Supporting information

Revealing the Structure of Transition Metal Complexes of Formaldoxime

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1. General information

All reactions were carried out in oven-dried (150°C) glassware. CH_2Cl_2, $CHCl_3$ and Et_3N were distilled over CaH_2; THF was distilled over $LiAlH_4$. $Na_2[Fe(ON{=}CH_2)_6]$ was prepared according to previously described protocol.[1] 1,4,7-Triazacyclononane trihydrochloride (*tacn*·3HCl**)**, *N*,*N*',*N*''-trimethyl-1,4,7-triazacyclononane (*Me*$_3$*tacn*), 1,8-bis(dimethylamino)naphthalene (proton sponge), *p*-thiocresol, naphthalene, Ph_3P, sodium ascorbate, hydroquinone, and all inorganic reagents were commercial grade and used as received. NMR spectra were recorded at room temperature with residual solvent peaks as internal standards.[2] Multiplicities are indicated by s (singlet), d (doublet), m (multiplet), and br (broad). ^{1}H spectra of complexes **2** and **4** were recorded from D_2O solutions with a Bruker Avance 400 spectrometer. Data acquisition and processing were performed with Topspin 2.1 and Mestrenova 12.0.0 software, respectively. The magnetic susceptibility of the paramagnetic iron and manganese complexes in a D_2O solution was evaluated by the Evans method[3] at 290 K using a Wilmad NMR tube with a coaxial insert. The inner (reference) tube was filled with D_2O with approximately 1% of DSS (Sodium trimethylsilylpropanesulfonate), the outer tube contained a D_2O solution of the paramagnetic complex with a known concentration and the same amount of Me_4Si. The molar magnetic susceptibility was calculated from the difference between the chemical shift of DSS in pure D_2O and its shift in the D_2O solution of the paramagnetic complex by the standard Evans method procedure.[4] The molar diamagnetic contribution to the paramagnetic susceptibility was estimated using Pascal's constants.[5]

Melting points were determined on a Kofler heating stage and were not corrected. HRMS experiments were performed on a mass-spectrometer with electrospray ionization and a time-of-flight (TOF) detector. Peaks in FT-IR spectra data are reported in cm^{-1} with the following relative intensities: s (strong), m (medium), w (weak), br (broad), sh (shoulder). UV-Vis spectra were recorded with the use of Jasco V-770 spectrophotometer or SF2000 spectrophotometer for the solutions of the investigated compounds. Raman spectra were measured on Princeton Instruments SpectraPro with CCD detector. Laser wavelength λ = 671.7 nm, spot size is about 2 μm. Intervals were 200 – 900 cm^{-1} and 800 – 1400 cm^{-1}, with 6 minutes exposition on each interval. GC-MS was performed on a Chromatec 5000 with Agilent DB-1MS column 122-0132.

Cyclic voltammetry experiments were performed for dimethylformamide solutions with 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte using a Metrohm Autolab PGSTAT128N potentiostat with a conventional one-compartment three-electrode cell (5 ml of solution). Platinum disk electrode (MF-2013, BASi), which was used as a working electrode, was thoroughly polished with 0.05 μm alumina slurry, sonicated for two minutes in

deionized water and rinsed before every measurement. A platinum wire counter electrode and a standard Ag/AgCl/NaClaq. reference electrode (RE-5B, BASi) were used. To account for a drift of the reference electrode, the ferrocene was added after the measurements as an internal standard, and all the potentials are reported relative to the Fc/Fc^+ redox couple. The solutions were thoroughly deaerated by passing argon through them before the CV experiments and above these solutions during the measurements.

The XPS spectra were measured using a KRATOS ES-300 photoelectron spectrometer with a nonmonochromated primary radiation source (AlKα line of hν = 1486.6 eV). Before the experiments, the spectrometer binding energy (BE) scale was calibrated based on the energy position of metallic gold $Au4f_{7/2}$ (84.0 eV) and copper $Cu2p_{3/2}$ (932.7 eV) lines.[6] Powders of the compounds were deposited on holder using a conductive double sided adhesive tape. The measurement accuracy of XPS binding energy was 0.1 eV. The BE scale was calibrated using the internal standard using the C1s line energy position (285.1 eV) for carbon atoms in $-CH_2-CH_2-$ framework of the complexes.[7] After the subtracting of the background by the Shirley method, the experimental spectra were fitted into individual components. The curve fitting for the overlapping spectral lines was carried out using a Lorentz-Gaussian line shape. The XPS spectra processing (decomposition into individual components, measurement of XPS signal area and determination of binding energies) was carried out using XPS-Calc program which was tested on a number of systems.[8, 9]

^{57}Fe Mössbauer absorption spectra of powdered samples were recorded using a conventional constant-acceleration Mössbauer spectrometer MC-1104Ем equipped with specialized nitrogen gas-flow cryostat. Spectra were recorded without external magnetic field at atmospheric pressure and within temperature range from 90 K to 295 K in transmission geometry with a ^{57}Co(Rh) source (MCo7.114).[10] For recording of Mössbauer absorption spectrum 26 mg of powdered sample was put into thin aluminum container (tablet) with approx. square 0.3 cm^2. The plane of the tablet was placed perpendicular to the direction of γ-rays propagation. Isomer shifts are given relatively to an α-Fe foil (30 μm MRA.2.6).[11] Simulations of the experimental data were performed with the Univem MS program.

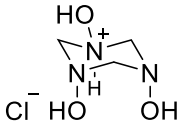
X-ray diffraction experiments were carried out at 120 K with a Bruker APEX2 DUO CCD diffractometer, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Using Olex2[12], the structures were solved with the ShelXT[13] structure solution program using Intrinsic Phasing and refined with the XL[14] refinement package using Least-Squares minimization against F^2 in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms of NH and OH groups, including those of solvent molecules, were located from the difference Fourier synthesis, positions of others were calculated, and they all were refined in isotropic approximation within

the riding model. Crystal data and structure refinement parameters for **tfoH$_3$·HCl**, complexes **1-3** and **5** are given in Table S1. CCDC 2061527 (for **tfoH$_3$·HCl**), 2035756 (for **1**), 2035755 (for **2**), 2035757 (for **3**), 2035754 (for **5**), contain the supplementary crystallographic data for this paper.

DFT calculations were performed with the Gaussian 16 Rev C.01[15] or ORCA 4.2.1[16] quantum chemistry programs.

2. Synthetic procedures for *tfoH₃*·HCl and 1-5

Synthesis of 1,3,5-trihydroxy-1,3,5-triazinan-1-ium chloride (*tfoH₃*·HCl).



To a stirred hydroxylamine hydrochloride solution (100 mg, 1.44 mmol) in H_2O (0.1 ml) was added a paraformaldehyde (43 mg, 1.44 mmol). The mixture was refluxed in a closed vial for 15 min until the formation of clear solution. The resulting solution was concentrated in a vacuum (80 Torr, 40°C). Then 150 uL of ethanol was added to the residue and the mixture was left to stay in a refrigerator at 4°C for 24 hours. Then precipitate was separated from mother liquor, washed with ethanol (3×150 μL) and was dried in a vacuum (0.2 Torr, 25 °C) to give 34 mg (yield 41%) of *tfoH₃*·HCl as a white solid. Mp. 108-112°C. *Caution*: the product starts to decompose above 50°C in a vacuum (0.1 Torr). ^{1}H NMR spectrum of *tfoH₃*·HCl is in agreement with literature data.[17] ^{1}H NMR (300 MHz, D_2O, δ, ppm): 4.61 (s, 6 H, 3 CH_2). FT-IR (KBr): 3242 (s,br), 3034 (s,sh), 2835 (s,br), 2622 (s), 2523 (m), 2419 (w), 1541 (s), 1405 (s,br), 1348 (m), 1307 (w), 1253 (w), 1203 (s), 1178 (s), 1131 (s), 1039 (s), 973 (s), 947 (s), 889 (s), 796 (s), 709 (m), 622 (br), 557 (s), 503 (m), 431 (s). Anal. Calcd for $C_3H_{10}ClN_3O_3$: C, 21.00; H, 5.87; N, 24.49. Found: C, 21.16; H, 5.78; N, 23.86. Single crystals of ***tfoH₃*·HCl**, suitable for X-ray diffraction were obtained by recrystallization from hot ethanolic solution.

Synthesis of *tfoH₃*·HCl from formaldehyde and hydroxylamine hydrochloride.

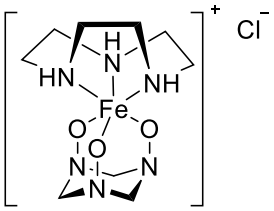
To a stirred formaldehyde solution (37 wt. % in H_2O, 4.4 mL, 59 mmol) at 0°C was added a hydroxylamine hydrochloride (4.0 g, 57 mmol). The mixture was stirred for 5 min at 0 °C, warmed up to room temperature, and stirred for additional 2 hours. The resulting solution was concentrated in a vacuum (80 Torr, 40°C). Then 5 mL of ethanol was added to the residue and the mixture was left to stay in a refrigerator at 4°C for 24 hours. Then another 10 mL of ethanol was added and solid material was filtered off and was dried in a vacuum (0.2 Torr, 25 °C) to give 2.0 g (yield 61%) of *tfoH₃*·HCl as a white solid. *Caution*: the product starts to decompose above 50°C in a vacuum (0.1 Torr). ^{1}H NMR spectrum of *tfoH₃*·HCl is in agreement with literature data.[17] ^{1}H NMR (300 MHz, HSQC, D_2O, δ, ppm): 4.53 (s, 6 H, 3 CH_2). ^{13}C NMR (75 MHz, HSQC, D_2O, δ, ppm): 74.3 (CH_2). ESI-HRMS m/z: $[M-Cl]^+$ Calcd for $[C_3H_{10}N_3O_3]^+$ 136.0717; Found 136.0718.

Synthesis of $^{15}N_3$-*tfoH₃*·HCl. Prepared from ^{15}N-hydroxylamine hydrochloride (100 mg, 1.42 mmol) and paraformaldehyde (43 mg, 1.44 mmol). 33 mg (yield 39%). FT-IR (KBr): 3253 (s,br), 3035 (s,sh), 2828 (s,br), 2662 (s), 2612 (s), 2511 (m), 2420 (w), 1539 (s), 1402 (s,br), 1349 (s), 1303 (w), 1246 (w), 1169 (s), 1119 (m), 1020 (s), 962 (m), 941 (s), 882 (s), 793 (s),

691 (m), 621 (br), 554 (s), 535 (m), 502 (m), 427 (s). ESI-HRMS m/z: $[M-Cl]^+$ Calcd for $[C_3H_{10}{}^{15}N_3O_3]^+$ 139.0628; Found 139.0649.

Synthesis of D_6-*tfoH$_3$*·HCl. Prepared from hydroxylamine hydrochloride (100 mg, 1.44 mmol) and D_2-paraformaldehyde (46 mg, 1.44 mmol). 40 mg (yield 47%). FT-IR (KBr): 3254 (s,br), 2828 (s,br), 2612 (s), 1540 (s), 1429 (s,br), 1374 (s),1205 (s),1182 (m), 1150 (s), 1097 (s), 1040 (s), 1011 (s), 986 (s), 889 (m), 817 (s,sh), 744 (s), 690 (m), 618 (br), 533 (m), 515 (s), 417 (m). ESI-HRMS m/z: $[M-Cl]^+$ Calcd for $[C_3H_4D_6N_3O_3]^+$ 142.1093; Found 142.1088.

Synthesis of 2,8,9-trioxa-1',3,4',5,7,7'-hexaaza-1-ferraspiro[tricyclo[3.3.1.1^{3,7}]decane- 1,10'-tricyclo [5.2.1.0^{4,10}]decan]-1-ylium chloride (2).



To a mixture of *tfoH$_3$*·HCl (34 mg, 0.2 mmol), *tacn*·3HCl (48 mg, 0.20 mmol), anhydrous $FeCl_3$ (32 mg, 0.20 mmol) and proton sponge (428 mg, 2.0 mmol) were added 5 mL of methanol. The reaction mixture was stirred for 1 hour at room temperature under air and then kept for additional 24 hours with a closed cap. The precipitate was centrifuged off and clear solution containing complex **2** was concentrated in a vacuum. The residue was dried at 0.1 Torr for 30 min and a mixture of Et_2O (10 mL) and CH_2Cl_2 (30 mL) was added to the crude product. The mixture was left to stay in a refrigerator at 4°C for 4 days. Then precipitate was separated from mother liquor and dried at 0.1 Torr for 30 min. The residue was placed in a centrifuge cup and centrifuged with CH_2Cl_2 (3×10 mL) and THF (2×10 mL). The residual solid was dissolved in 3 mL of methanol (dark maroon solution) and centrifuged. Clear solution was separated from small amount of undissolved material and concentrated in vacuum. This operation was repeated twice. Solid material was dried in vacuum at 0.1 Torr to give 31 mg (yield 42%) of **2** as a black solid. Mp. above 280°C. FT-IR (KBr): 3449 (br), 3240 (s), 3053 (s), 2978 (s), 2924 (m), 2883 (s), 2828 (w), 1631 (br), 1485 (w), 1450 (s), 1419 (m), 1360 (m), 1329 (w), 1261 (m), 1229 (w), 1167 (m), 1101 (s), 1042 (s), 972 (s), 929 (s), 874 (m), 830 (m), 779 (s), 746 (m), 632 (s), 604 (m), 530 (s), 460 (m), 431 (m). UV−vis spectrum: (MeOH, c = 6.4 × 10^{-6} M) peaks λ nm: 273 (max. extinction coefficient ε_{max} = 5.4×10^4), 345 (ε_{max} = 2.8×10^4), 492 (ε_{max} = 1.9×10^4), 578 (ε_{max} = 7.7×10^3).). UV−vis / NIR spectrum: (powder sample) peaks λ nm: 353, 490, 576. Raman Spectrum: 217 (intensity: 340, Fe-O),[18] 289 (intens.: 161), 362 (intens.: 190), 387 (intens.: 202), 429 (intens.: 209), 462 (intens.: 120), 500 (intens.: 508, v_s Fe-O and Fe-N),[18, 19] 524 (intens.: 792), 538 (intens.: 358), 632 (intens.: 227), 748 (intens.: 105), 976 (intens.: 148), 1250 (intens.: 2354, twisting CH_2 from *tfo* and *tacn*),[18, 19]1357 (intens.: 115), 1424 (intens.: 5818,

scissoring CH_2 from *tfo* and *tacn*).[18-20] ESI-HRMS m/z: $[M-Cl]^+$ Calcd for $[C_9H_{21}FeN_6O_3]^+$ 317.1019; Found 317.1021. Anal. Calcd for $C_9H_{21}ClFeN_6O_3 \cdot 0.5CH_3OH$: C, 30.95; H, 6.29; N, 22.80. Found: C, 31.54; H, 5.95; N, 22.82.

Preparation of crystals for X-ray analysis of complex **2**.

To a mixture of *tfoH₃*·HCl (22 mg, 0.13 mmol), *tacn*·3HCl (31 mg, 0.13 mmol), anhydrous $FeCl_3$ (20 mg, 0.13 mmol) was added 1 mL of methanol and Et_3N (0.16 mL, 1.18 mmol). The reaction mixture was stirred for 2 hours at room temperature under air and then for additional 24 hours with a closed cap. The resulting mixture was evaporated and residue was triturated with CH_3CN:Et_2O mixture (1 mL : 3 mL), then triturated with CH_3CN:Et_2O (0.5 mL : 1 mL) mixture and finally with CH_3CN (0.3 mL). Solid was collected and dried at 0.1 Torr. The crude product was dissolved in 1 mL of methanol and the solution was filtered through syringe filter. Slow diffusion of an Et_2O layer into the methanol solution produced black crystals of **2** suitable for X-Ray diffraction analysis.

Synthesis of complex 2 from formaldehyde and hydroxylamine.

To a stirred 37% aqueous solution of formaldehyde (60 μL, 0.8 mmol) in 5 mL of CH_3OH at 0°C was added a 50% aqueous solution of hydroxylamine (49 μL, 0.8 mmol). The mixture was stirred for 3 min at 0°C. Then *tacn*·3HCl (48 mg, 0.20 mmol), anhydrous $FeCl_3$ (32 mg, 0.20 mmol) and proton sponge (428 mg, 2 mmol) were successively added. The reaction mixture was warmed up to room temperature and was stirred for 1 hour under air and then for additional 24 hours with a closed cap. The precipitate was centrifuged off and clear solution was evaporated. The residue was dried in vacuum at 0.1 Torr for 30 min and a mixture of Et_2O (10 mL) and CH_2Cl_2 (30 mL) was added to the crude product. The mixture was left to stay in a refrigerator at 4°C for 3 days. Then precipitate was separated from mother liquor, dried in vacuum at 0.1 Torr for 30 min, and placed in a centrifuge cup. Precipitate was centrifuged with CH_2Cl_2 (3×10 mL) and THF (2×10 mL) in centrifuge cup. The residue was dissolved in 3 mL of methanol (dark maroon solution) and centrifuged. Clear solution was separated from small amount of undissolved material and concentrated in a vacuum. This operation was repeated twice. Solid material was dried in vacuum at 0.1 Torr to give 18 mg (yield 24%) of **2** as a black solid. ESI-HRMS m/z: $[M-Cl]^+$ Calcd for $[C_9H_{21}FeN_6O_3]^+$ 317.1019; Found 317.1021.

Synthesis of complex 2 from $Na_2[Fe(ON{=}CH_2)_6]$.

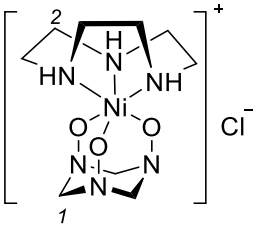
To a mixture of $Na_2[Fe(ON{=}CH_2)_6]$ (50 mg, 0.13 mmol) and *tacn*·3HCl (31 mg, 0.13 mmol) was added 1 mL of methanol. The reaction mixture was stirred for 1 hour at room temperature under air. The crude material was centrifuged off and clear solution was concentrated in a vacuum. The residue was dried at 0.1 Torr for 30 min. Then crude material was

triturated with 1 mL of CH_2Cl_2 and solid material was dried in vacuum at 0.1 Torr to give 15 mg (yield 33%) of **2**.

Synthesis of [Fe(tacn)($^{15}N_3$-tfo)]Cl. Prepared from $^{15}N_3$-*tfoH*$_3$·HCl (26 mg, 0.15 mmol) and anhydrous $FeCl_3$ (24 mg, 0.15 mmol). 33 mg (yield 62%). FT-IR (KBr): 3435 (br), 3240 (s), 3053 (m), 2982 (m), 2924 (s), 2882 (s), 1728 (s), 1646 (br), 1453 (s), 1418 (m), 1354 (sh), 1279 (br), 1261 (m), 1229 (w), 1145 (w), 1097 (s), 1069 (w), 1043 (s,sh), 961 (s), 923 (s), 872 (m), 830 (m), 780 (s), 729 (m), 622 (s), 532 (s), 455 (m), 435 (w). ESI-HRMS m/z: $[M\text{-}Cl]^+$ Calcd for $[C_9H_{21}Fe^{15}N_3N_3O_3]^+$ 320.0930; Found 320.0940.

Synthesis of [Fe(tacn)(D_6-tfo)]Cl. Prepared from D_6-*tfoH*$_3$·HCl (27 mg, 0.15 mmol) and anhydrous $FeCl_3$ (24 mg, 0.15 mmol). 37 mg (yield 69%). FT-IR (KBr): FT-IR (KBr): 3434 (br), 3241 (s), 3053 (s), 2931 (w), 2884 (s), 2829 (w), 1636 (br), 1453 (m), 1355 (sh), 1263 (m), 1228 (w), 1127 (w), 1092 (s), 1065 (s), 1047 (s), 1027 (s), 959 (s), 924 (w), 868 (s), 827 (s), 798 (s), 734 (w), 719 (s), 609 (m), 590 (s), 520 (s), 453 (w), 424 (w). ESI-HRMS m/z: $[M\text{-}Cl]^+$ Calcd for $[C_9H_{15}D_6FeN_6O_3]^+$ 323.1396; Found 323.1398.

Synthesis of 2,8,9-trioxa-1',3,4',5,7,7'-hexaaza-1-nickelaspiro[tricyclo[3.3.1.1^{3,7}]decane-1,10'-tricyclo [5.2.1.0^{4,10}]decan]-1-ylium chloride (3).



To a mixture of *tfoH*$_3$·HCl (34 mg, 0.20 mmol), *tacn*·3HCl (48 mg, 0.20 mmol), anhydrous $NiCl_2$ (26 mg, 0.20 mmol) and proton sponge (428 mg, 2.0 mmol) were added 5 mL of methanol. The reaction mixture was stirred for 1 hour at room temperature under air and then for additional 24 hours with a closed cap. The precipitate was centrifuged off and clear solution was concentrated in a vacuum. The residue was dried at 0.1 Torr for 30 min and a mixture of Et_2O (10 mL) and CH_2Cl_2 (30 mL) was added to the crude product. The mixture was left to stay in a refrigerator at 4°C for 2 days. Then, the precipitate was separated from mother liquor (off-white solid was not collected), dried in vacuum at 0.1 Torr for 30 min. The residue was placed in a centrifuge cup and centrifuged with CH_2Cl_2 (5×8 mL) and THF (2×10 mL). Solid residue was dissolved in 3 mL of methanol (dark maroon solution) and concentrated in a vacuum. The resulting crude material was dissolved in 1 mL of methanol; clear solution was separated from a small amount of off-white solid and evaporated again. This operation was repeated with 0.4 mL of methanol and then with 0.2 mL of methanol (until clear solution is formed upon dissolution in

methanol). The residue was dried in vacuum at 0.1 Torr to give 22 mg (yield 28%) of **3** as a black solid. Mp. above 280°C. ^{1}H NMR (300 MHz, HSQC, COSY, D_2O, δ, ppm, *J*/Hz): 2.73 (d, *J* = 11.6 Hz, 3 H, *H*C-1), 3.04 (m, 6 H, *H*C-2), 3.30 (m, 6 H, *H*C-2), 3.38 (br. s, CH_3OH), 3.97 (br, 3 H, N*H*), 5.13 (d, *J* = 11.6 Hz, 3 H, *H*C-1). ^{13}C NMR (75 MHz, HSQC, D_2O, δ, ppm): 45.9 (*C*-2), 86.0 (*C*-1). FT-IR (KBr): 3434 (br), 3255 (s;br), 3195 (s;br), 2944 (m), 2893 (br), 1631 (m;br), 1454 (m), 1428 (m), 1366 (m), 1327 (m), 1278 (w), 1220 (m), 1103 (s), 1049 (s), 1015 (s), 955 (m), 925 (s), 874 (m), 831 (m), 762 (m), 625 (s), 592 (m), 539 (w), 508 (m), 445 (m), 419 (w). UV−vis spectrum: (MeOH, c = 8.5 × 10^{-6} M) peaks λ nm: 211 (max. extinction coefficient ε_{max} = 2.5×10^4), 256 (ε_{max} = 1.7×10^4), 303 (ε_{max} = 4.8×10^4), 367 (ε_{max} = 2.8×10^4). UV−vis / NIR spectrum: (powder sample) peaks λ nm: 384. ESI-HRMS m/z: $[M\text{-}Cl]^+$ Calcd for $[C_9H_{21}N_6NiO_3]^+$ 319.1023; Found 319.1016. Anal. Calcd for $C_9H_{21}ClNiN_6O_3{\cdot}1CH_3OH$: C, 31.00; H, 6.50; N, 21.69. Found: C, 30.74; H, 6.13; N, 21.29.

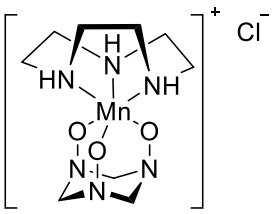
*Preparation of crystals for X-ray analysis of complex **3**.*

To a mixture of *tfoH₃*·HCl (64 mg, 0.38 mmol), *tacn*·3HCl (90 mg, 0.38 mmol) and $NiCl_2{\cdot}6H_2O$ (90 mg, 0.38 mmol) were added 3 mL of methanol and Et_3N (0.53 mL, 3.8 mmol). The reaction mixture was stirred for 1 hours at room temperature under air and then for additional 24 hours with a closed cap. The resulting mixture was concentrated in a vacuum and the residue was triturated with $CHCl_3$:Et_2O mixture (1 mL : 1 mL). Crude material was separated from mother liquor and was dried at 0.1 Torr for 6 hours at 70°C. The resulting solid material was triturated with $CHCl_3$:Et_2O mixture (1 mL : 1 mL) and the precipitate was centrifuged off and dried in vacuum until constant weight. Then 1 mL of methanol was added and mixture was filtered through syringe filter. Slow diffusion of an Et_2O layer into the methanol solution produced black crystals of **3**·CH_3OH suitable for X-Ray diffraction analysis.

Synthesis of [Ni(tacn)($^{15}N_3$-tfo)]Cl. Prepared from $^{15}N_3$-*tfoH₃*·HCl (26 mg, 0.15 mmol) and anhydrous $NiCl_2$ (20 mg, 0.15 mmol). 24 mg (yield 44%). FT-IR (KBr): 3437 (br), 3253 (br), 3196 (s;br), 2932 (m), 2872 (br), 1728 (w), 1634 (br), 1454 (m), 1424 (m), 1375 (w), 1354 (w), 1314 (m), 1278 (m), 1203 (m), 1100 (s), 1039 (m,br) 1004 (s), 954 (m), 920 (s), 873 (m), 832 (m), 799 (w), 741 (m), 615 (s), 542 (w), 505 (w), 441 (m), 421 (w). ESI-HRMS m/z: $[M\text{-}Cl]^+$ Calcd for $[C_9H_{21}Ni^{15}N_3N_3O_3]^+$ 322.0934; Found 322.0935.

Synthesis of [Ni(tacn)(D_6-tfo)]Cl. Prepared from D_6-*tfoH₃*·HCl (27 mg, 0.15 mmol) and anhydrous $NiCl_2$ (20 mg, 0.15 mmol). 16 mg (yield 30%). FT-IR (KBr): 3434 (br), 3252 (s;br), 3196 (s;br), 2929 (br), 2871 (m), 1724 (w), 1635 (m;br), 1490 (w), 1455 (m), 1357 (m,sh), 1277 (w), 1232 (w), 1185 (m), 1148 (s), 1101 (s), 1081 (m), 1053 (s), 1029 (s), 955 (s), 871 (s), 823 (s), 799 (m), 743 (w), 710 (w), 618 (w), 598 (s), 582 (s), 505 (s), 459 (w),428 (w). ESI-HRMS m/z: $[M\text{-}Cl]^+$ Calcd for $[C_9H_{15}D_6NiN_6O_3]^+$ 325.1399; Found 325.1400.

Synthesis of 2,8,9-trioxa-1',3,4',5,7,7'-hexaaza-1-manganaspiro [tricyclo[3.3.1.1^{3,7}]decane-1,10'-tricyclo [5.2.1.0^{4,10}]decan]-1-ylium chloride (4).



To a mixture of *tfoH$_3$*·HCl (64 mg, 0.38 mmol), *tacn*·3HCl (90 mg, 0.38 mmol) and $Mn(OAc)_3$·$2H_2O$ (102 mg, 0.38 mmol) were added 3 mL of methanol. After 15 minutes of stirring, Et_3N (0.53 mL, 3.8 mmol) was added. The reaction mixture was stirred for 1 hours at room temperature under air and then for additional 24 hours with a closed cap. The resulting mixture was concentrated at 80 Torr. The residue was triturated with $CHCl_3$:Et_2O mixture (5 mL : 5 mL). The solid material was separated from mother liquor and dried in vacuum for 8 hours at 100°C (off-white solid was not collected). The resulting crude material was triturated with 5 mL of $CHCl_3$ and dried at 0.1 Torr to give 47 mg (yield 35%) of **4** as a black solid. Mp. above 250°C. ESI-HRMS m/z: $[M-Cl]^+$ Calcd for $[C_9H_{21}MnN_6O_3]^+$ 316.1050; Found 316.1047. Anal. Calcd for $C_9H_{21}ClMnN_6O_3$: C, 30.74; H, 6.02; N, 23.90. Found: C, 30.74; H, 6.07; N, 23.89.

Synthesis of complex 4 from $MnCl_2$ and proton sponge.

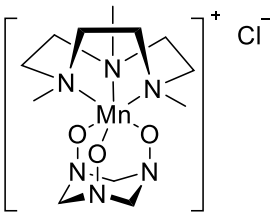
To a mixture of *tfoH$_3$*·HCl (34 mg, 0.20 mmol), anhydrous $MnCl_2$ (25 mg, 0.20 mmol), *tacn*·3HCl (48 mg, 0.20 mmol) and proton sponge (428 mg, 2.0 mmol) were added 5 mL of methanol. The reaction mixture was stirred for 1 hour at room temperature under air and then for additional 48 hours with a closed cap. The precipitate was centrifuged off and the solution was concentrated in a vacuum. The residue was dried at 0.1 Torr for 1 hour and a mixture of Et_2O (20 mL) and CH_2Cl_2 (30 mL) was added to crude product. The mixture was left to stay in a refrigerator at 4°C for 3 days. Then precipitate was separated from mother liquor, dried at 0.1 Torr for 30 min (off-white solid was not collected). The resulting brown solid was placed in a centrifuge cup and centrifuged with CH_2Cl_2 (3×10 mL). The residual solid was dissolved in 3 mL of methanol (dark maroon solution) and centrifuged. Clear solution was separated from small amount of undissolved material and concentrated in vacuum. To the residual solid was added 1 mL of methanol, the clear solution was separated from insoluble crystals and concentrated in a vacuum. Last operation was repeated with 0.4 mL of methanol (until clear solution is formed upon dissolution in methanol). The residue was dried at 0.1 Torr to give 20 mg (yield 26%) of **4** as a black solid. FT-IR (KBr): 3438 (br), 3214 (s), 3031 (m), 2980 (m), 1634 (br), 1454 (m), 1417 (m), 1262 (w), 1166 (w), 1109 (m), 1097 (m), 1069 (w), 1037 (s,sh), 963 (s), 932 (s), 871 (w), 830 (w), 779 (s), 746 (w), 632 (s), 591 (m), 531 (s), 463 (m), 425 (w). UV−vis / NIR spectrum: (powder sample) peaks λ nm: 305, 351, 451, 543. ESI-HRMS m/z: [M-

Cl]$^+$ Calcd for [$C_9H_{21}MnN_6O_3$]$^+$ 316.1050; Found 316.1050. Anal. Calcd for $C_9H_{21}ClMnN_6O_3 \cdot 1CH_3OH$: C, 31.30; H, 6.57; N, 21.90. Found: C, 31.31; H, 6.71; N, 22.33.

Synthesis of [Mn(tacn)($^{15}N_3$-tfo)]Cl. Prepared from $^{15}N_3$-*tfoH*$_3$·HCl (26 mg, 0.15 mmol) and anhydrous $MnCl_2$ (19 mg, 0.15 mmol). 20 mg (yield 38%). FT-IR (KBr): 3440 (br), 3214 (s), 3032 (m), 2980 (m), 2922 (m), 2867 (s), 1635 (br), 1454 (m), 1417 (m), 1264 (br), 1147 (w), 1109 (m), 1098 (m), 1069 (w), 1037 (s,sh), 956 (s), 932 (s), 924 (s), 872 (w), 830 (w), 778 (s), 730 (w), 621 (s), 592 (m), 530 (s), 459 (m), 425 (w). ESI-HRMS m/z: [M-Cl]$^+$ Calcd for [$C_9H_{21}Mn^{15}N_3N_3O_3$]$^+$ 319.0961; Found 319.0959.

Synthesis of [Mn(tacn)(D_6-tfo)]Cl. Prepared from D_6-*tfoH*$_3$·HCl (27 mg, 0.15 mmol) and anhydrous $MnCl_2$ (19 mg, 0.15 mmol). 15 mg (yield 28%). FT-IR (KBr): 3436 (br), 3216 (s), 3032 (m), 2959 (s), 2930 (s), 2867 (s), 1729 (s), 1633 (br), 1455 (m), 1376 (w), 1355 (w), 1284 (s), 1130 (m), 1055 (m,sh), 1027 (m), 959 (s), 906 (m), 868 (s), 827 (s), 796 (w), 737 (w), 721 (s), 604 (s), 588 (s), 526 (s), 437 (w). ESI-HRMS m/z: [M-Cl]$^+$ Calcd for [$C_9H_{15}D_6MnN_6O_3$]$^+$ 322.1427; Found 322.1418.

Synthesis of 1',4',7'-trimethyl-2,8,9-trioxa-1'λ4,3,4'λ4,5,7,7'λ4-hexaaza-1-manganaspiro[tricyclo[3.3.1.1^{3,7}]decane-1,10'-tricyclo[5.2.1.0^{4,10}]decan]-1-ylium chloride (5).



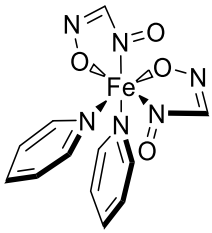
To a mixture of *tfoH*$_3$·HCl (34 mg, 0.20 mmol), anhydrous $MnCl_2$ (25 mg, 0.20 mmol) and proton sponge (300 mg, 1.40 mmol) were added 5 mL of methanol and Me_3*tacn* (0.39 mL, 0.20 mmol). The reaction mixture was stirred for 1 hour at room temperature under air and then for additional 24 hours with a closed cap. The precipitate was centrifuged off and the solution was concentrated in a vacuum. The residue was dried at 0.1 Torr for 1 hour and a mixture of Et_2O (20 mL) and CH_2Cl_2 (30 mL) was added to crude product. The mixture was left to stay in a refrigerator at 4°C for 4 days. Then precipitate was separated from mother liquor, dried at 0.1 Torr for 30 min (off-white solid was not collected). The resulting brown solid was placed in a centrifuge cup and centrifuged with CH_2Cl_2:Et_2O mixture (5 mL : 5 mL) and with CH_2Cl_2:Et_2O mixture (4.5 mL : 2.5 mL). To the residual solid was added 3 mL of methanol, the clear solution was separated from insoluble crystals and concentrated in a vacuum. Last operation was repeated with 1 mL of methanol and then with 0.4 mL of methanol (until clear solution is formed upon dissolution in methanol). The residue was dried at 0.1 Torr to give 14 mg (yield 15%) of **5** as a black solid. Mp. above 280°C. FT-IR (KBr): 3382 (br), 2994 (m), 2934 (m), 2849 (m), 2624

(w;br), 1697 (w), 1658 (w) 1599 (w), 1501 (m), 1462 (s), 1415 (m), 1382 (m), 1345 (w), 1290 (s), 1252 (w), 1202 (w), 1160 (s), 1121 (w), 1058 (s), 1003 (s), 970 (s), 931 (s), 901 (m), 868 (w), 784 (s), 738 (s), 661 (w), 619 (s), 591 (m), 509 (s), 451 (s). UV−vis spectrum: (MeOH, c = 5.8×10^{-6} M) peaks λ nm: 211 (max. extinction coefficient $\varepsilon_{max} = 2.7\times10^4$), 252 ($\varepsilon_{max} = 3.7\times10^4$), 297 ($\varepsilon_{max} = 3.6\times10^4$), 451 ($\varepsilon_{max} = 2.6\times10^4$), 542 ($\varepsilon_{max} = 6.8\times10^3$). ESI-HRMS m/z: $[M\text{-}Cl]^+$ Calcd for $[C_{12}H_{27}MnN_6O_3]^+$ 358.1520; Found 358.1525. Anal. Calcd for $C_{12}H_{27}ClMnN_6O_3{\cdot}2CH_3OH{\cdot}H_2O$: C, 35.34; H, 7.84; N, 17.66. Found: C, 34.89; H, 7.47; N, 17.42.

*Preparation of crystals for X-ray analysis of complex **5**.*

To a mixture of *tfoH₃*·HCl (34 mg, 0.20 mmol), SrO (73 mg, 0.70 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (54 mg, 0.20 mmol) were added 3 mL of methanol and Me_3*tacn* (0.39 mL, 0.20 mmol). The reaction mixture was stirred for 1 hour at room temperature under air and then for additional 24 hours with a closed cap. The precipitate was centrifuged off and clear solution was concentrated in a vacuum. The residue was dried at 0.1 Torr until constant weight. Then 1 mL of methanol was added and the solution was filtered through syringe filter. Slow diffusion of an Et_2O layer into the methanol solution produced black crystals of **4**·CH_3OH suitable for X-Ray diffraction analysis.

Synthesis of 5,5-bis(1λ4-pyridin-1-yl)-1,6-dioxa-2,4λ5,7,9λ5-tetraaza-5-ferraspiro[4.4]nonane-4,9-dione (**1**).



To a solution of anhydrous $FeCl_3$ (150 mg, 0.93 mmol) in methanol (5 mL) were consequently added *tfo*·HCl (159 mg, 0.93 mmol) and pyridine (0.63 mL, 7.8 mmol). The purple-brown solution was stirred at room temperature overnight under air. The resulting dark-olive solution was concentrated under reduced pressure. The residue was dried in vacuum to remove the unreacted pyridine and then dissolved in water (20 mL). Aqueous layer was washed with the mixture of EtOAc:Et_2O until the organic layer became colorless. Then, $CHCl_3$ (20 mL) was added to the aqueous layer and the mixture was stirred overnight with an access of air. The resulting deep-blue chloroform layer was separated and concentrated in vacuum to give 7 mg of dark blue crystals of complex **1** (yield: 2%). Mp. above 280°C. FT-IR (KBr): 3480 (br), 3074 (w), 2922 (w), 2851 (w), 1605 (m), 1487 (w), 1449 (s), 1407 (s), 1385 (s), 1373 (s), 1357 (s), 1238 (m), 1219 (m), 1096 (m), 1066 (m), 1030 (s), 876 (w), 830 (m), 799 (w), 763 (m), 695 (m),

643 (w), 606 (w). UV−vis spectrum: (CH_2Cl_2, c = 2.3 × 10^{-3} M) peaks λ nm: 600 (max. extinction coefficient ε_{max} = 0.8×10^3). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{12}H_{13}FeN_6O_4]^+$ 361.0342; Found 361.0339. For growth of crystals of **1** which are suitable for X-ray diffraction analysis 25 mg of **1** were dissolved in 1 mL of methanol and mixture was filtered through syringe filter. Slow diffusion of an Et_2O layer into the methanol solution produced dark blue crystals of **1** which were suitable for X-Ray diffraction analysis.

3. Oxidation reactivity and catalytic activity of metal-tfo complexes

Aerobic oxidation of *p*-thiocresol catalyzed by Fe[(*tacn*)(*tfo*)]$^+$Cl$^-$.

A solution of *p*-thiocresol (25 mg, 0.2 mmol, 1000 equiv.) in methanol (250 μL) was added to a 1 mM solution of Fe[(*tacn*)(*tfo*)]$^+$Cl$^-$ in methanol (200 μL). The mixture was stirred in a closed vessel equipped with a magnetic stirrer and an air-filled balloon for 24 hours. The resulting solution was concentrated under reduced pressure. Hexane (2 mL) and water (1 mL) were added to the residue. The organic phase was collected and the aqueous layer was washed with hexane (2 × 2 mL). The combined organic phase was dried over sodium sulfate, concentrated under reduced pressure and dried until constant weight to give 19.7 mg (80 %) of *p*-tolyl disulfide as a white solid.

Aerobic oxidation of *p*-thiocresol catalyzed by Ni[(*tacn*)(*tfo*)]$^+$Cl$^-$.

To a 1 mM solution of the Ni[(*tacn*)(*tfo*)]$^+$Cl$^-$ (1.2 mL) in methanol was added 29.8 mg of *p*-thiocresol (0.24 mmol, 200 equiv.) and triethylamine (2 μL, 0.014 mmol, ca. 10 equiv.). The mixture was stirred in a closed vessel equipped with a magnetic stirrer and an air-filled balloon for 24 hours. The resulting solution was concentrated under reduced pressure. Hexane (2 mL) and water (1 mL) were added to the residue. The organic phase was collected and the aqueous layer was washed with hexane (2 × 2 mL). The combined organic phase was dried over sodium sulfate, concentrated under reduced pressure and dried until constant weight to give 23.1 mg (78 %) of *p*-tolyl disulfide as a white solid.

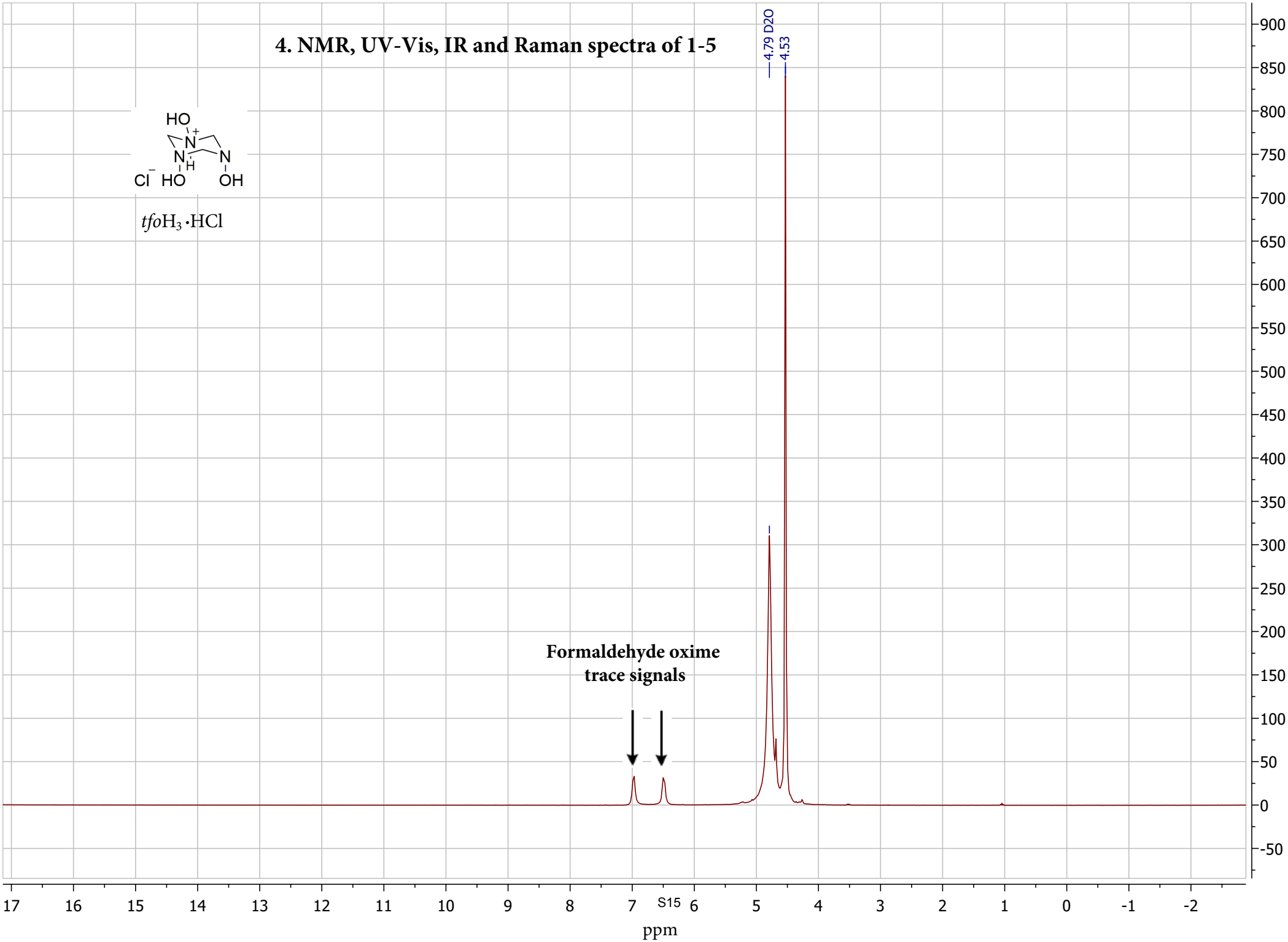
Aerobic oxidation of *p*-thiocresol catalyzed by Mn[(*Me$_3$tacn*)(*tfo*)]$^+$Cl$^-$.

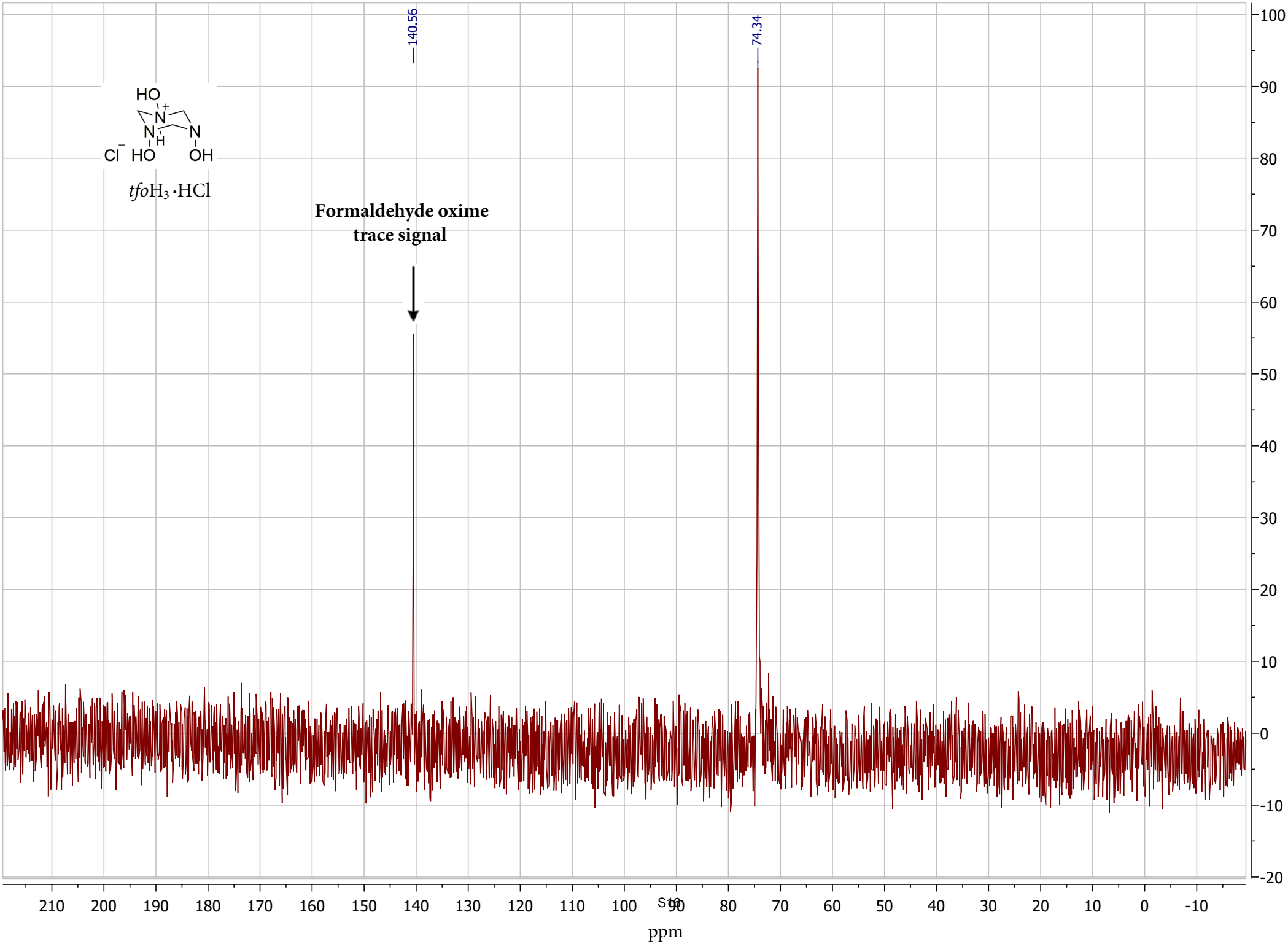
To a 1 mM solution of the Mn[(*Me$_3$tacn*)(*tfo*)]$^+$Cl$^-$ (1.2 mL) in methanol was added 29.8 mg of *p*-thiocresol (0.24 mmol, 200 equiv.) and triethylamine (2 μL, 0.014 mmol, ca. 10 equiv.). The mixture was stirred in a closed vessel equipped with a magnetic stirrer and an air-filled balloon for 24 hours. The mixture was concentrated under reduced pressure. Hexane (2 mL) and water (1 mL) were added to the residue. The organic phase was collected and the aqueous layer was washed with hexane (2 × 2 mL). The combined organic phase was dried over sodium sulfate, concentrated under reduced pressure and dried until constant weight to give 24.0 mg (81 %) of *p*-tolyl disulfide as a white solid.

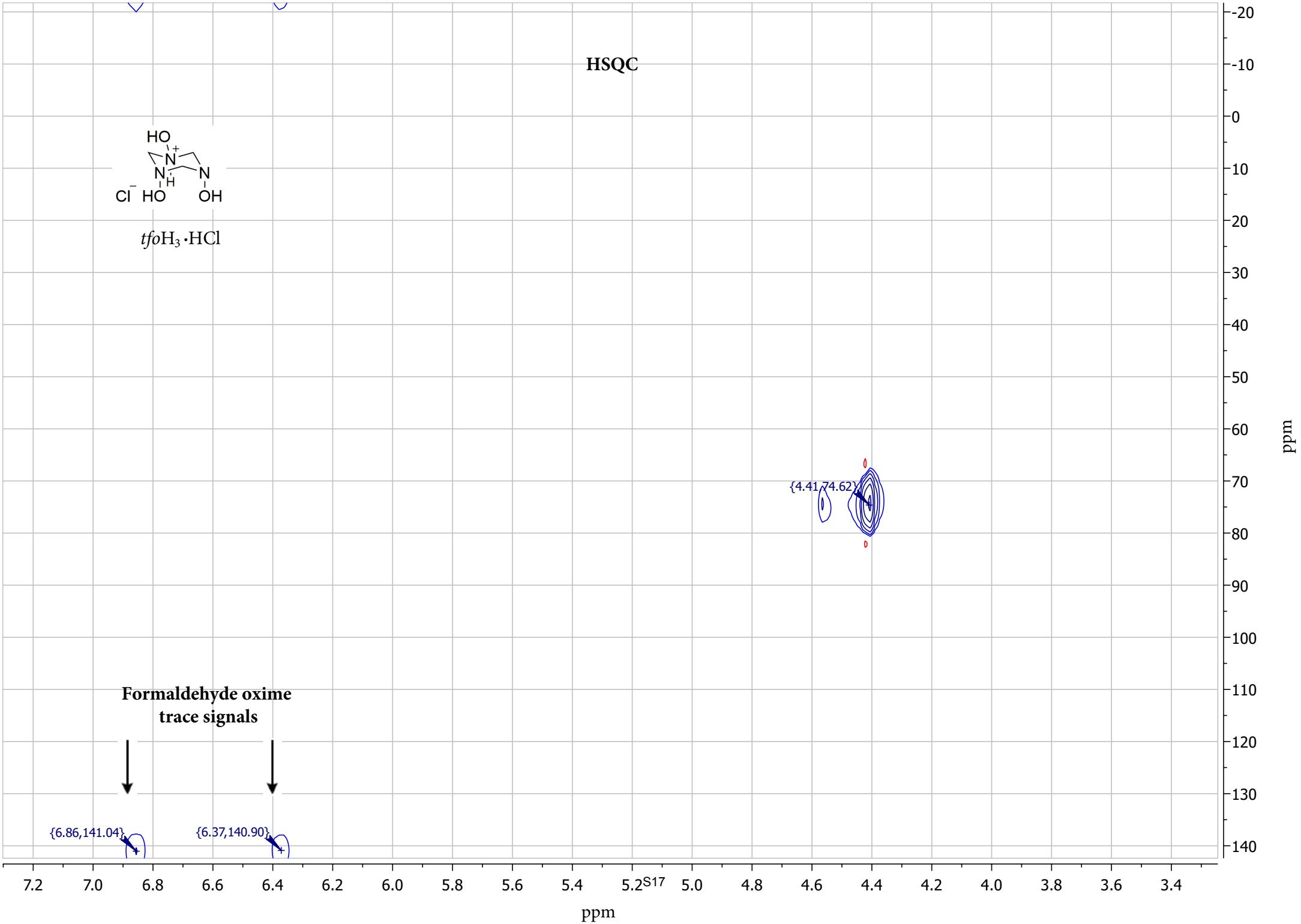
***p*-Tolyl disulfide.** White solid. Mp. 46 °C. Lit. 43-46 °C.[21] GC-MS: r.t. 10.1 min; m/z = 246 ([M]$^{+\bullet}$). ^{1}H NMR spectrum of *p*-tolyl disulfide is in agreement with literature data.[21] ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.32 (s, 6 H), 7.09 (m, 4 H), 7.37 (m, 4 H).

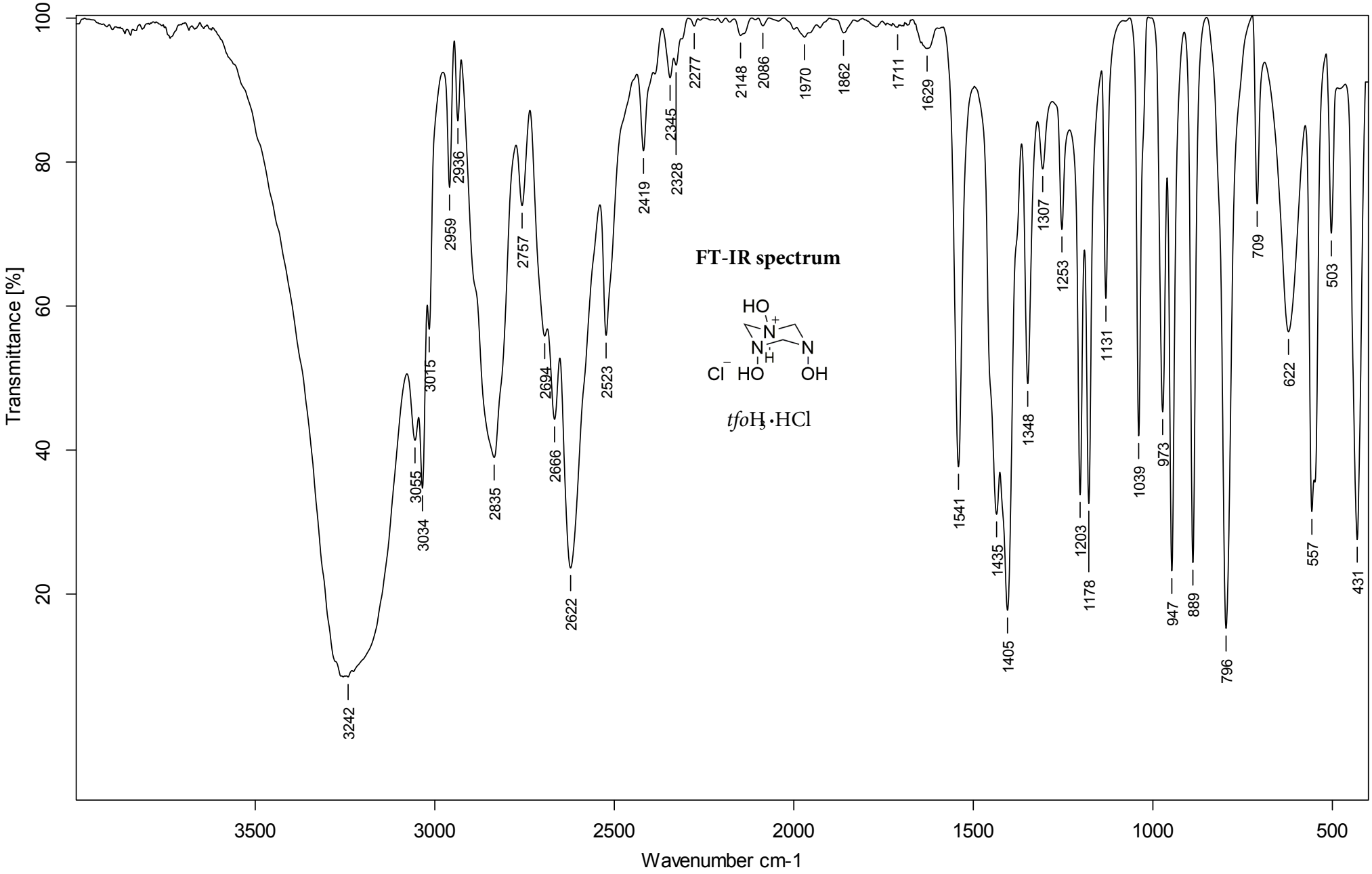
4. NMR, UV-Vis, IR and Raman spectra of 1-5

tfoH_3·HCl




140.56
74.34
HO
N
N
N
H
Cl⁻ HO
OH
tfoH3·HCl
Formaldehyde oxime
trace signal
ppm


HSQC
HO
N+
N
N
H
Cl−
HO
OH
tfoH3 ·HCl
{4.41,74.62}
Formaldehyde oxime
trace signals
{6.86,141.04}
{6.37,140.90}
ppm
ppm


FT-IR spectrum
tfoH3·HCl
Transmittance [%]
Wavenumber cm-1
3242
3055
3034
3015
2959
2936
2835
2757
2694
2666
2622
2523
2419
2345
2328
2277
2148
2086
1970
1862
1711
1629
1541
1435
1405
1348
1307
1253
1203
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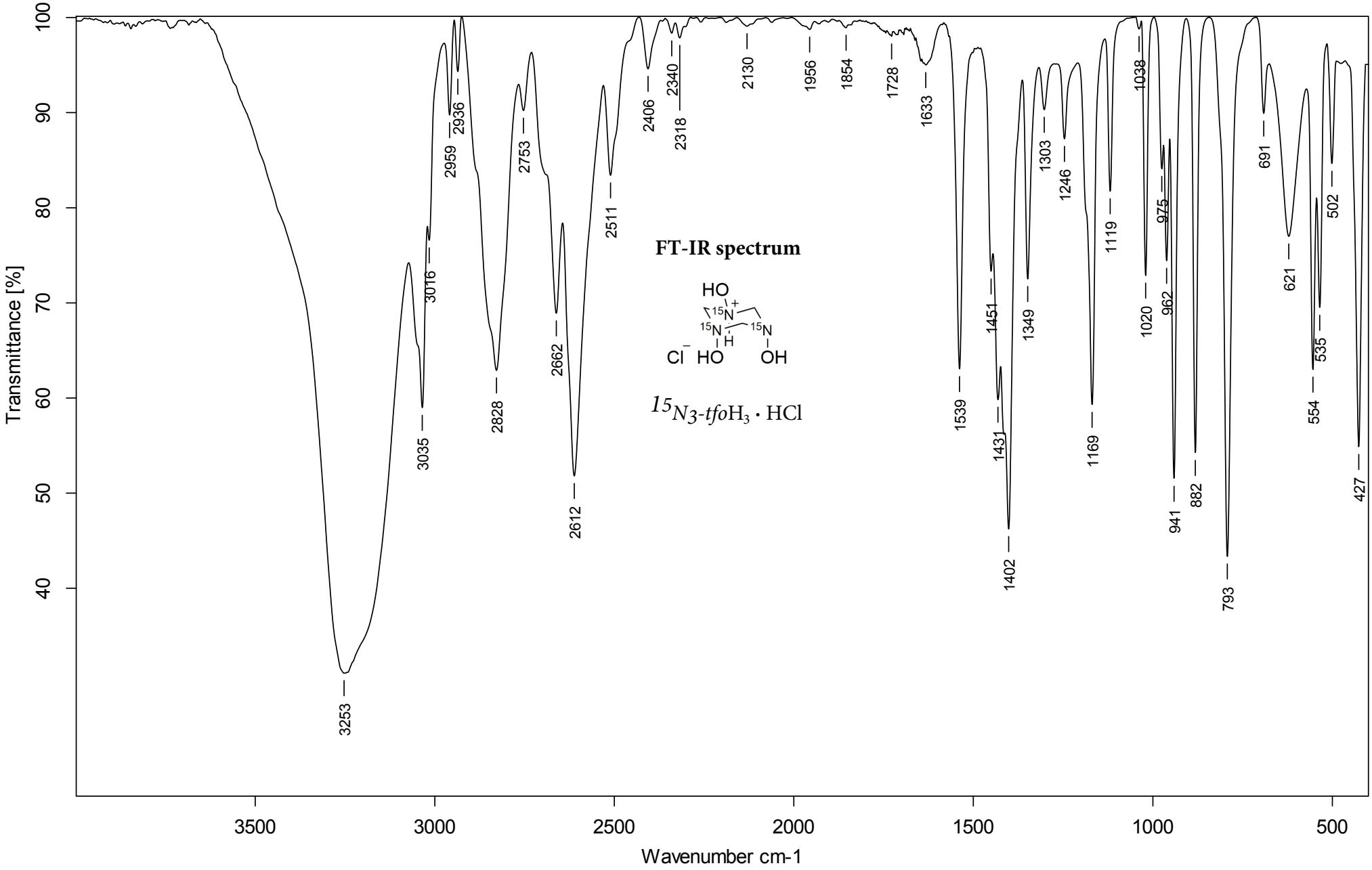
973
947
889
796
709
622
557
503
431


FT-IR spectrum
$^{15}N_3$-tfoH$_3$ · HCl
Transmittance [%]
Wavenumber cm-1
3253
3035
3016
2959
2936
2828
2753
2662
2612
2511
2406
2340
2318
2130
1956
1854
1728
1633
1539
1451
1431
1402
1349
1303
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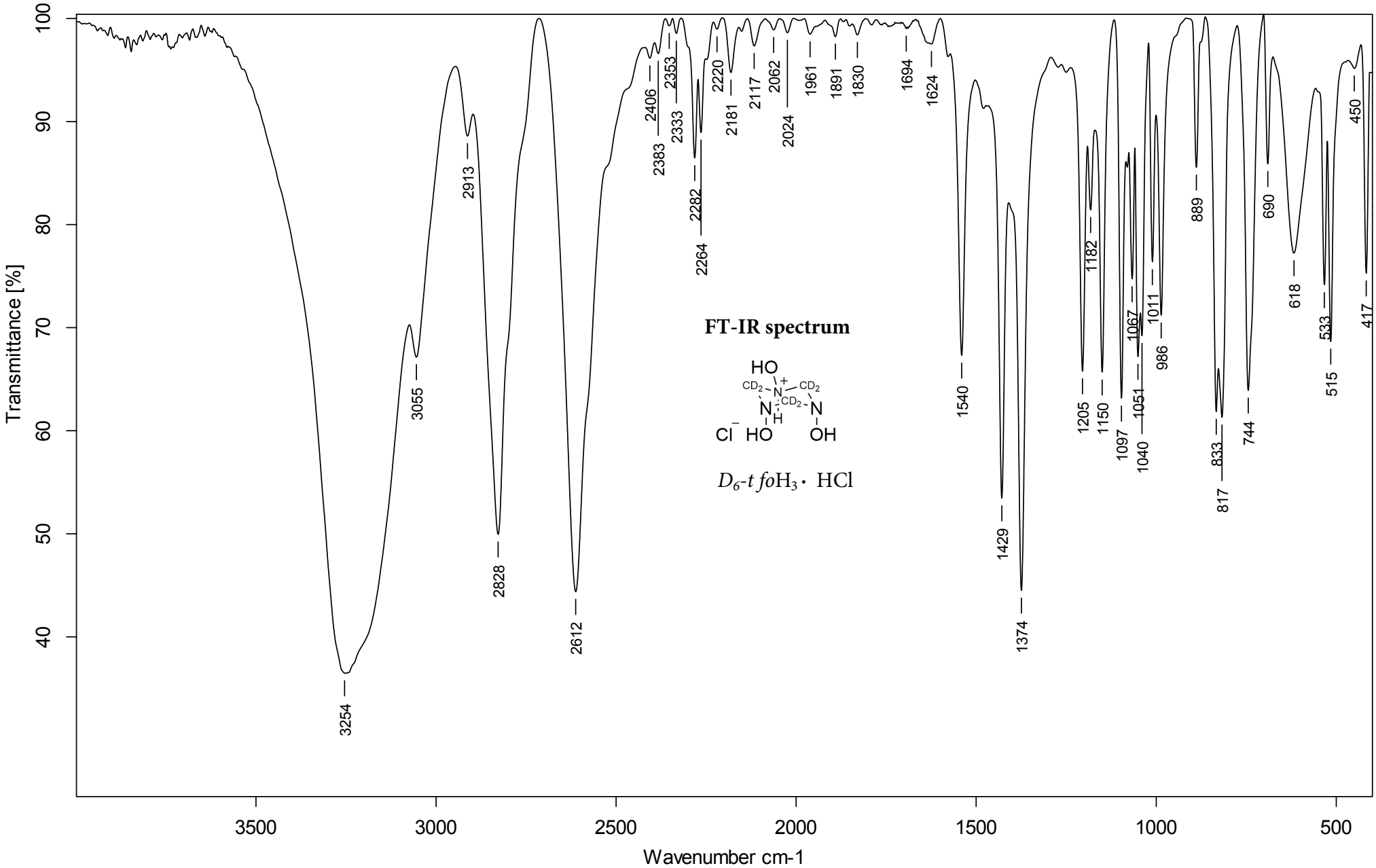
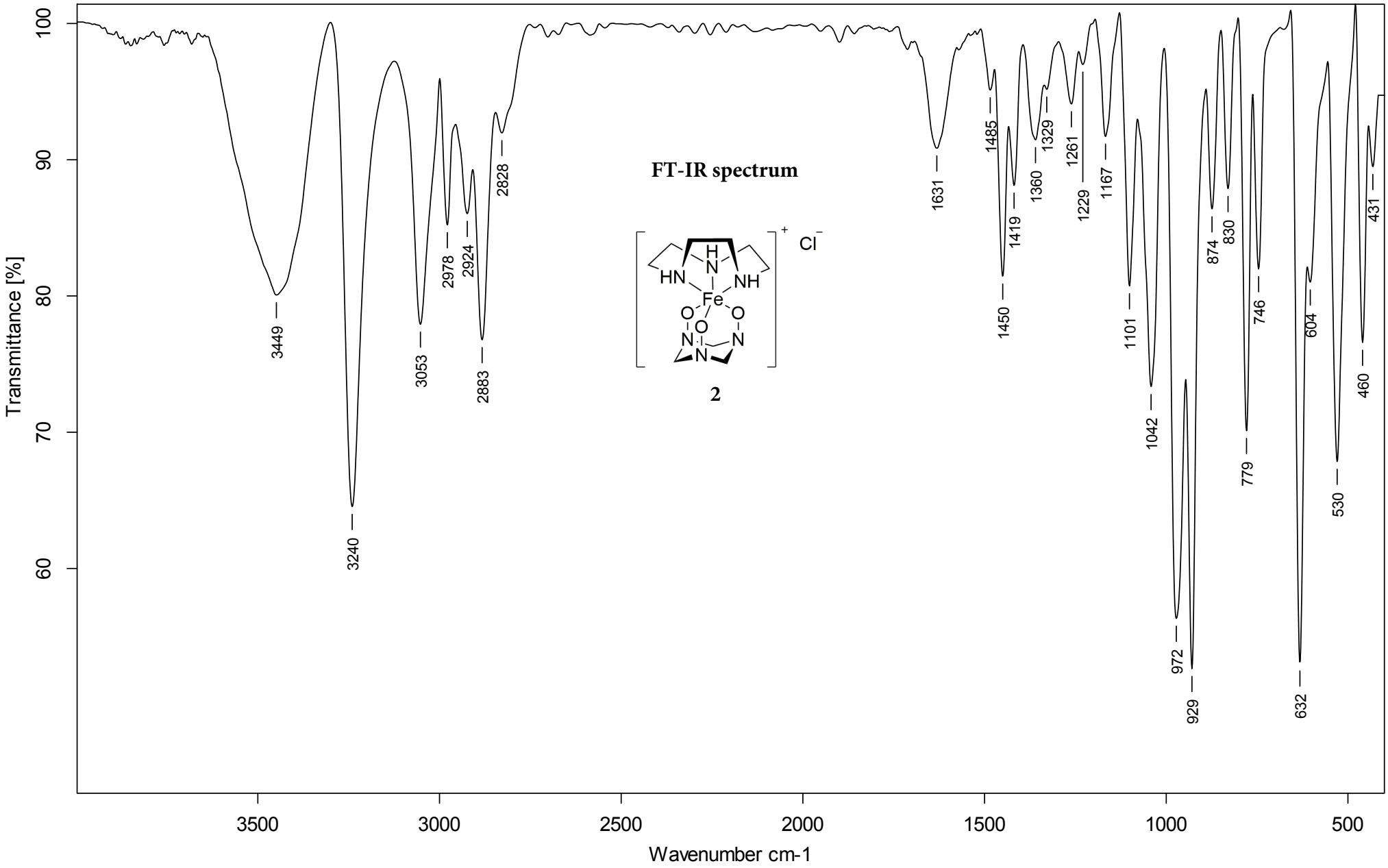
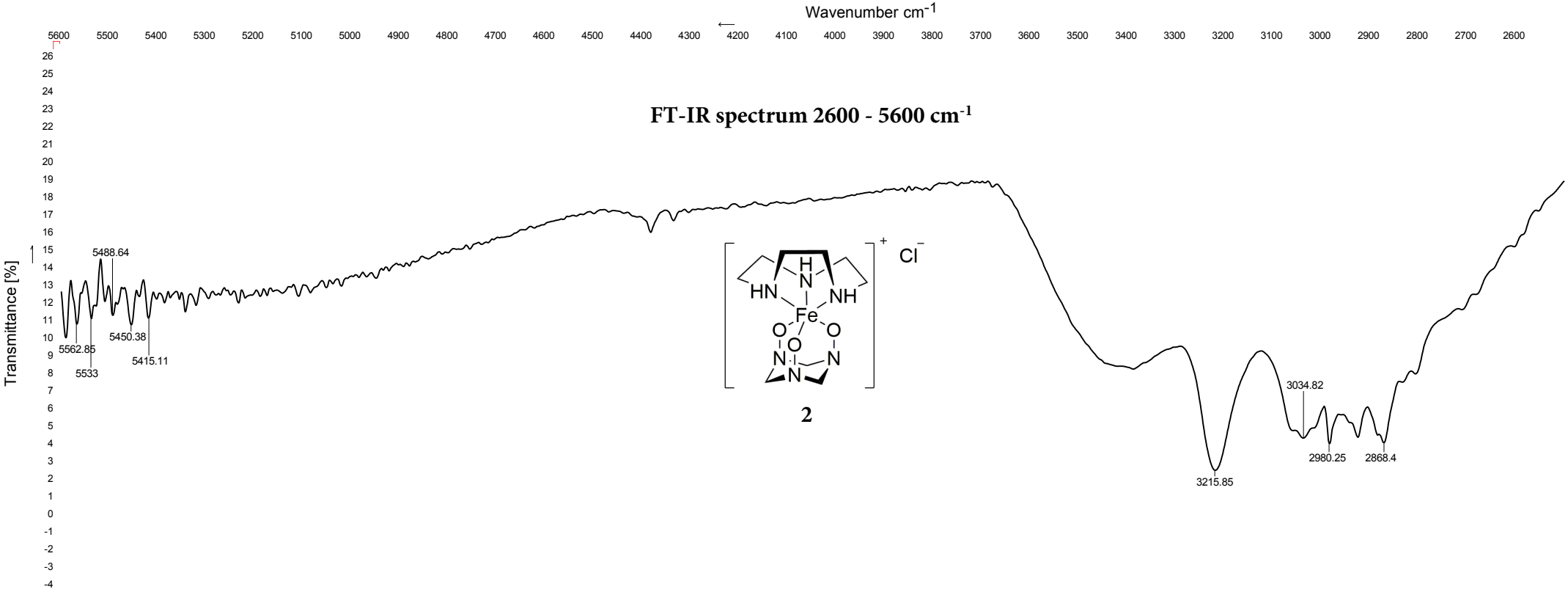
941
882
793
691
621
554
535
502
427

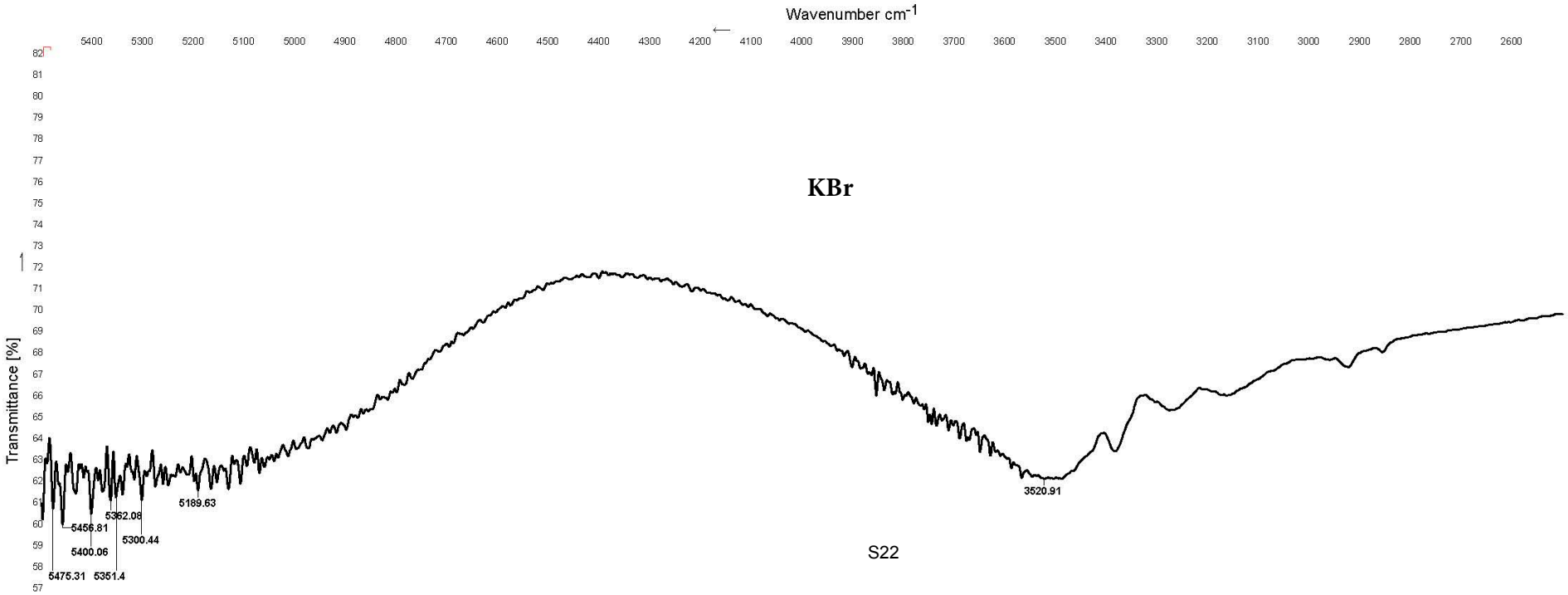

FT-IR spectrum
D_6-tfoH$_3$ · HCl
Transmittance [%]
Wavenumber cm-1
3254
3055
2913
2828
2612
2406
2383
2353
2333
2282
2264
2220
2181
2117
2062
2024
1961
1891
1830
1694
1624
1540
1429
1374
1205
1182
1150
1097
1067
1051
1040
1011
986
889
833
817
744
690
618
533
515
450
417

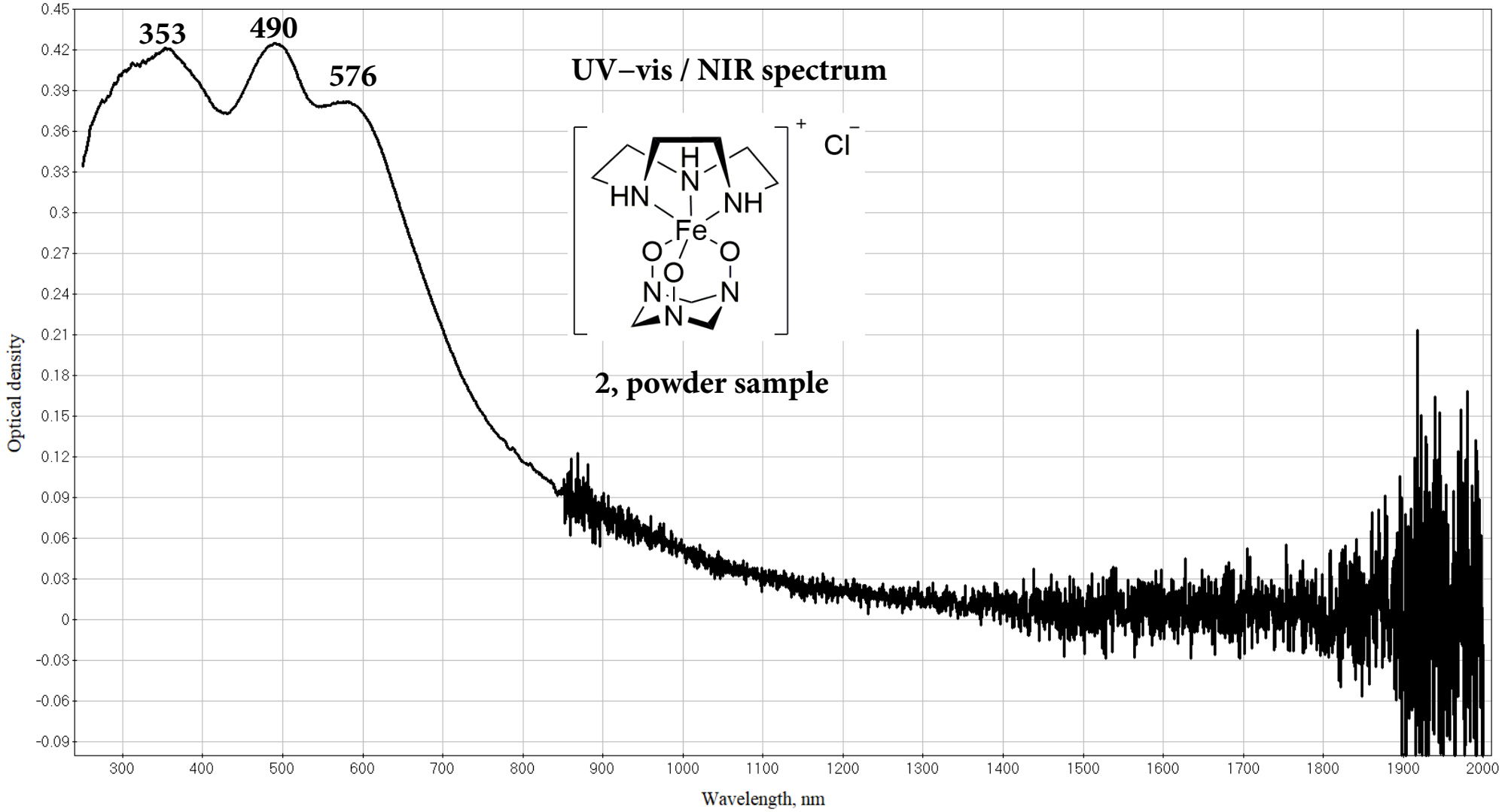

FT-IR spectrum
2
Transmittance [%]
Wavenumber cm-1
3449
3240
3053
2978
2924
2883
2828
1631
1485
1450
1419
1360
1329
1261
1229
1167
1101
1042
972
929
874
830
779
746
632
604
530
460
431

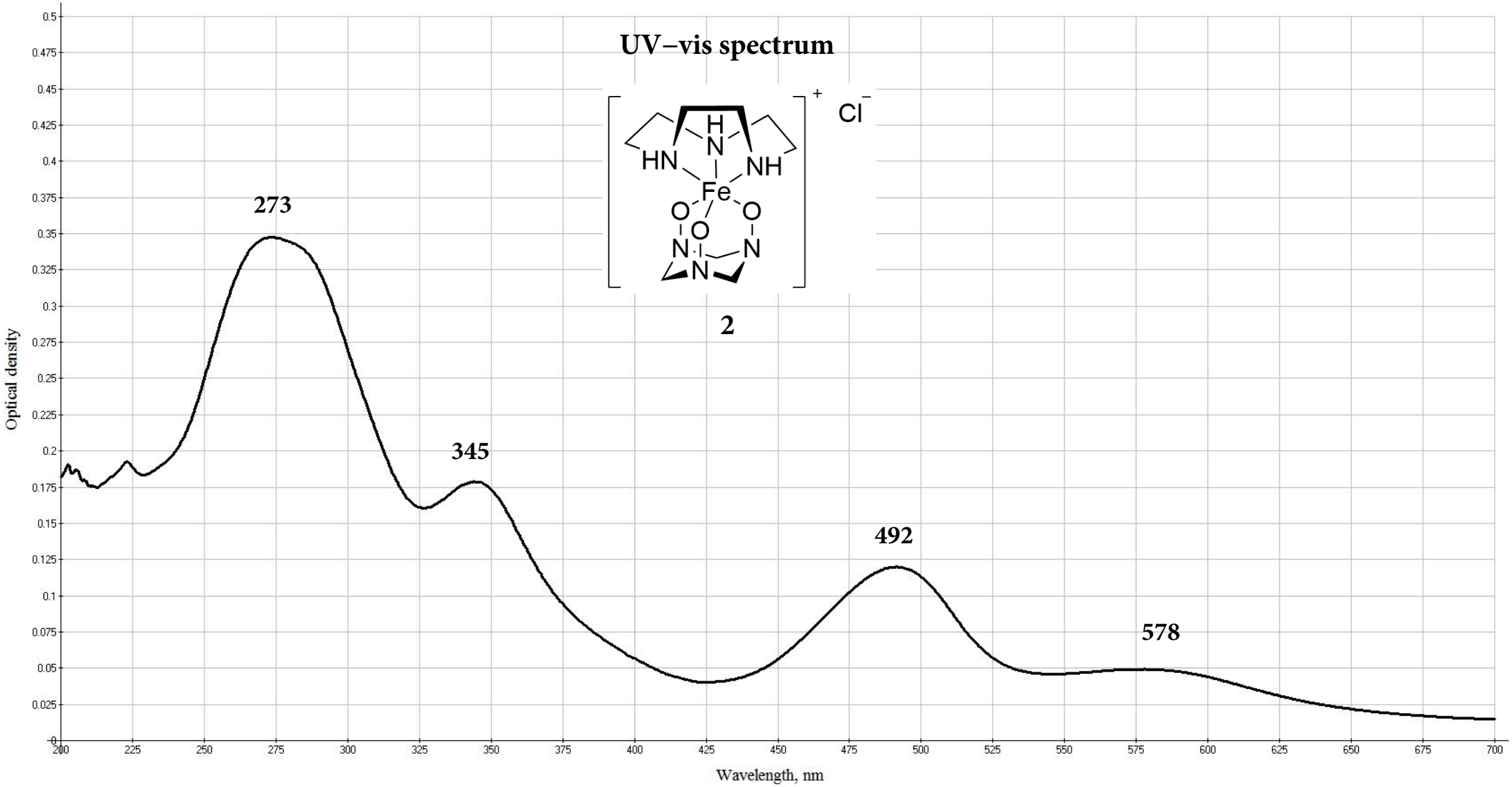
FT-IR spectrum 2600 - 5600 cm^{-1}



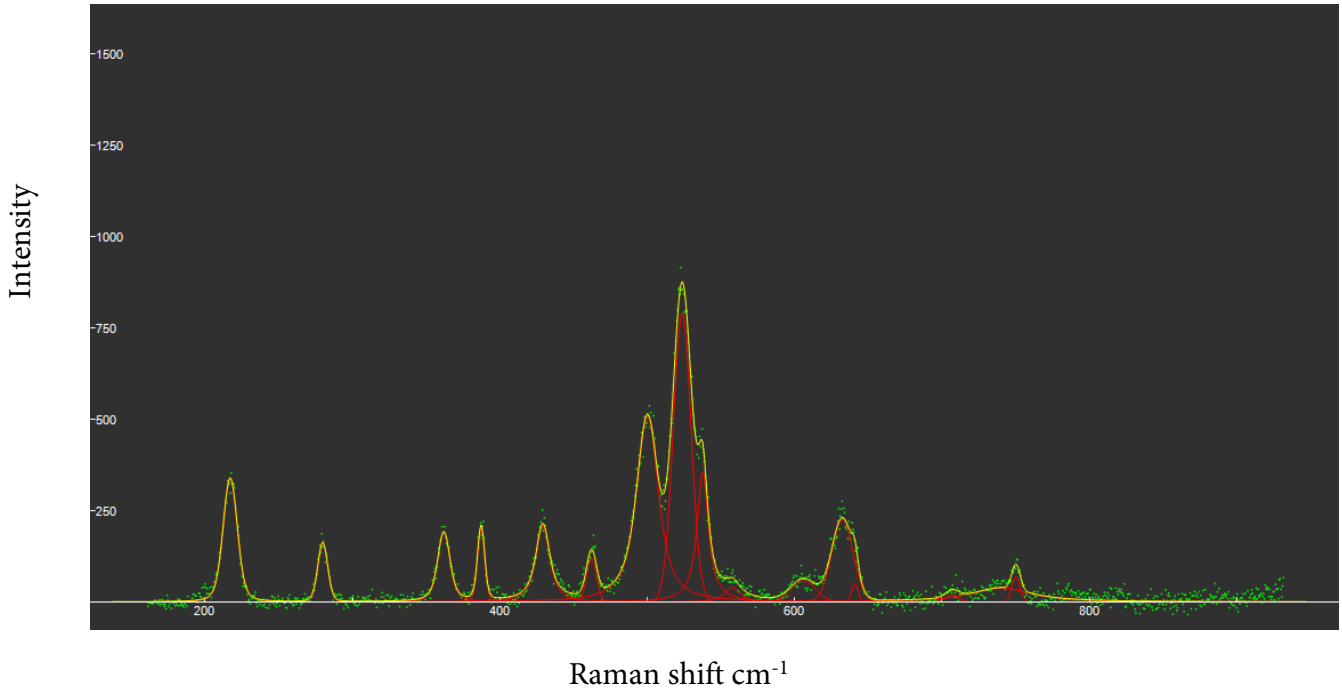
KBr

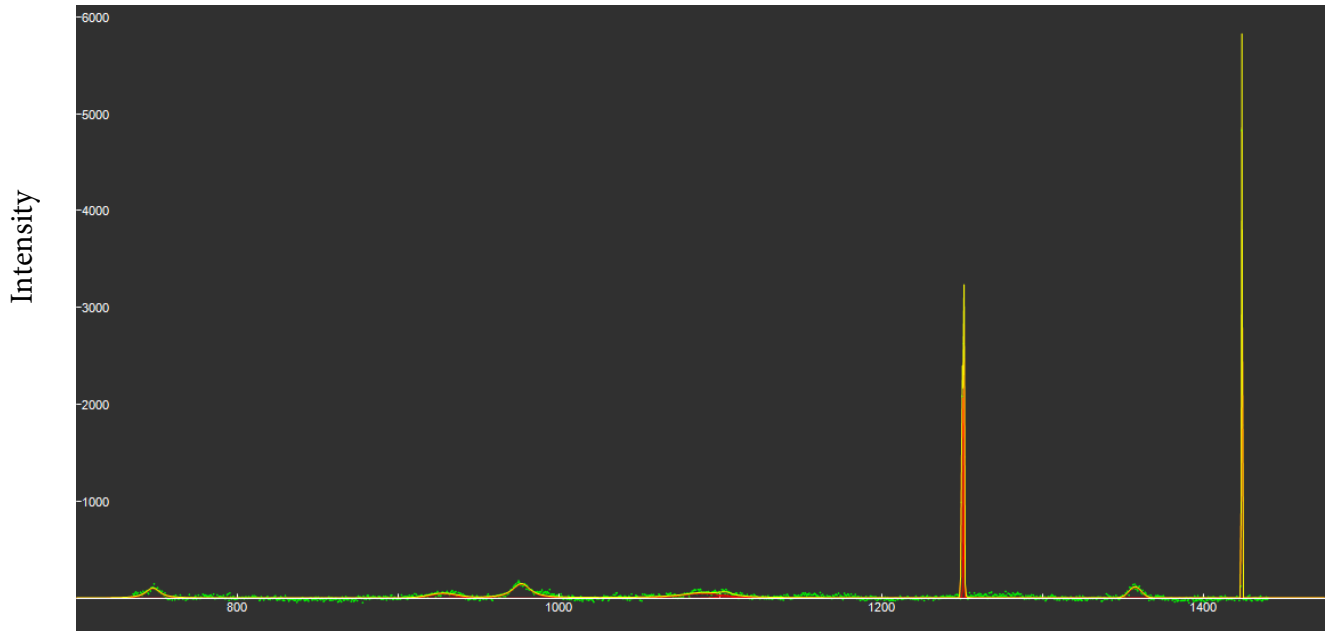


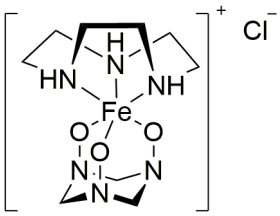

UV–vis / NIR spectrum
353
490
576
2, powder sample
Optical density
Wavelength, nm
0.45
0.42
0.39
0.36
0.33
0.3
0.27
0.24
0.21
0.18
0.15
0.12
0.09
0.06
0.03
0
-0.03
-0.06
-0.09
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000


UV–vis spectrum
Cl
2
273
345
492
578
Optical density
Wavelength, nm

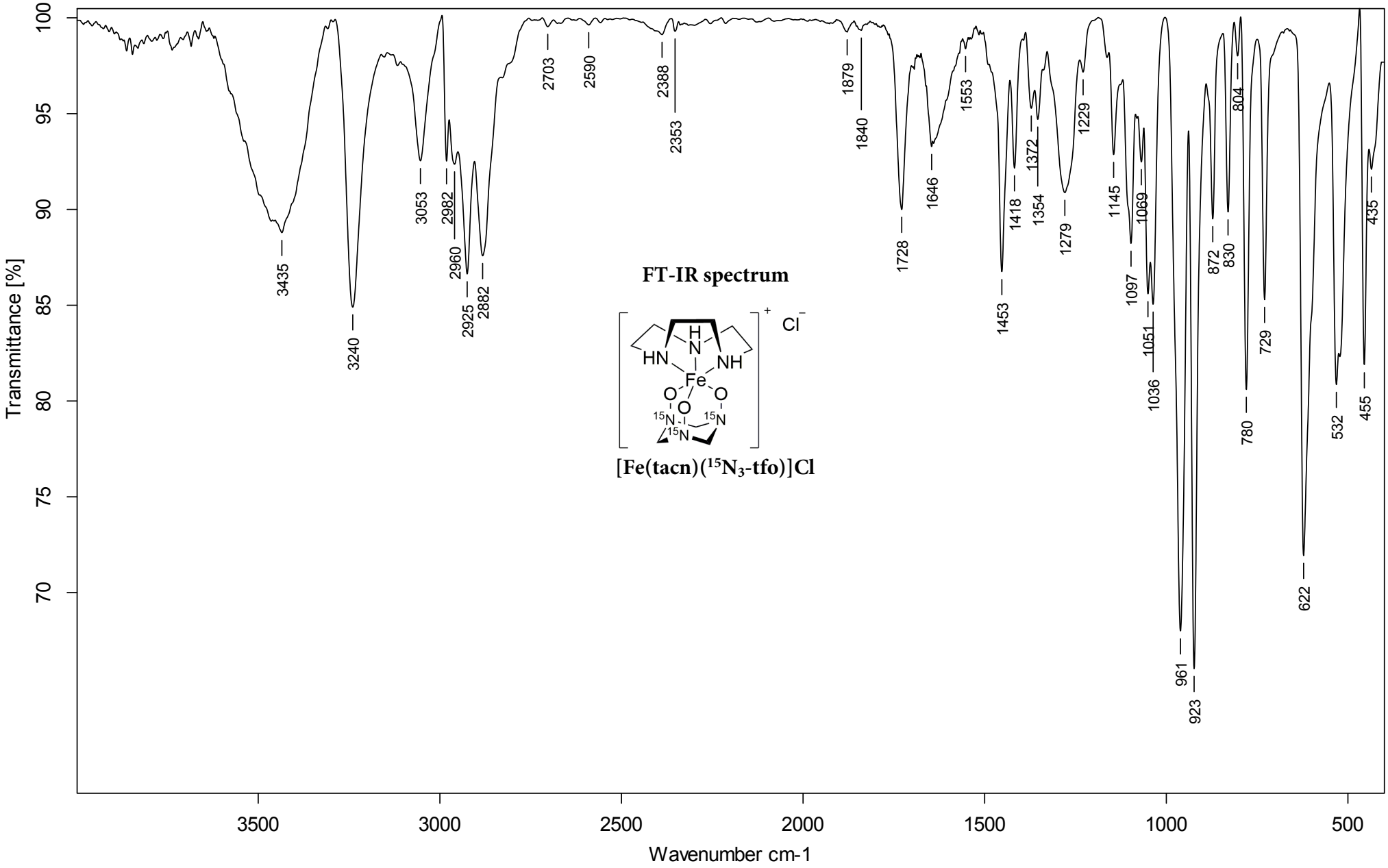
Raman spectrum







2


FT-IR spectrum
[Fe(tacn)(15N3-tfo)]Cl
Transmittance [%]
Wavenumber cm-1
3435
3240
3053
2982
2960
2925
2882
2703
2590
2388
2353
1879
1840
1728
1646
1553
1453
1418
1372
1354
1279
1229
1145
1097
1069
1051
1036
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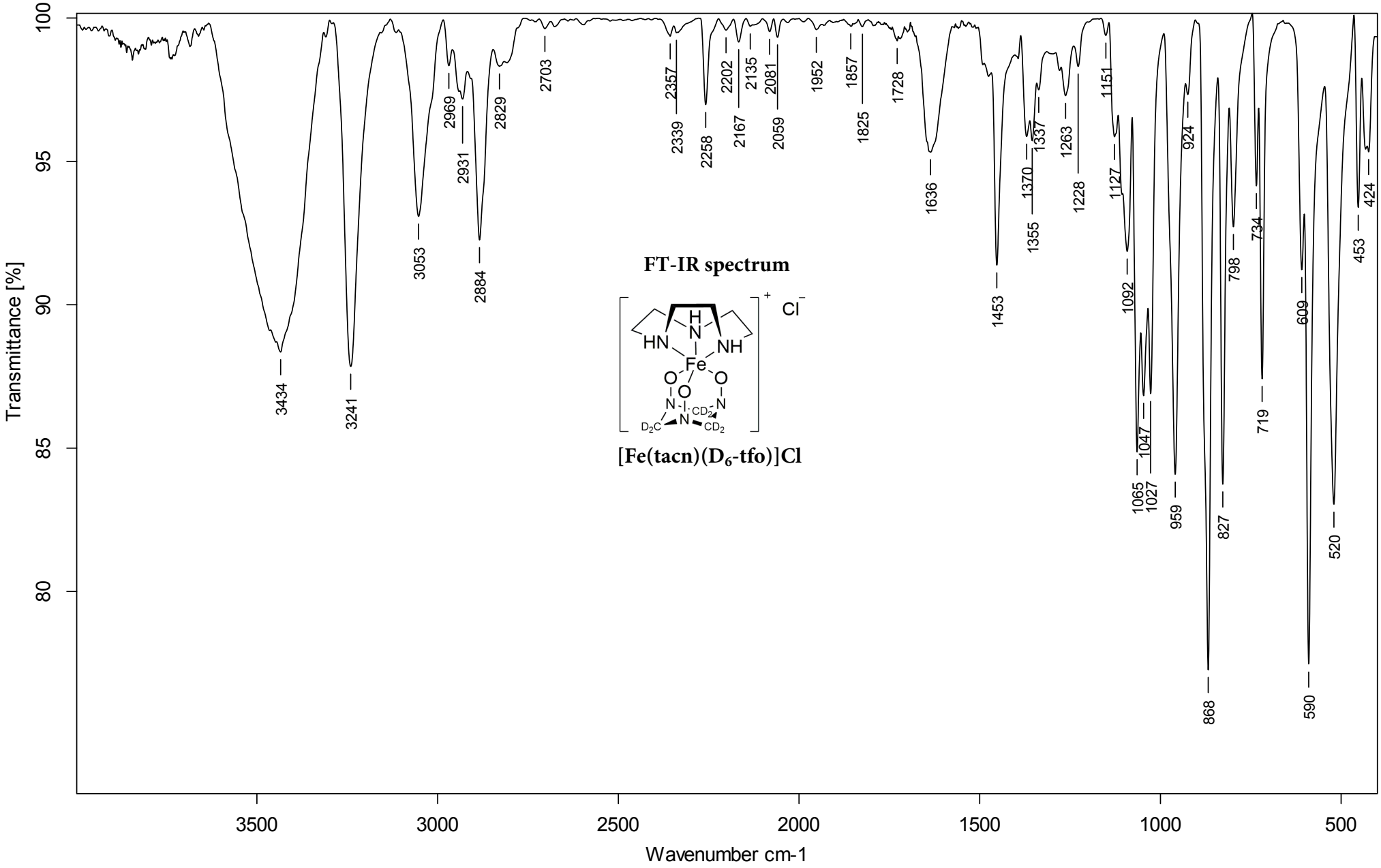
872
830
804
780
729
622
532
455
435


FT-IR spectrum
[Fe(tacn)(D6-tfo)]Cl
Transmittance [%]
Wavenumber cm-1
3434
3241
3053
2969
2931
2884
2829
2703
2357
2339
2258
2202
2167
2135
2081
2059
1952
1857
1825
1728
1636
1453
1370
1355
1337
1263
1228
1151
1127
1092
1065
1047
1027
959
924
868
827
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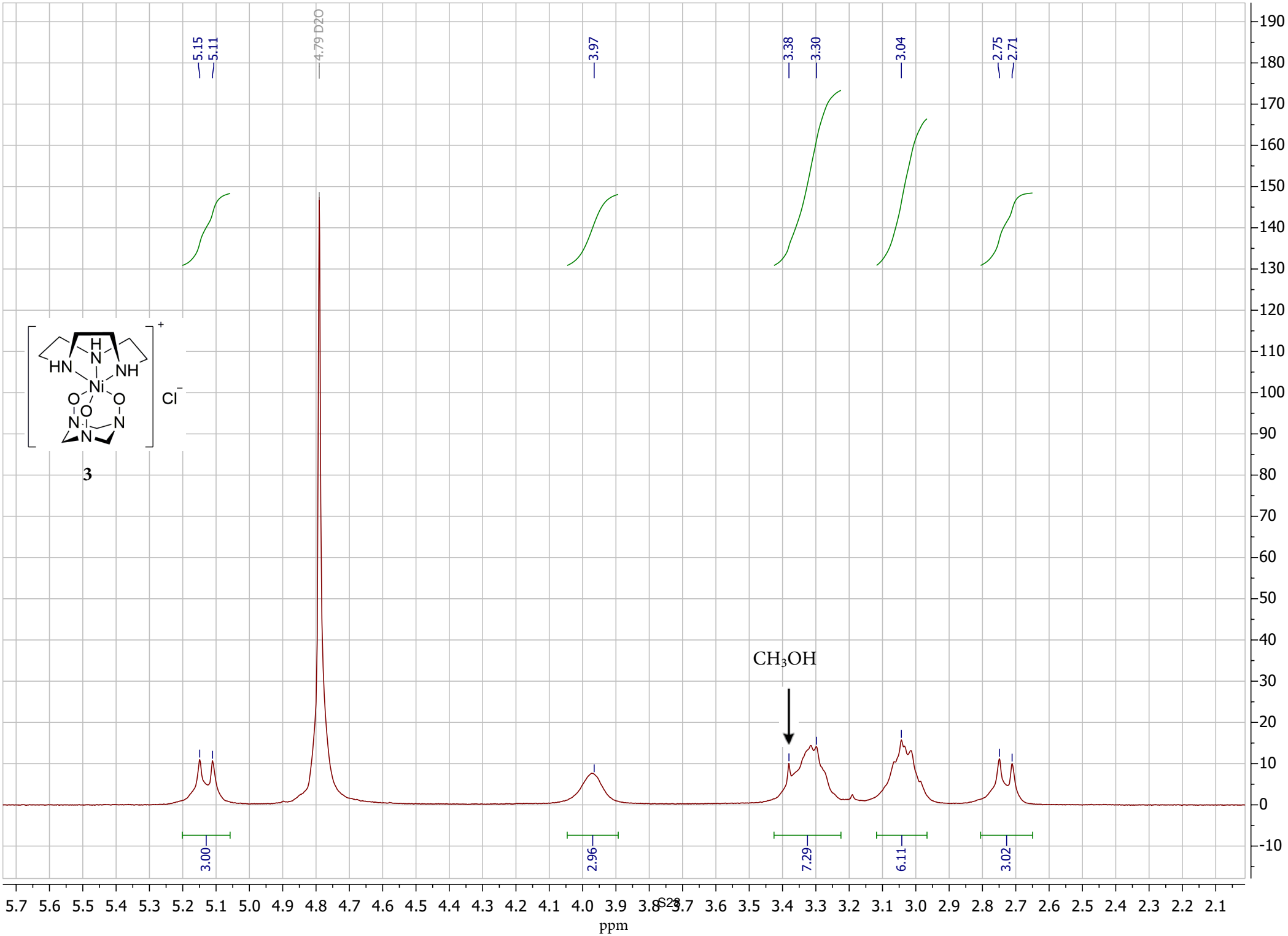
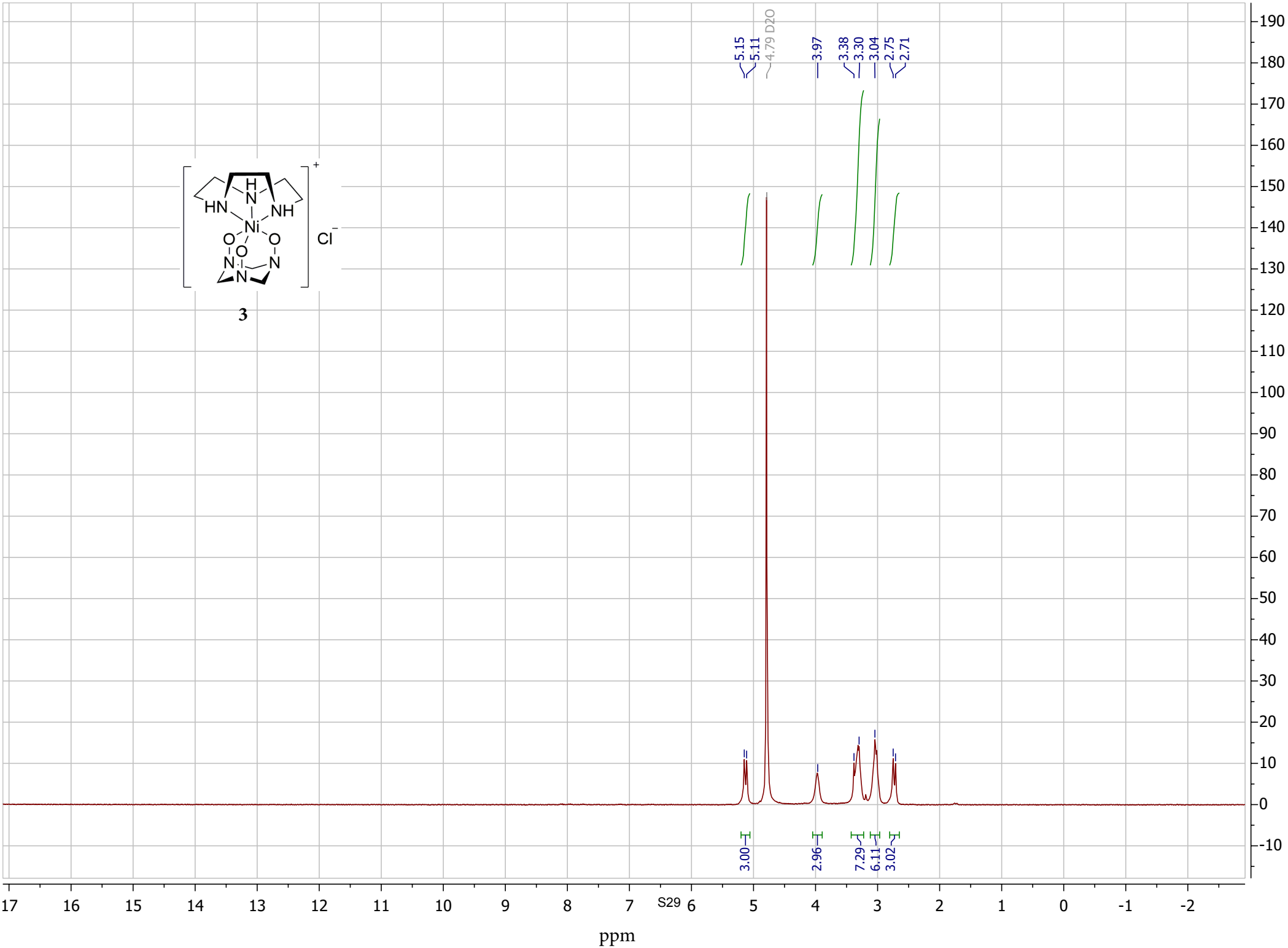
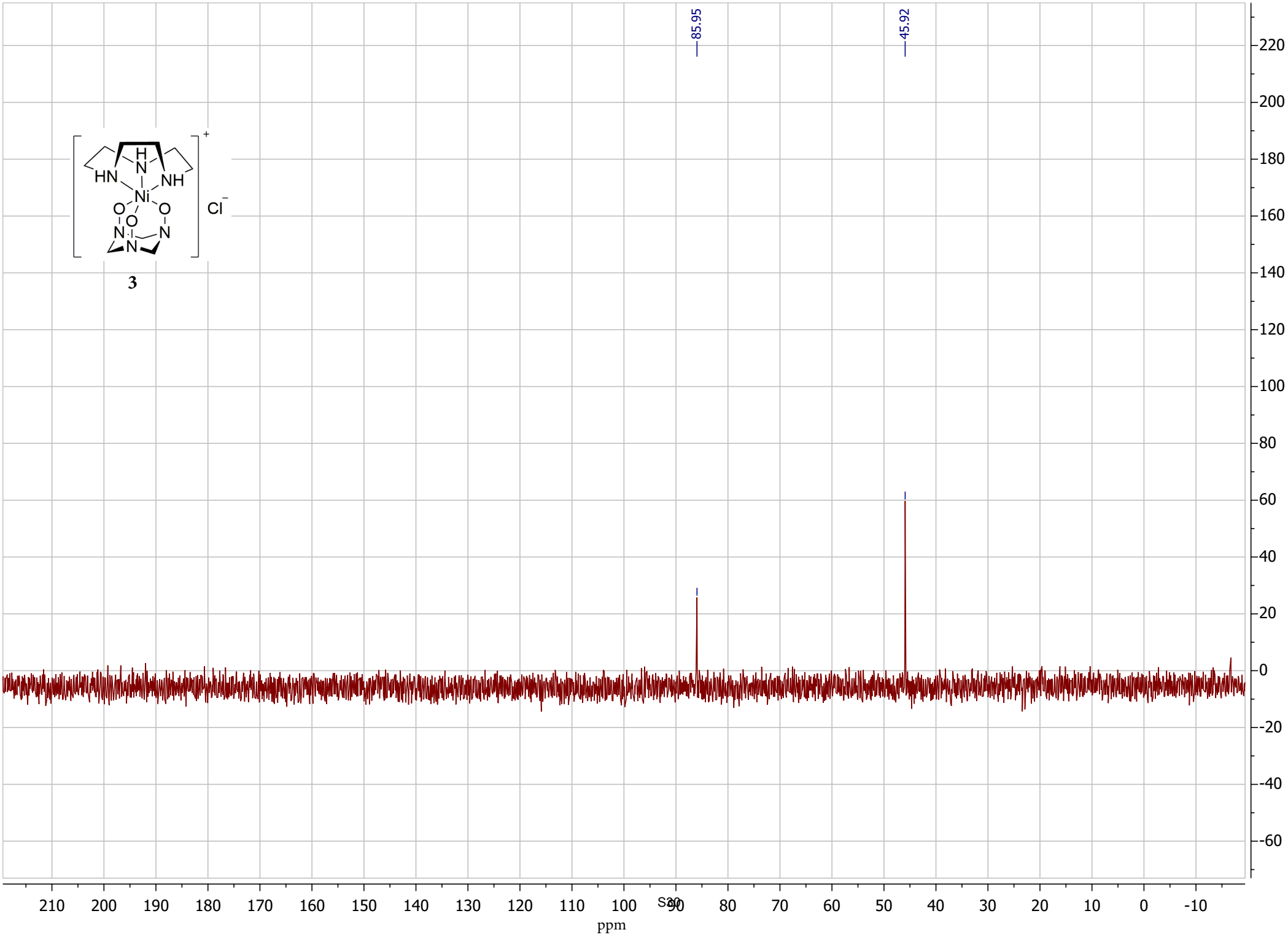
2500
2000
1500
1000
500
100
95
90
85
80


5.15
5.11
4.79 D2O
3.97
3.38
3.30
3.04
2.75
2.71
3.00
2.96
7.29
6.11
3.02
CH3OH
Cl−
3
ppm

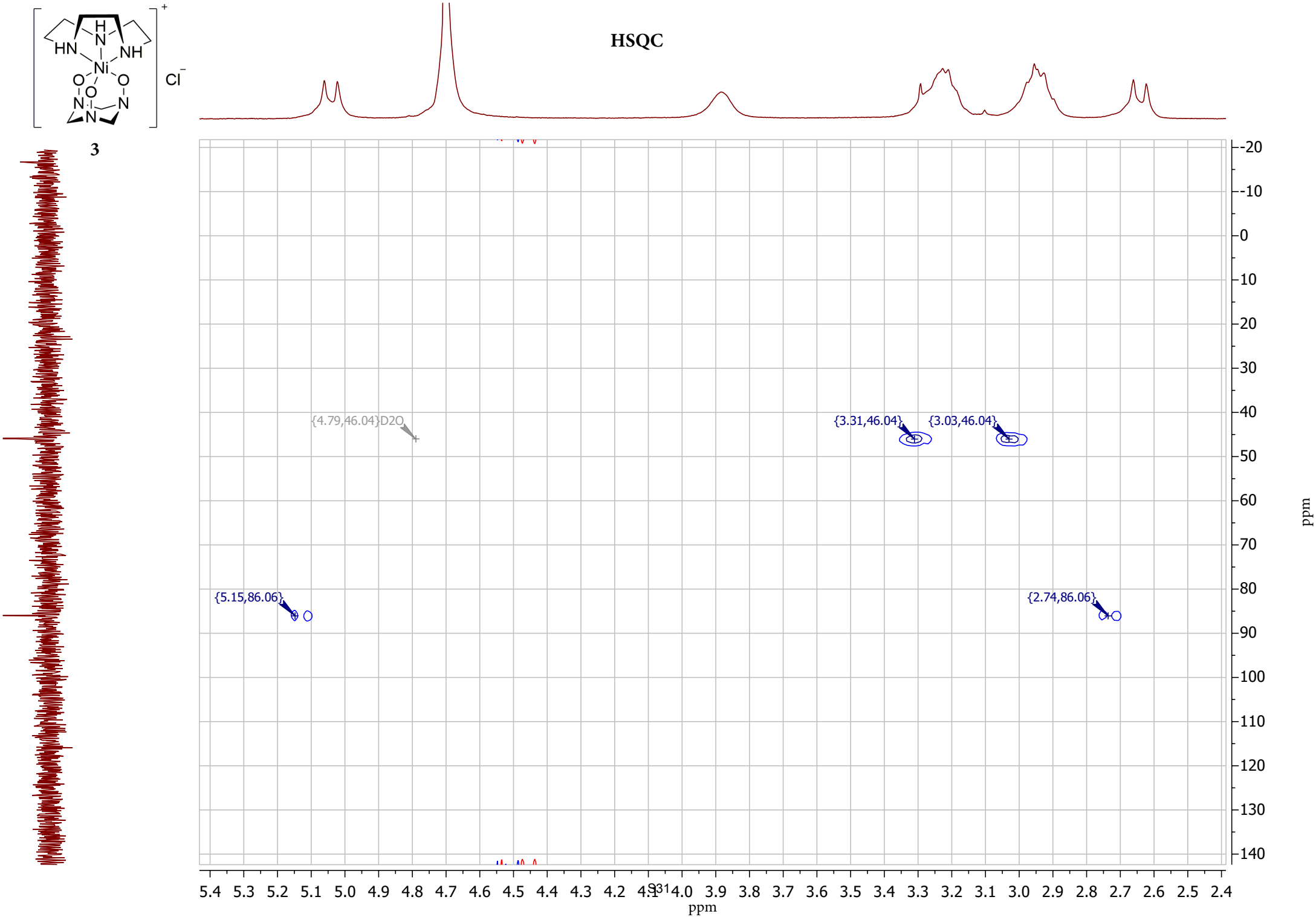

5.15
5.11
4.79 D2O
3.97
3.38
3.30
3.04
2.75
2.71
3.00
2.96
7.29
6.11
3.02
Cl⁻
3
ppm

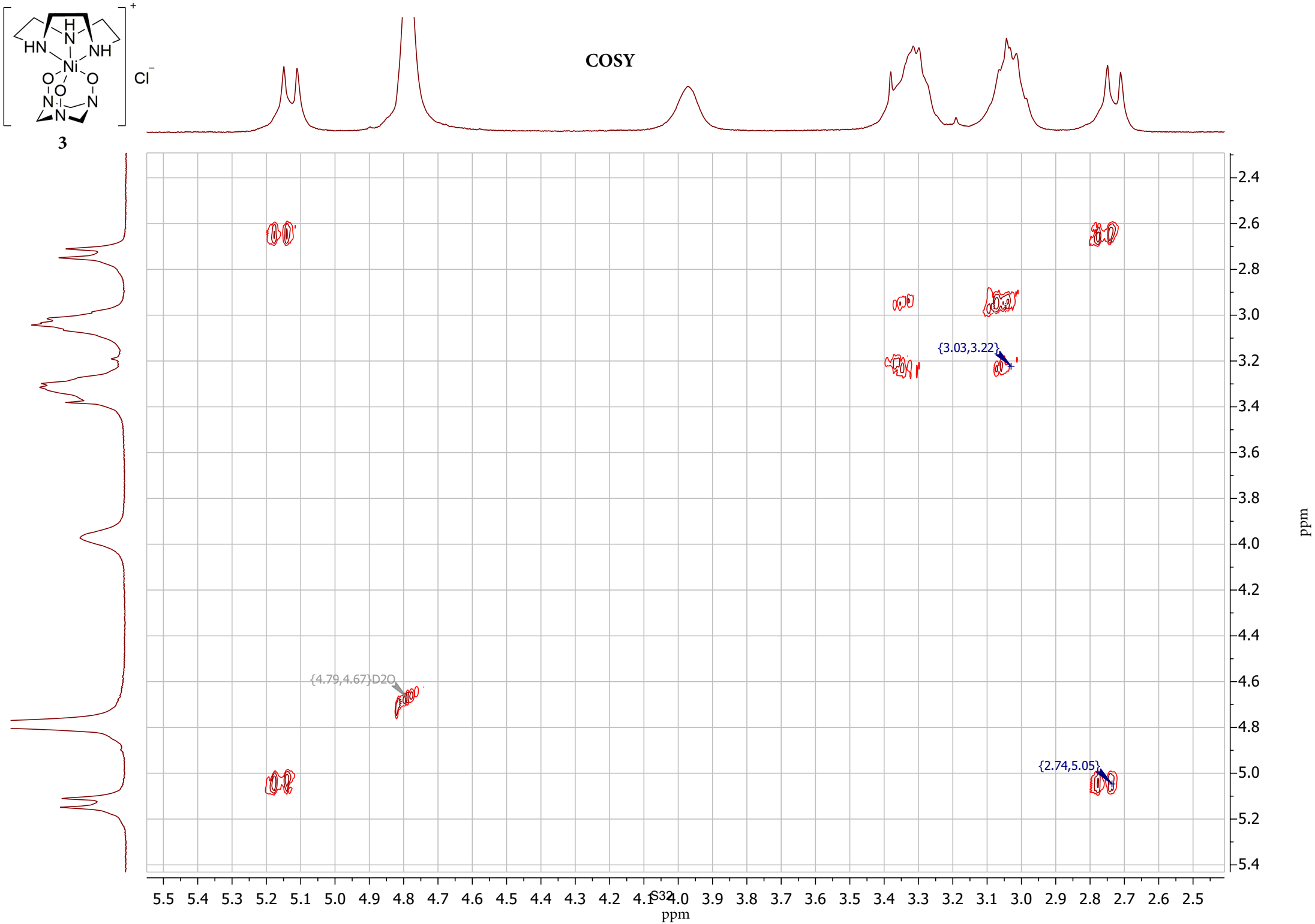

85.95
45.92
3
ppm

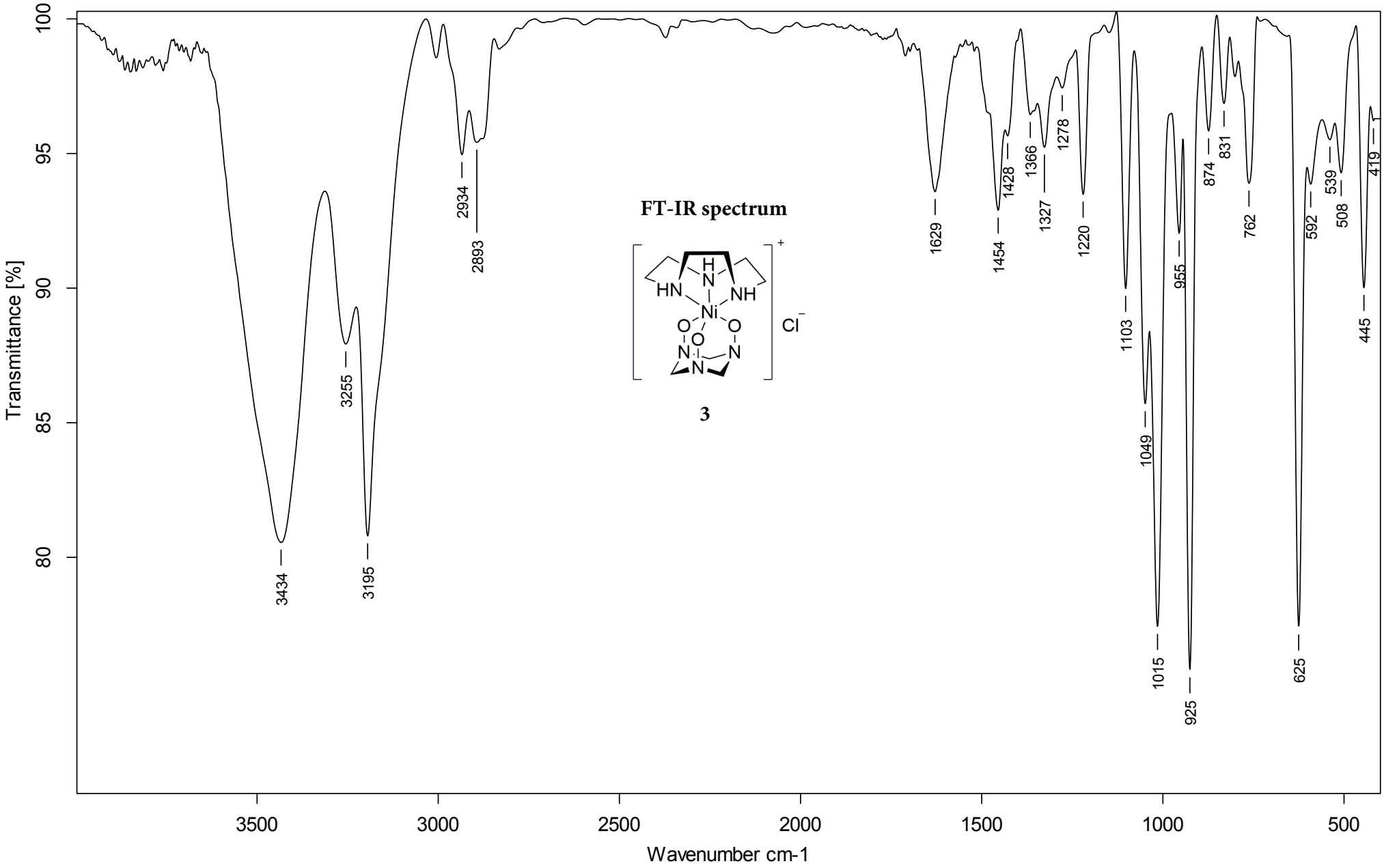
HN
NH
Ni
O
N
Cl

3

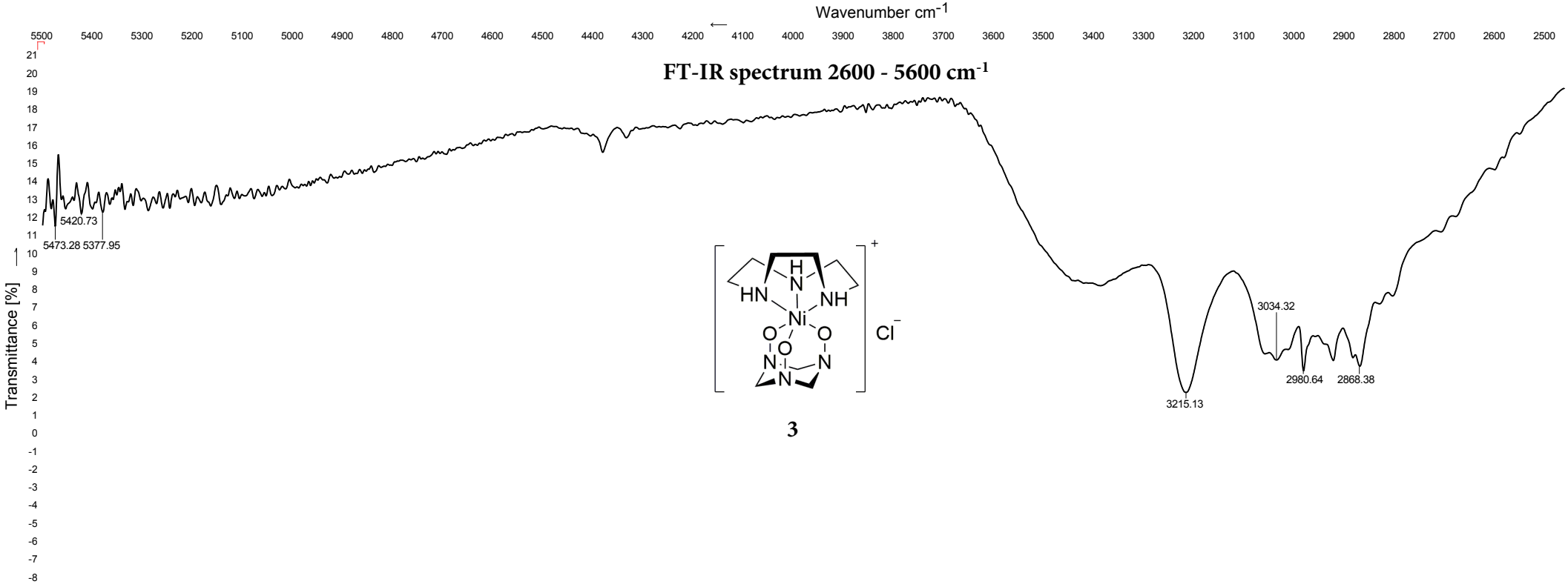
HSQC


{4.79,46.04}D2O
{3.31,46.04}
{3.03,46.04}
{5.15,86.06}
{2.74,86.06}
ppm
ppm


3
COSY
{3.03,3.22}
{4.79,4.67}D2O
{2.74,5.05}
ppm
ppm

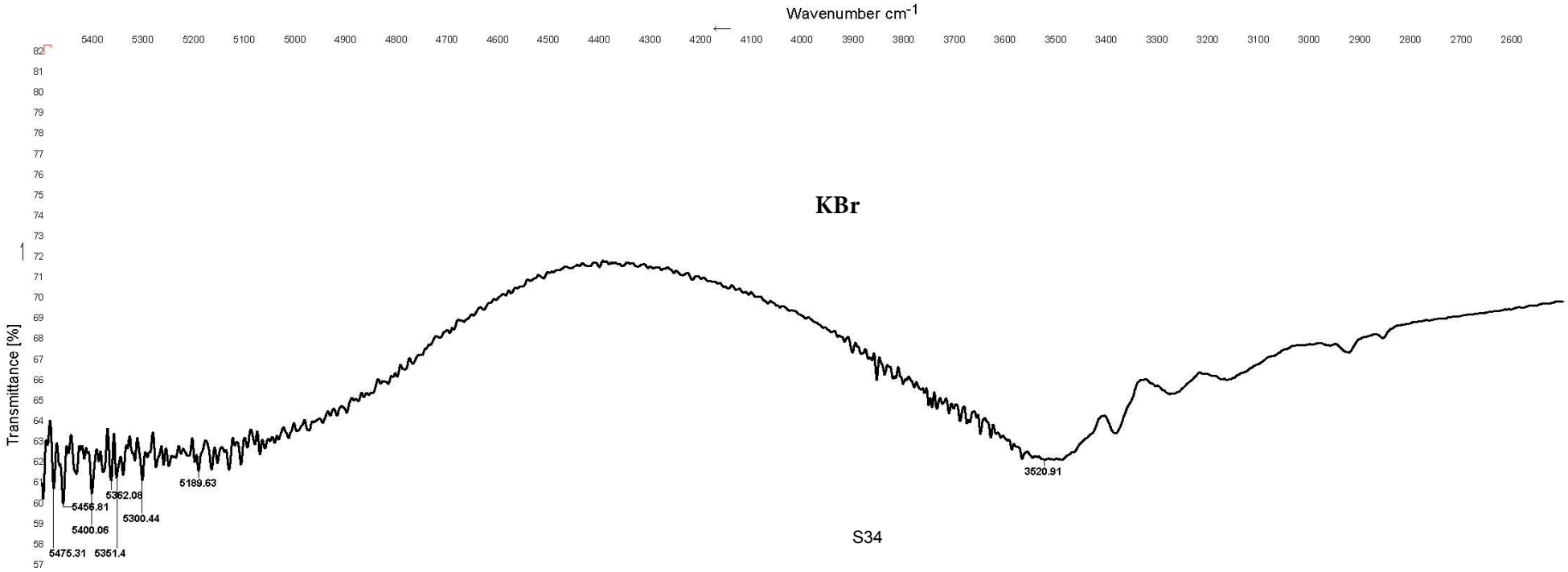

FT-IR spectrum
3
Transmittance [%]
Wavenumber cm-1
100
95
90
85
80
3500
3000
2500
2000
1500
1000
500
3434
3255
3195
2934
2893
1629
1454
1428
1366
1327
1278
1220
1103
1049
1015
955
925
874
831
762
625
592
539
508
445
419
Cl⁻

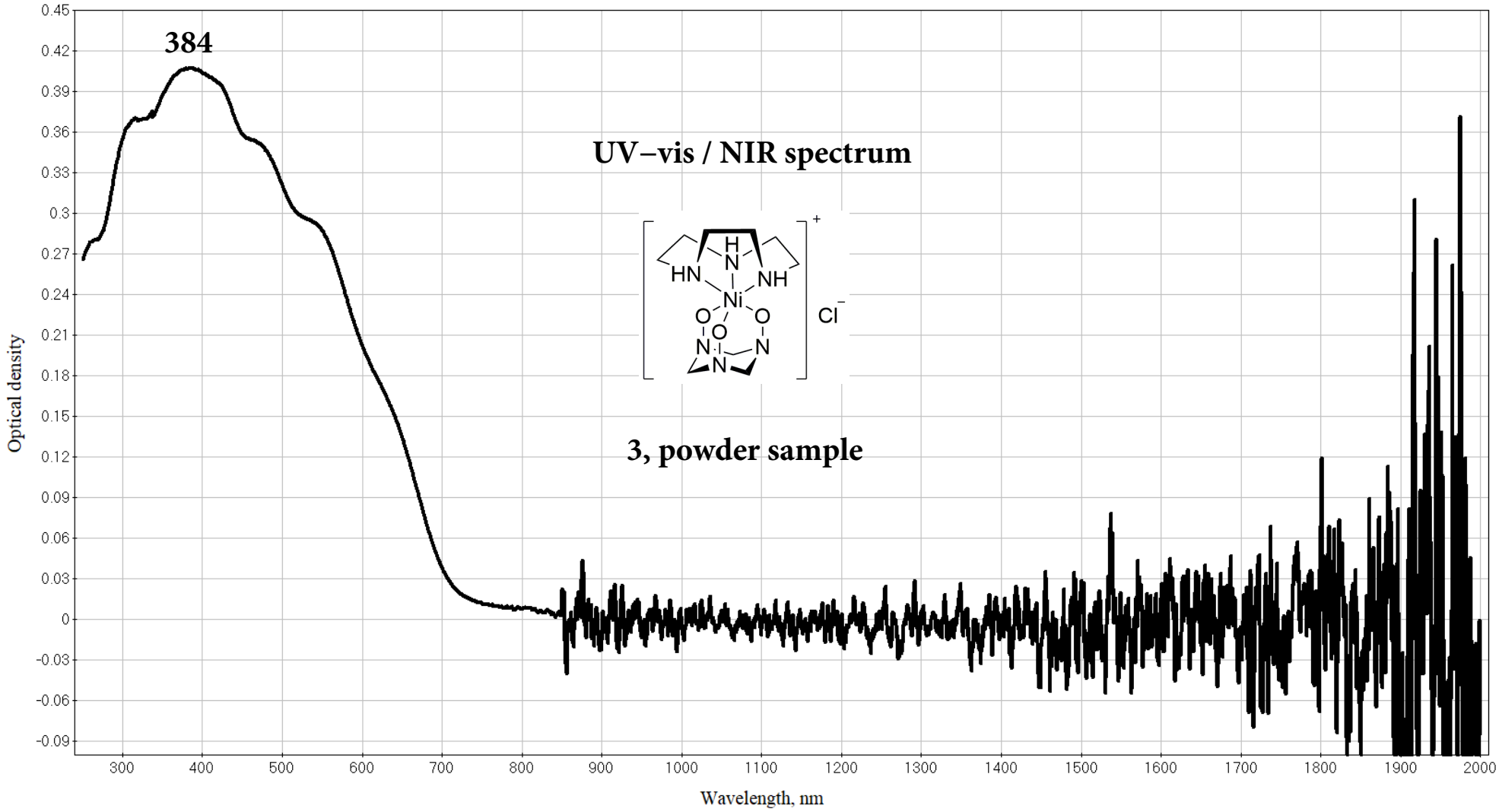
FT-IR spectrum 2600 - 5600 cm^{-1}

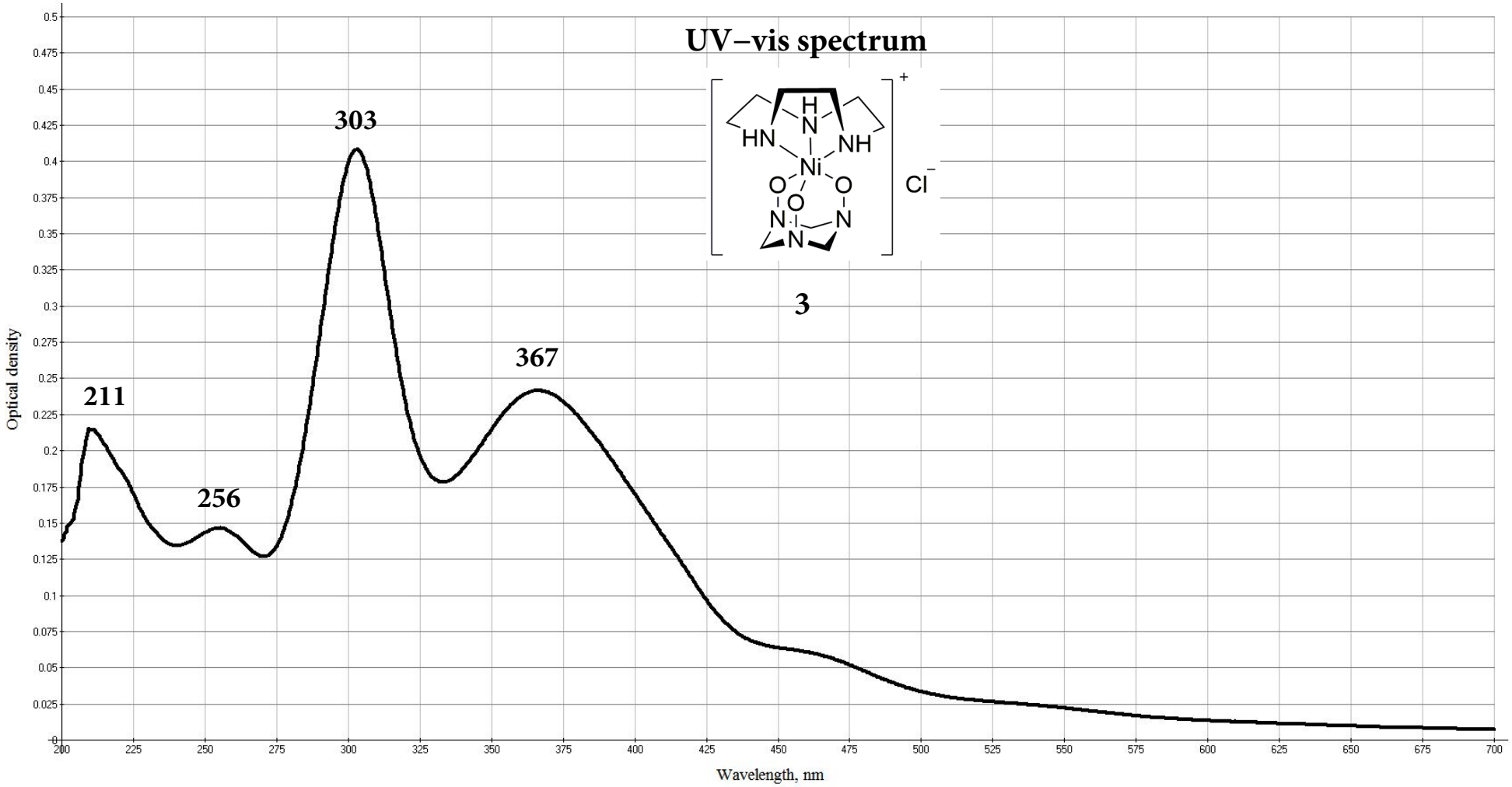


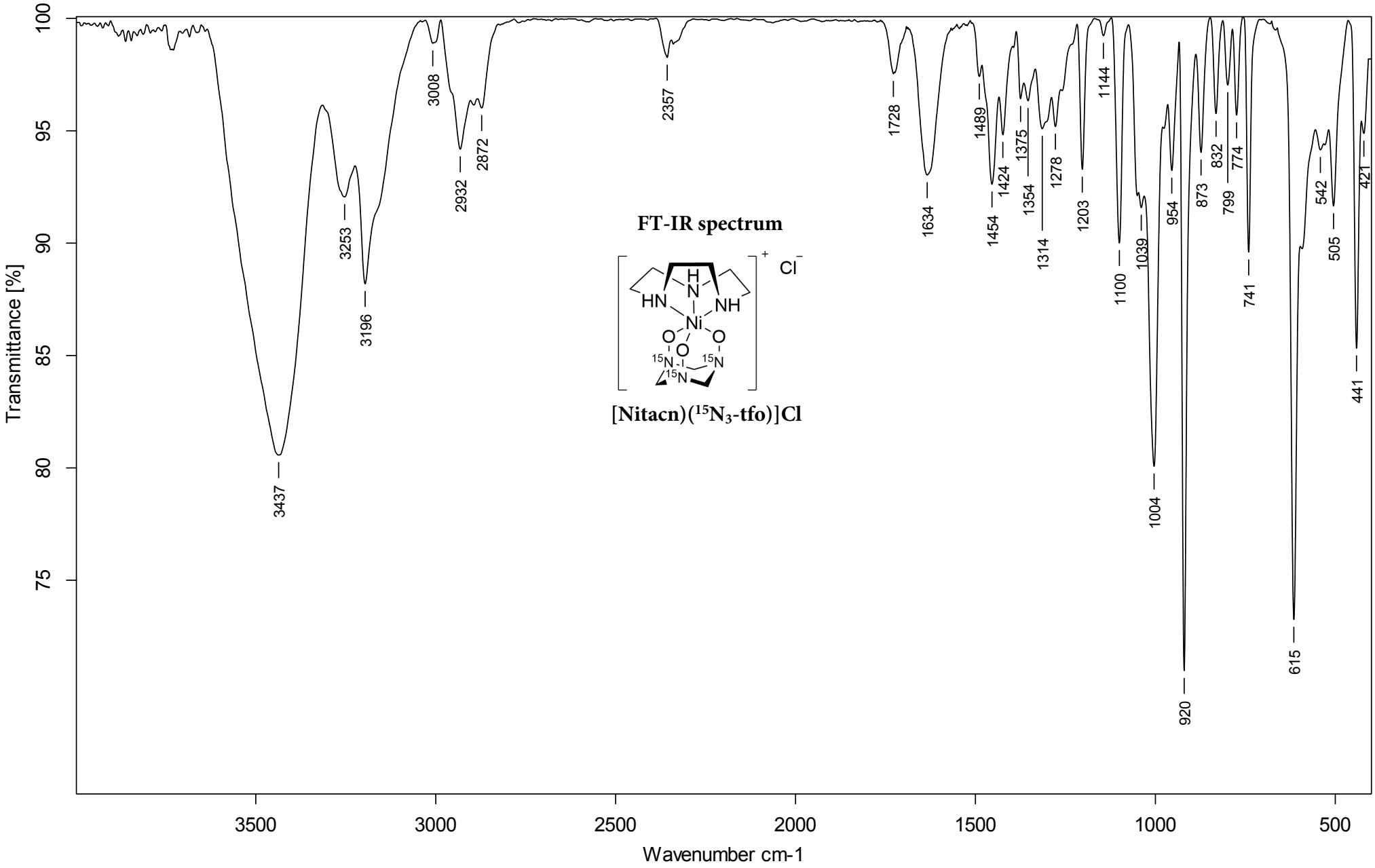
3

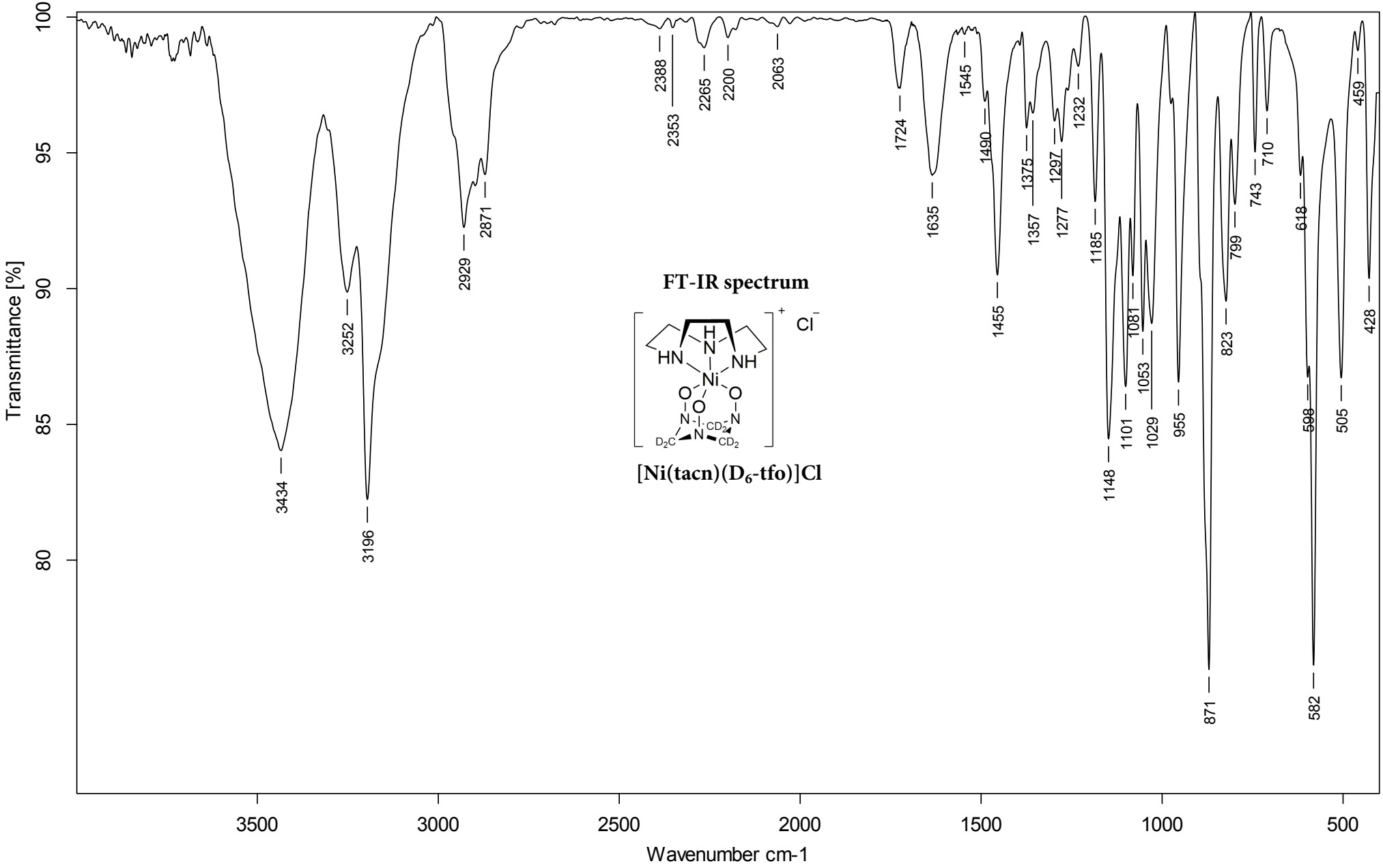
KBr

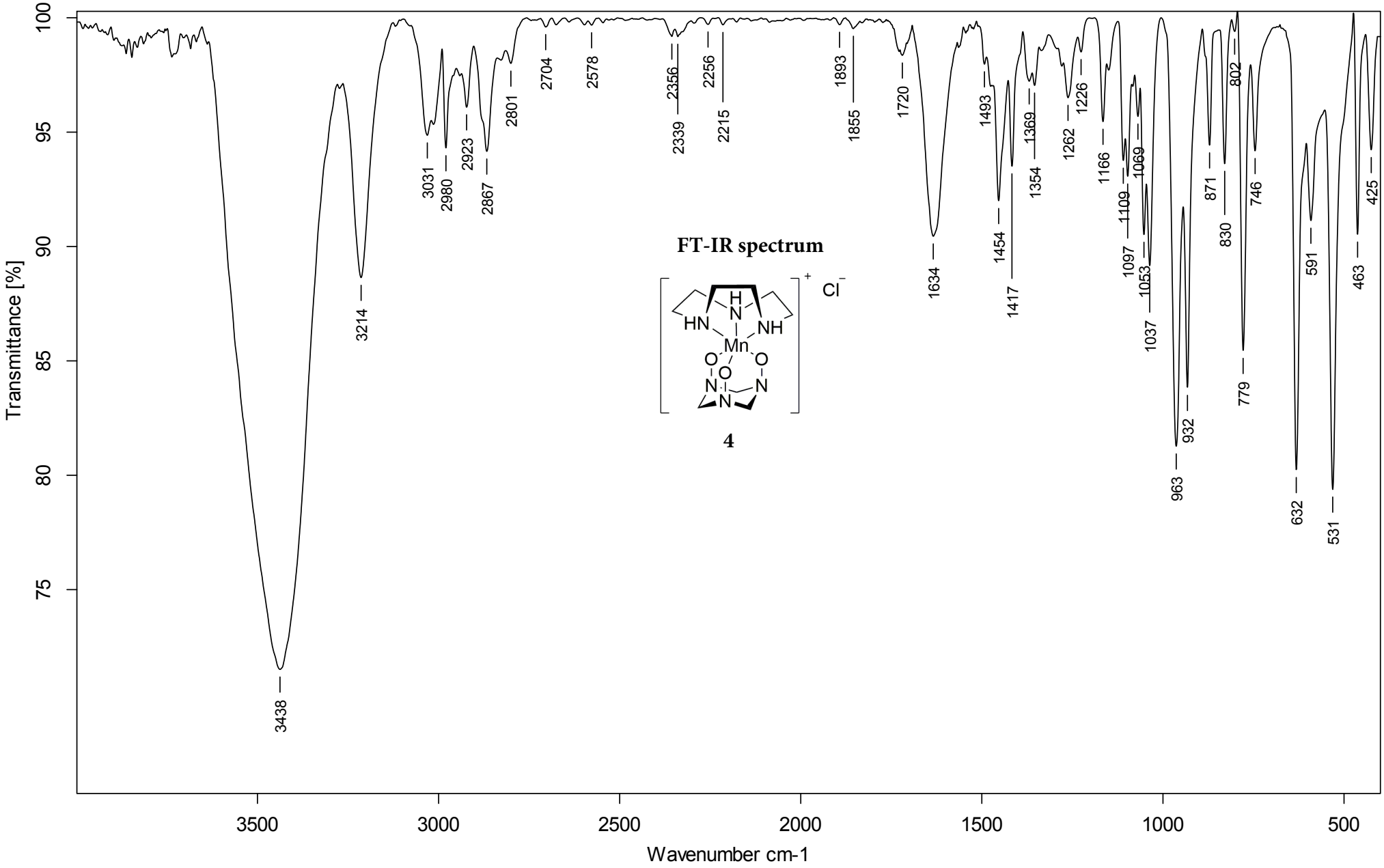


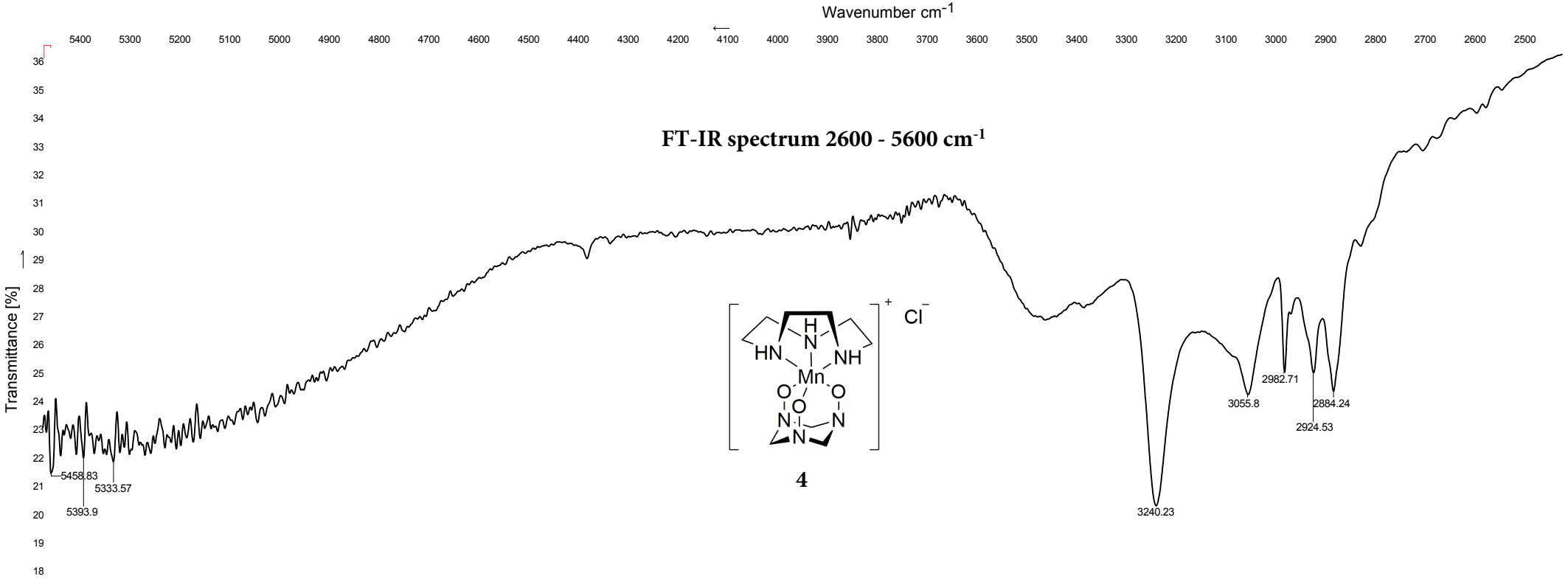

384
UV–vis / NIR spectrum
3, powder sample
Optical density
Wavelength, nm
0.45
0.42
0.39
0.36
0.33
0.3
0.27
0.24
0.21
0.18
0.15
0.12
0.09
0.06
0.03
0
-0.03
-0.06
-0.09
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000

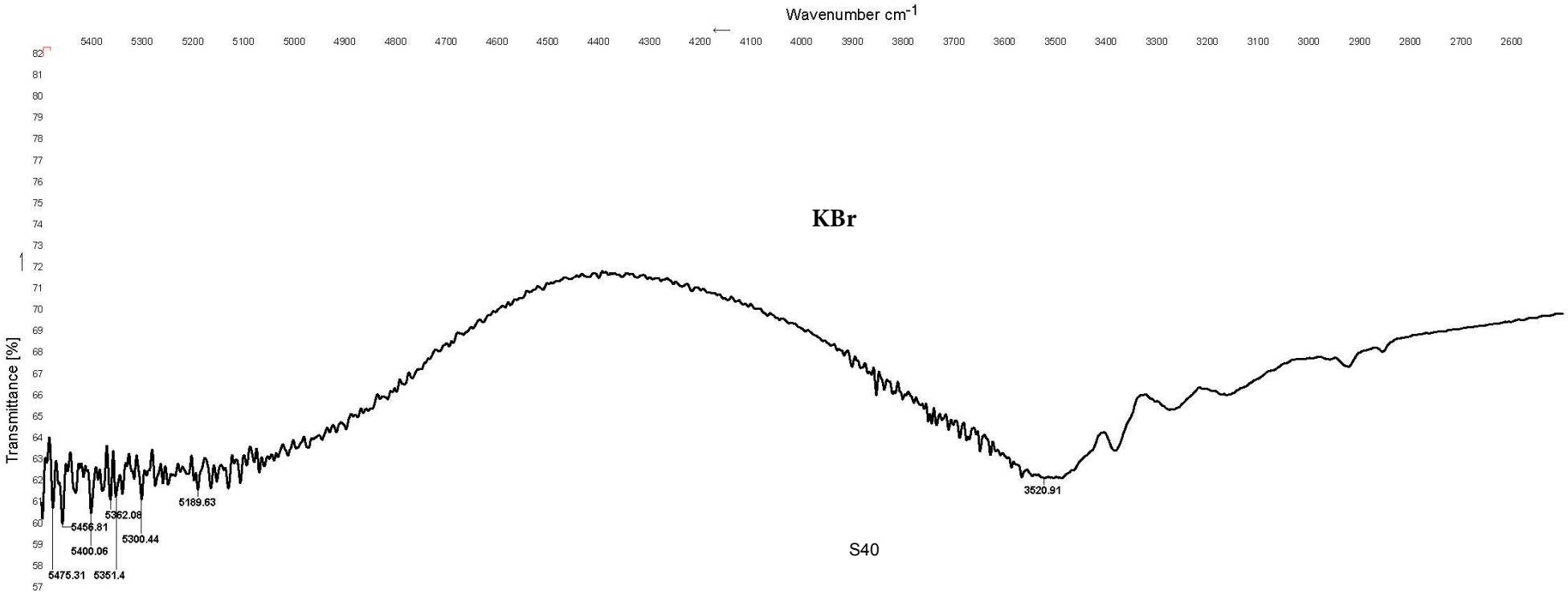

UV–vis spectrum
303
367
211
256
3
Optical density
Wavelength, nm

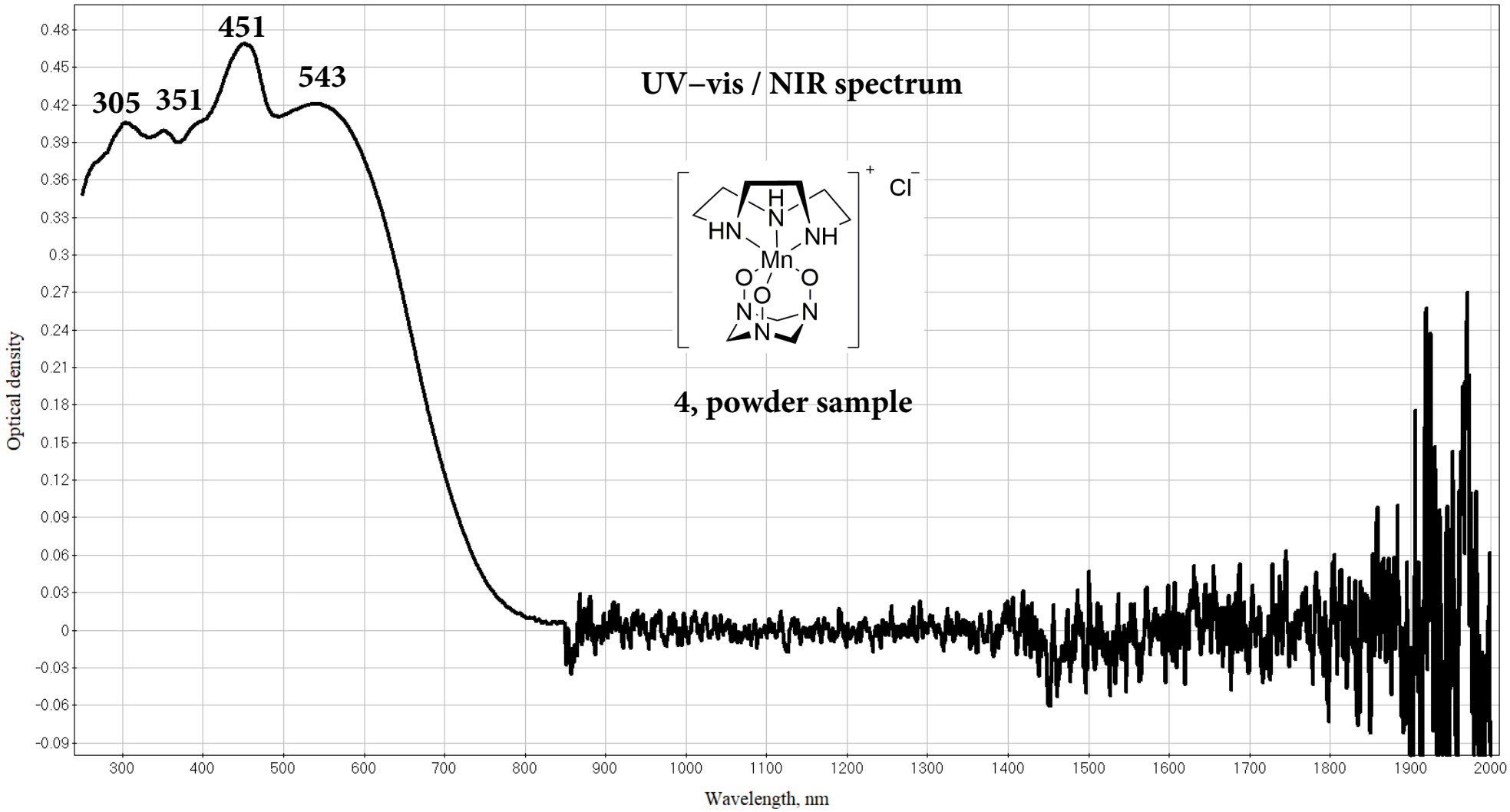

FT-IR spectrum
[Nitacn)(15N3-tfo)]Cl
Transmittance [%]
Wavenumber cm-1
3437
3253
3196
3008
2932
2872
2357
1728
1634
1489
1454
1424
1375
1354
1314
1278
1203
1144
1100
1039
1004
954
920
873
832
799
774
741
615
542
505
441
421

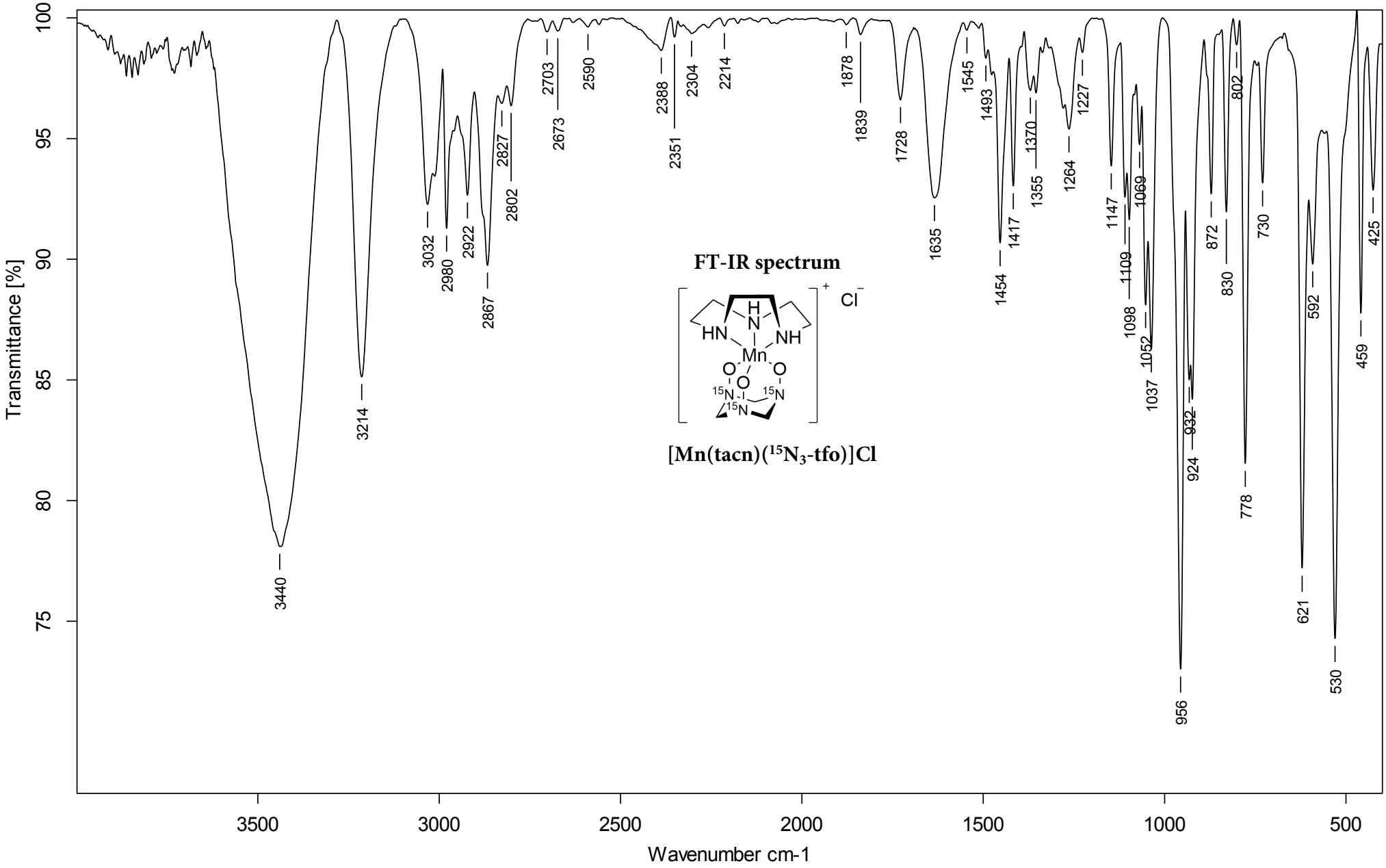

FT-IR spectrum
[Ni(tacn)(D6-tfo)]Cl
Transmittance [%]
Wavenumber cm-1
3434
3252
3196
2929
2871
2388
2353
2265
2200
2063
1724
1635
1545
1490
1455
1375
1357
1297
1277
1232
1185
1148
1101
1081
1053
1029
955
871
823
799
743
710
618
598
582
505
459
428

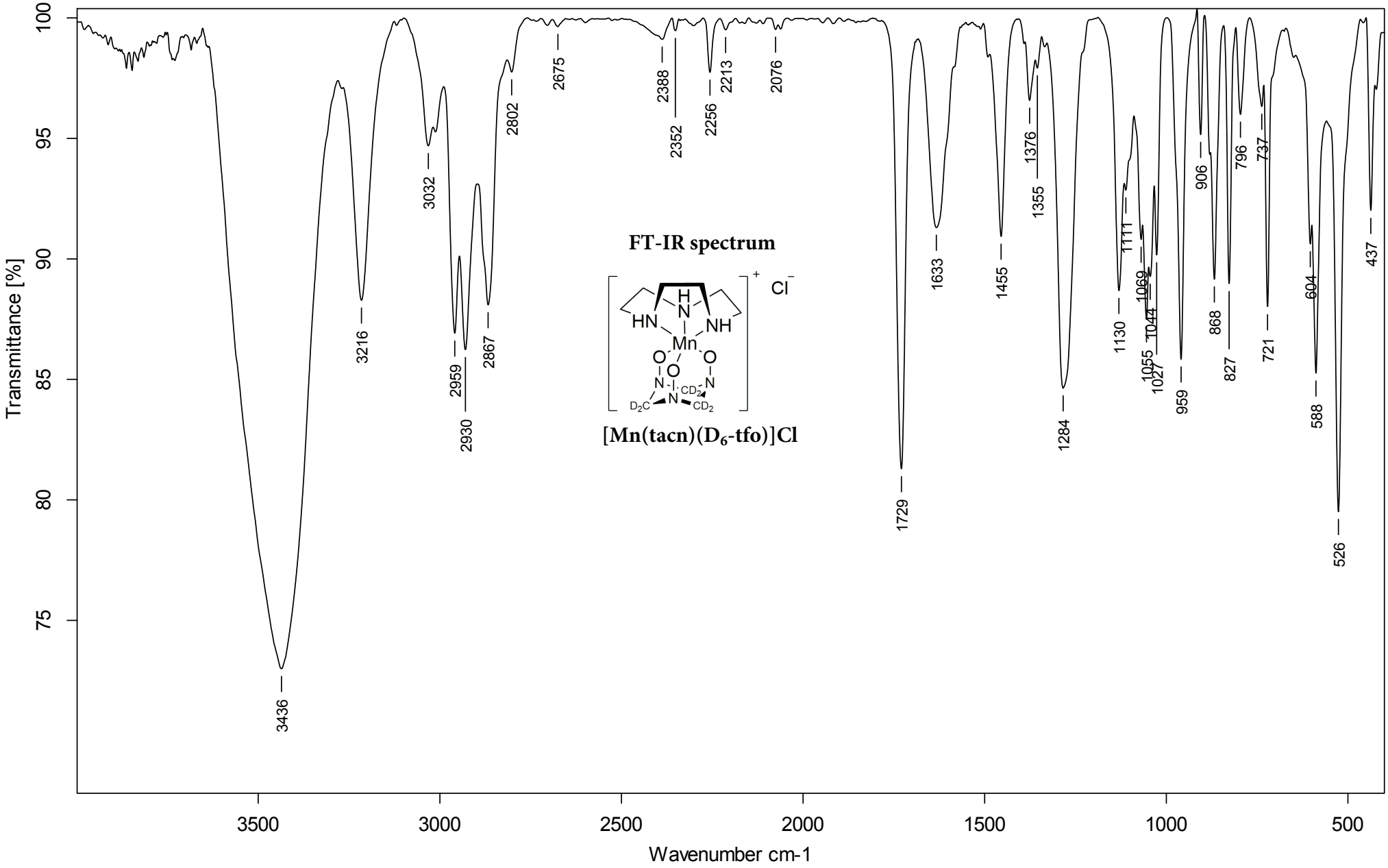

FT-IR spectrum
4
Transmittance [%]
Wavenumber cm-1
100
95
90
85
80
75
3500
3000
2500
2000
1500
1000
500
3438
3214
3031
2980
2923
2867
2801
2704
2578
2356
2339
2256
2215
1893
1855
1720
1634
1493
1454
1417
1369
1354
1262
1226
1166
1109
1097
1069
1053
1037
963
932
871
830
802
779
746
632
591
531
463
425
Cl⁻
HN
NH
Mn
O
N

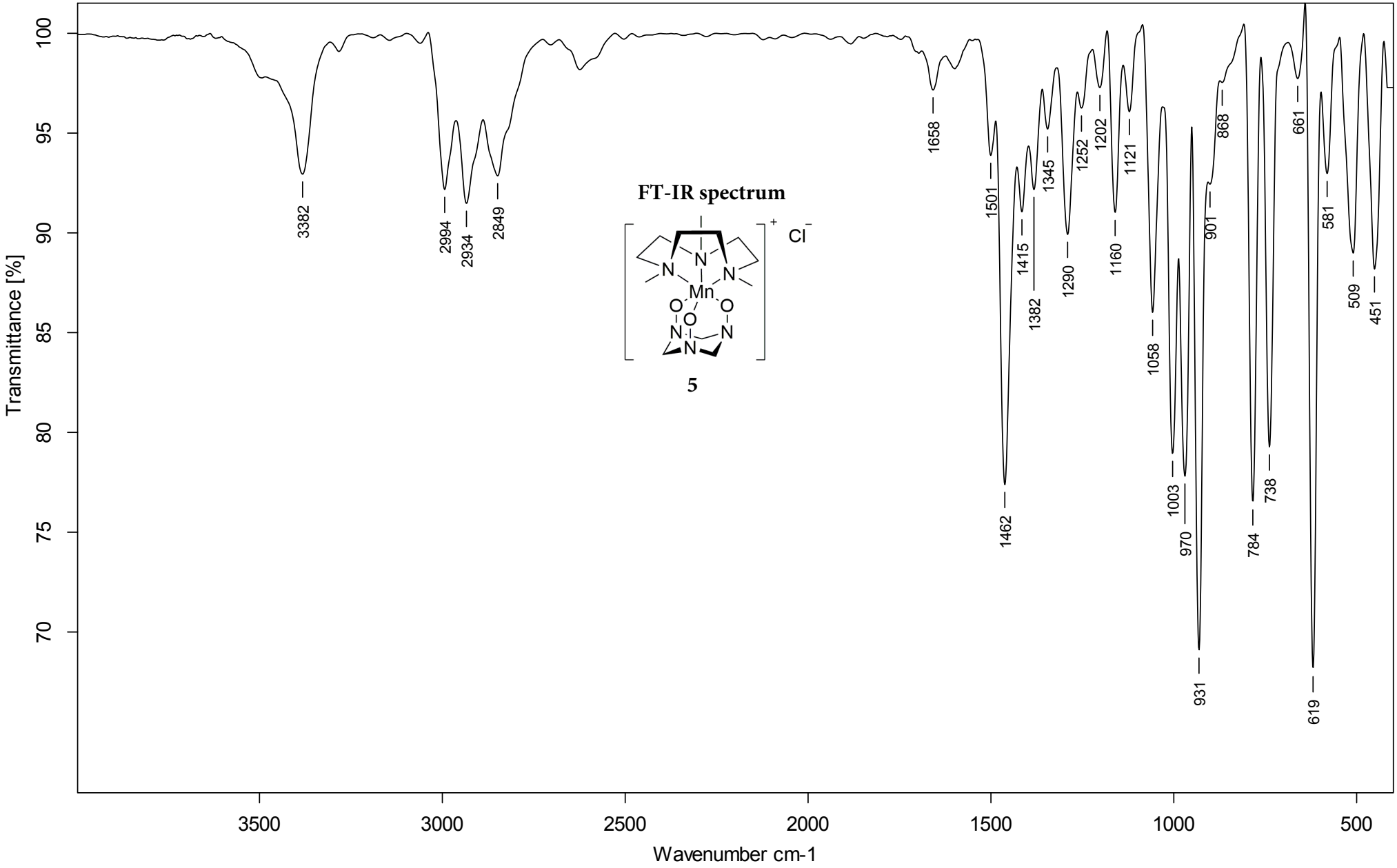

FT-IR spectrum 2600 - 5600 cm-1
Wavenumber cm-1
Transmittance [%]
5458.83
5333.57
5393.9
3240.23
3055.8
2982.71
2884.24
2924.53
Cl−
4

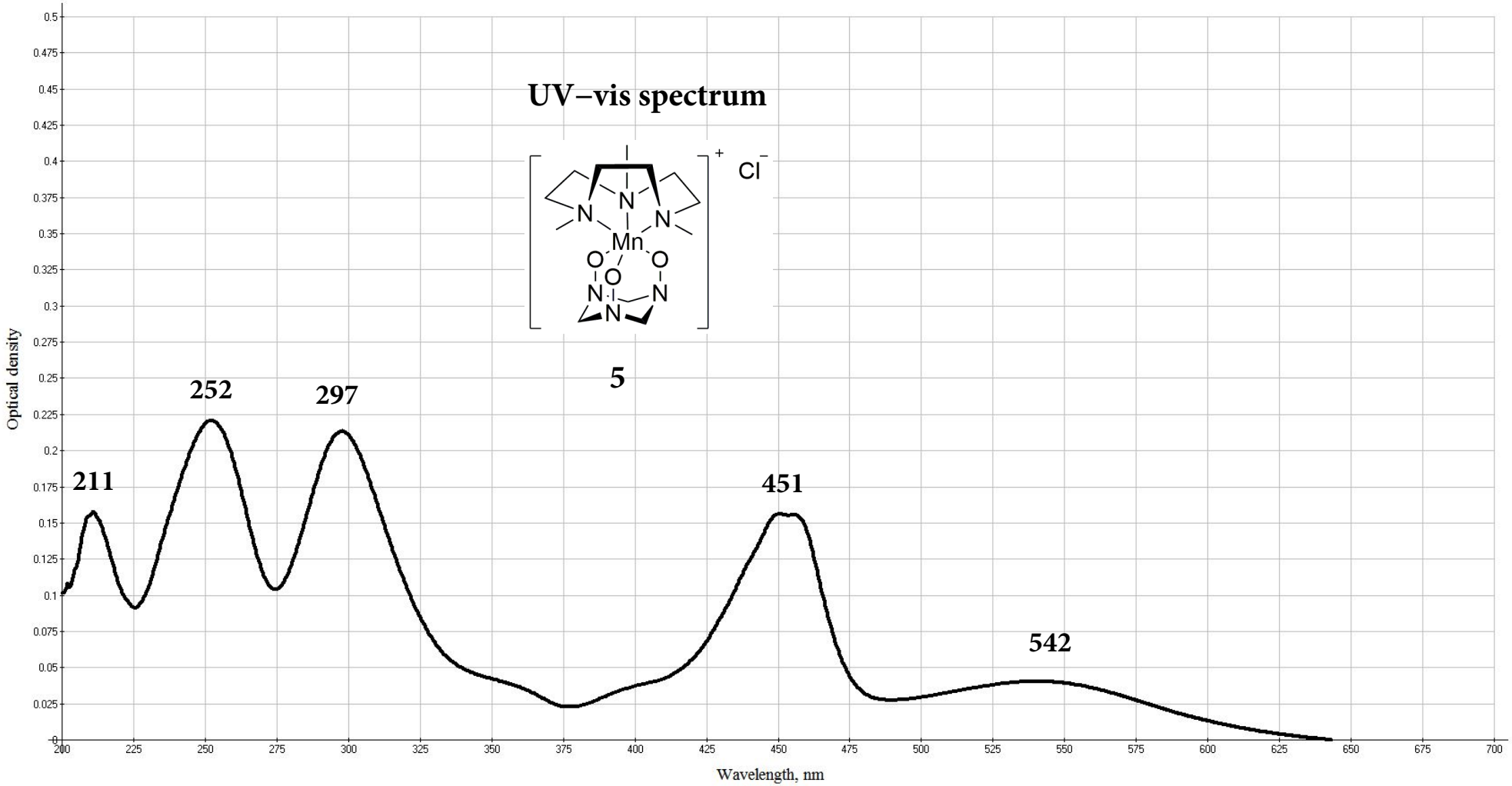

KBr
Wavenumber cm-1
Transmittance [%]
5189.63
5456.81
5362.08
5300.44
5400.06
5475.31
5351.4
3520.91

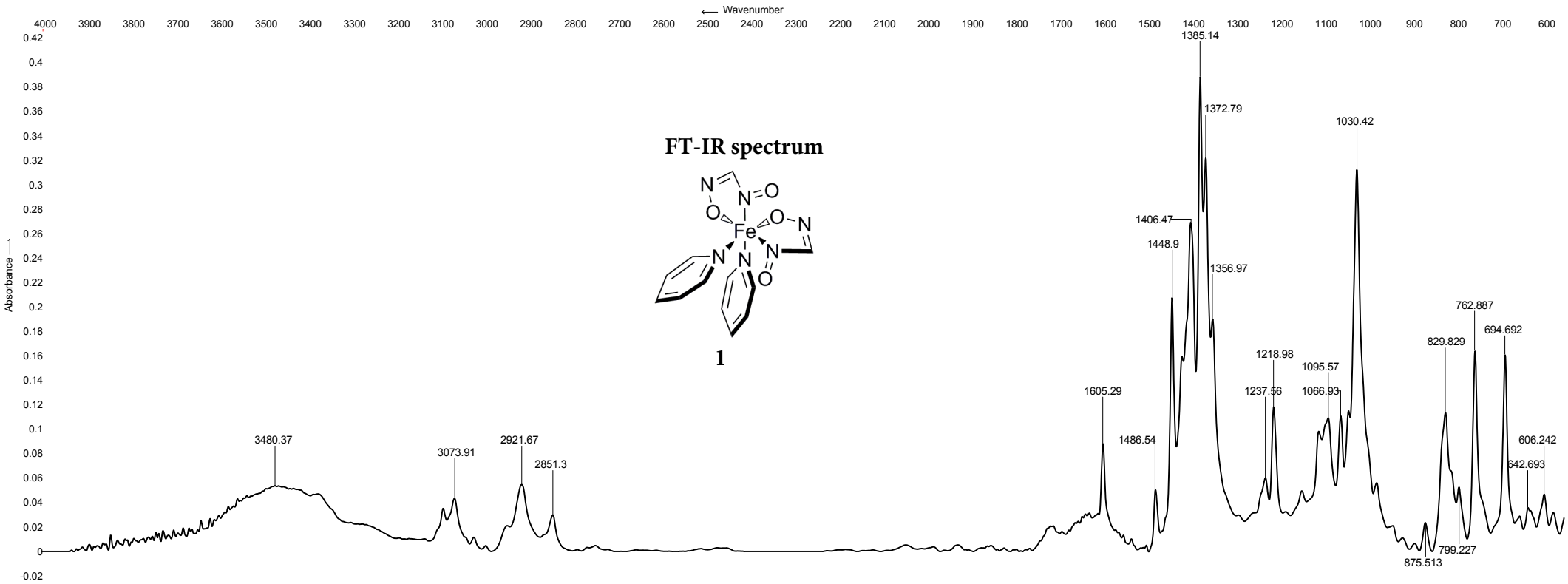

UV–vis / NIR spectrum
4, powder sample
305
351
451
543
Optical density
Wavelength, nm
Cl⁻
Mn

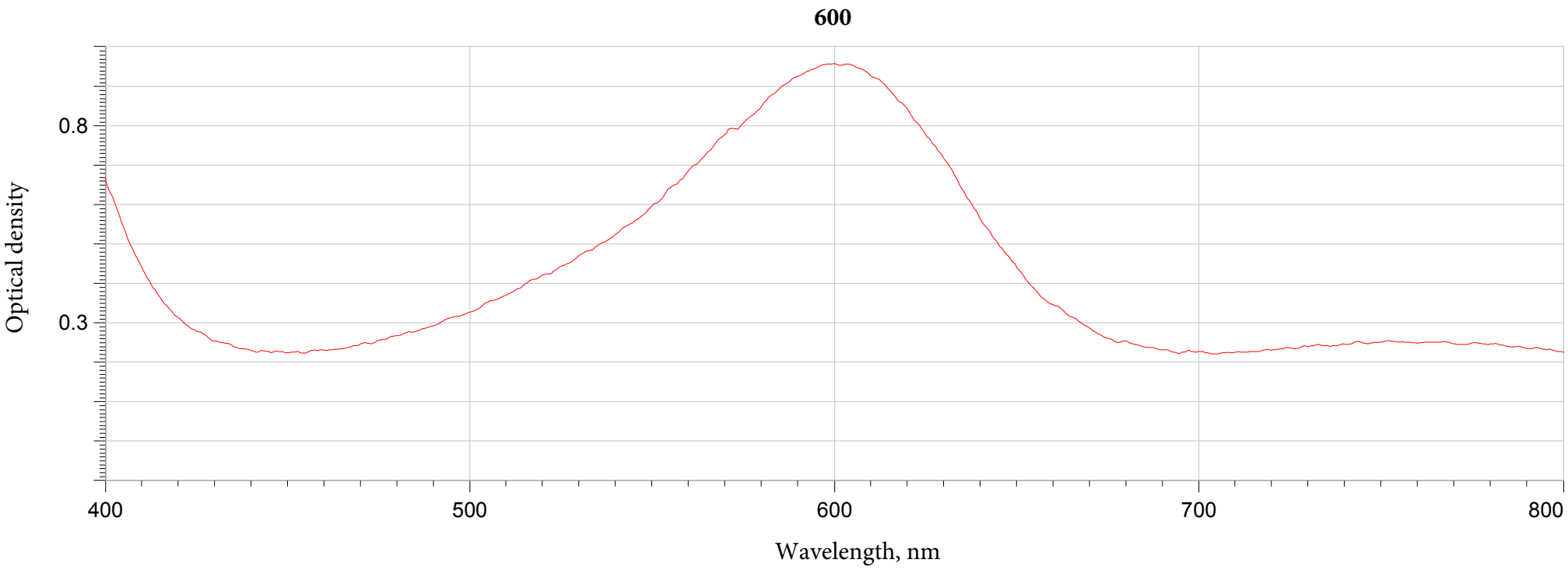

FT-IR spectrum
[Mn(tacn)(15N3-tfo)]Cl
Transmittance [%]
Wavenumber cm-1
3440
3214
3032
2980
2922
2867
2827
2802
2703
2673
2590
2388
2351
2304
2214
1878
1839
1728
1635
1545
1493
1454
1417
1370
1355
1264
1227
1147
1109
1098
1069
1052
1037
956
932
924
872
830
802
778
730
621
592
530
459
425
100
95
90
85
80
75
3500
3000
2500
2000
1500
1000
500


FT-IR spectrum
[Mn(tacn)(D6-tfo)]Cl
Transmittance [%]
Wavenumber cm-1
3436
3216
3032
2959
2930
2867
2802
2675
2388
2352
2256
2213
2076
1729
1633
1455
1376
1355
1284
1130
1111
1069
1055
1044
1027
959
906
868
827
796
737
721
604
588
526
437

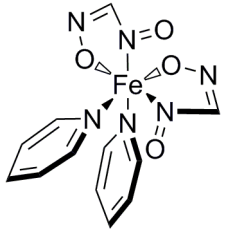

FT-IR spectrum
5
Cl⁻
Transmittance [%]
Wavenumber cm-1
3382
2994
2934
2849
1658
1501
1462
1415
1382
1345
1290
1252
1202
1160
1121
1058
1003
970
931
901
868
784
738
661
619
581
509
451


UV–vis spectrum
Cl⁻
5
211
252
297
451
542
Optical density
Wavelength, nm


FT-IR spectrum
1
Wavenumber
Absorbance
3480.37
3073.91
2921.67
2851.3
1605.29
1486.54
1448.9
1406.47
1385.14
1372.79
1356.97
1237.56
1218.98
1095.57
1066.93
1030.42
875.513
829.829
799.227
762.887
694.692
642.693
606.242

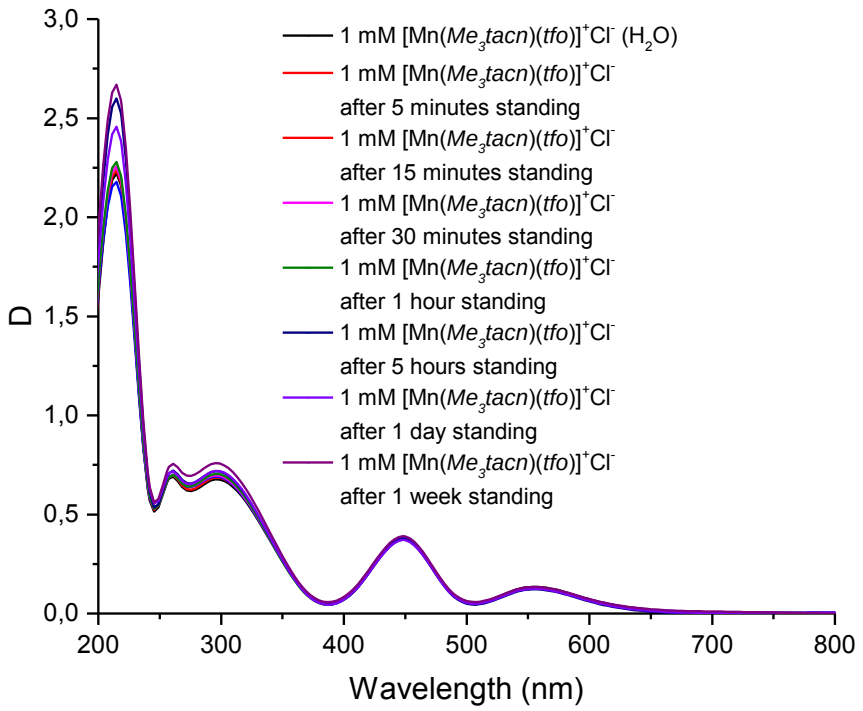


UV–vis spectrum

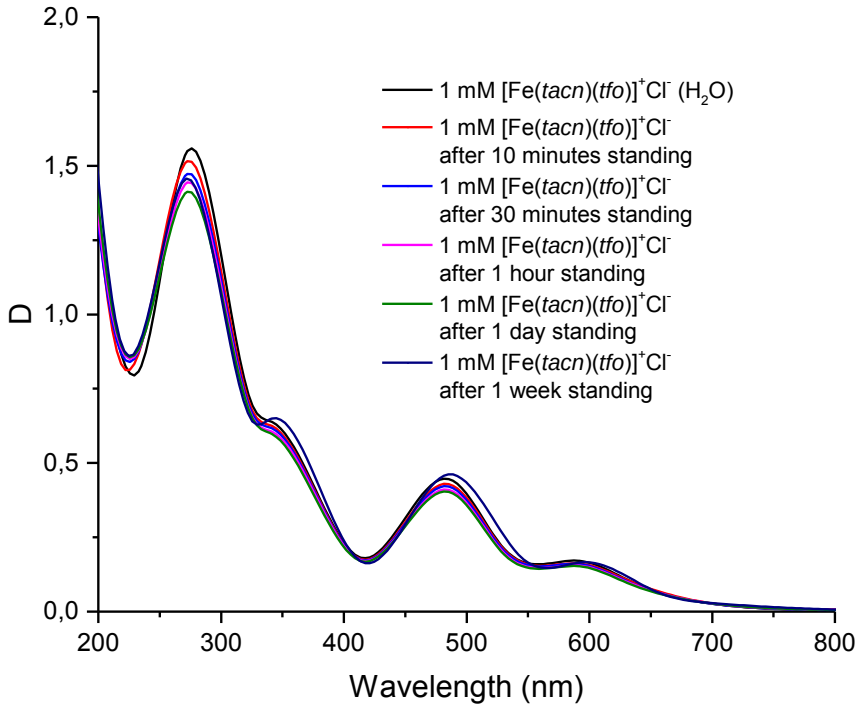


1

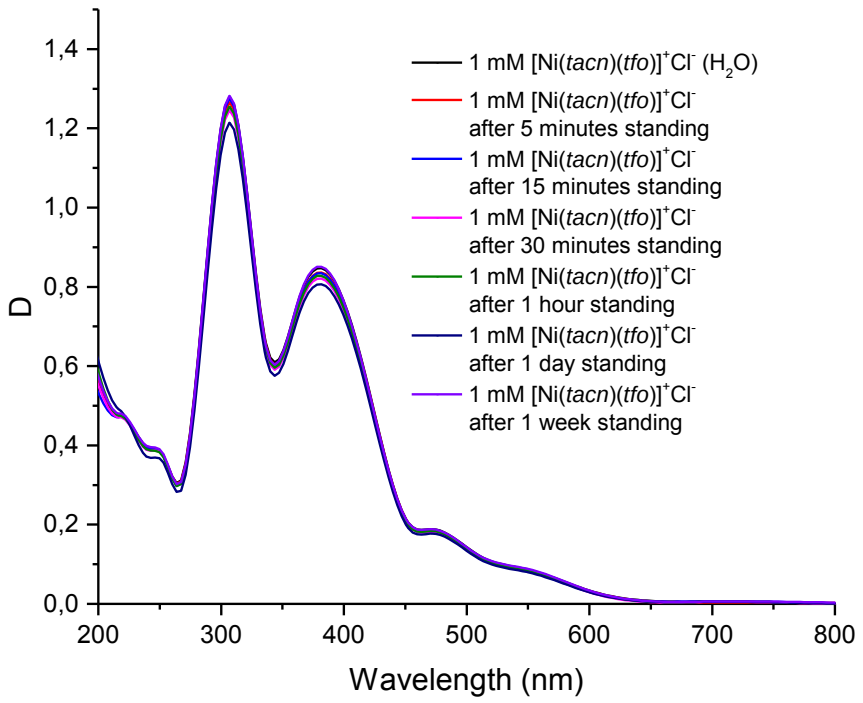
Stability of tfo-complexes 2,3 and 5 in water (UV-Vis monitoring)



Reference – H_2O

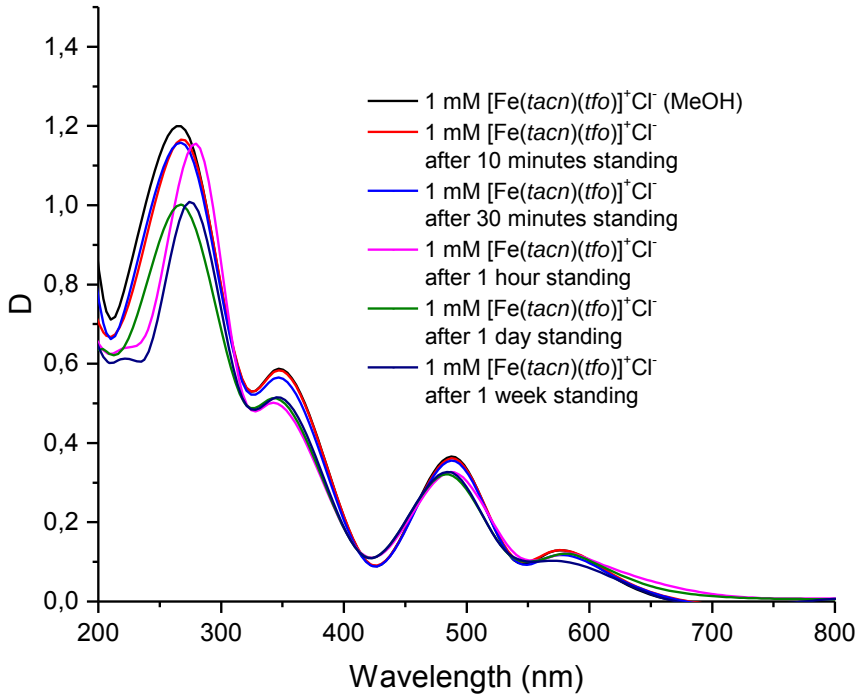


Reference – H_2O

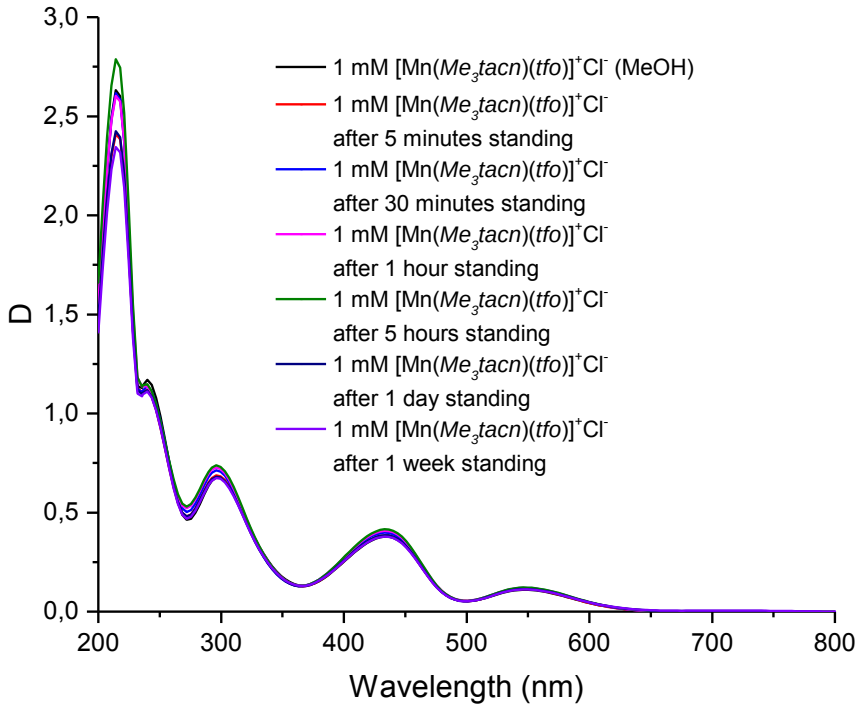


Reference – H_2O

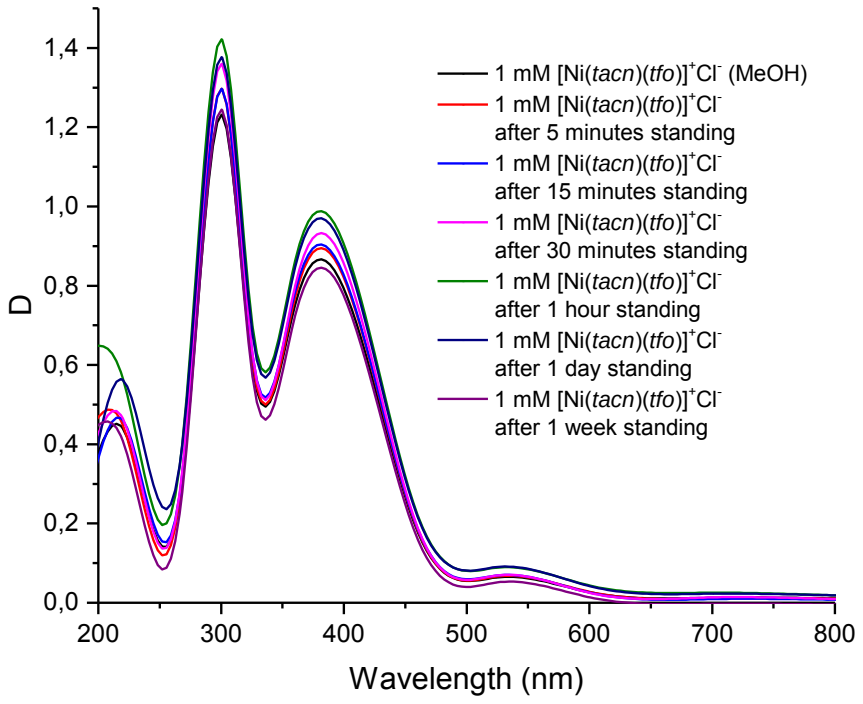
Stability of tfo-complexes 2,3 and 5 in methanol (UV-Vis monitoring)



Reference – MeOH

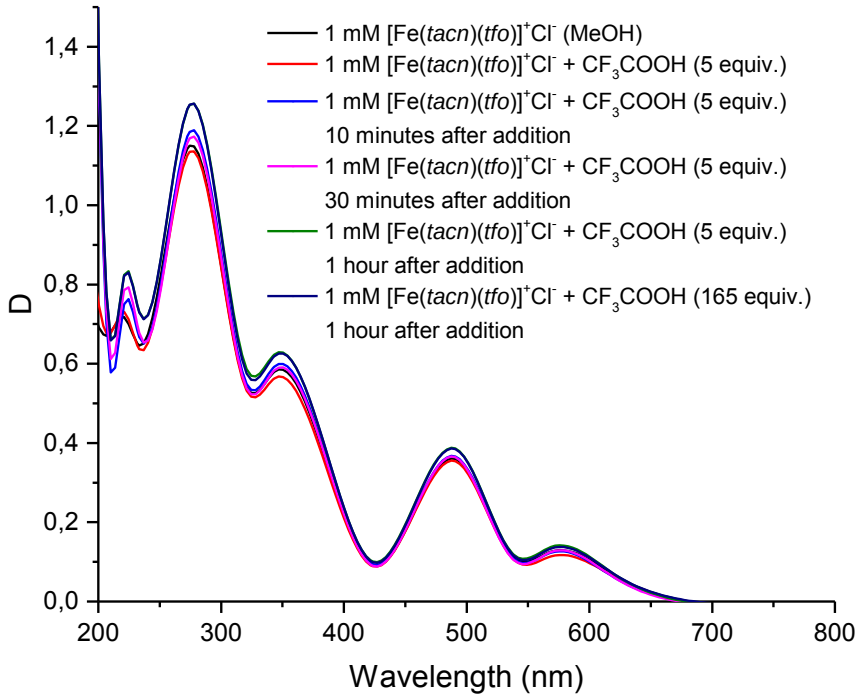


Reference – MeOH

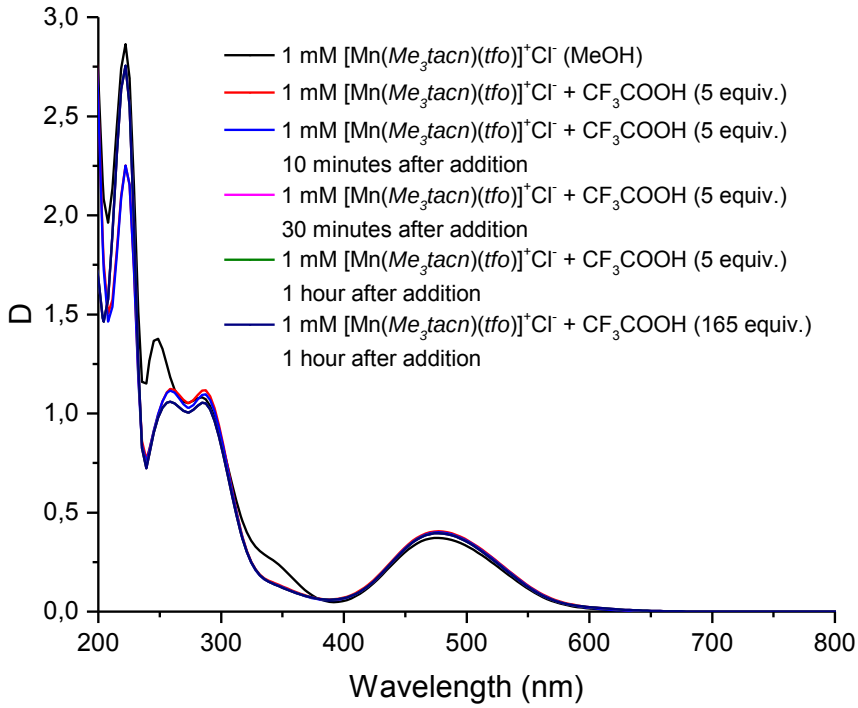


Reference – MeOH

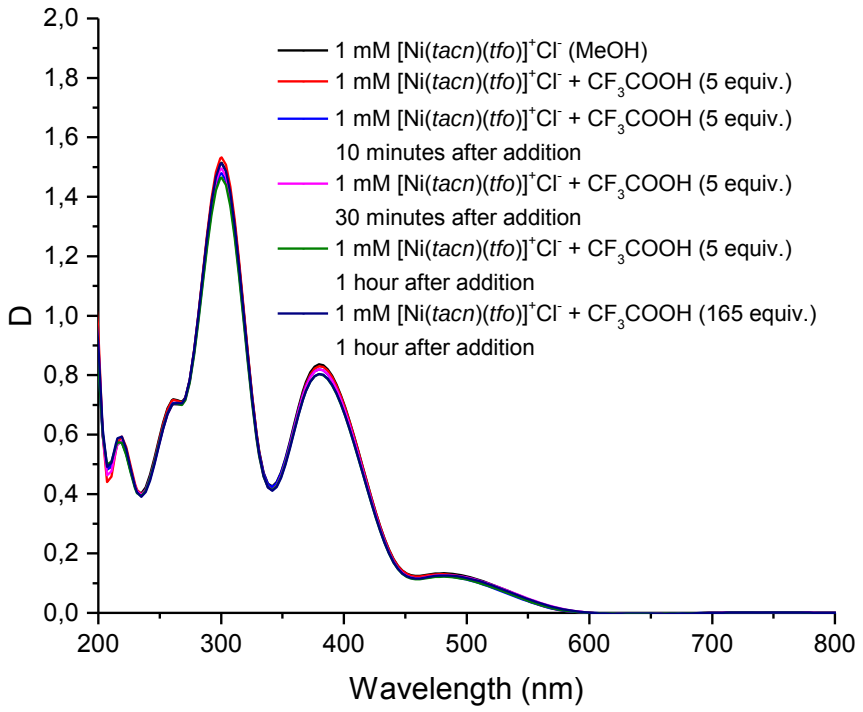
Stability of tfo-complexes 2,3 and 5 in the presence of CF_3COOH (UV-Vis monitoring)



Reference – MeOH



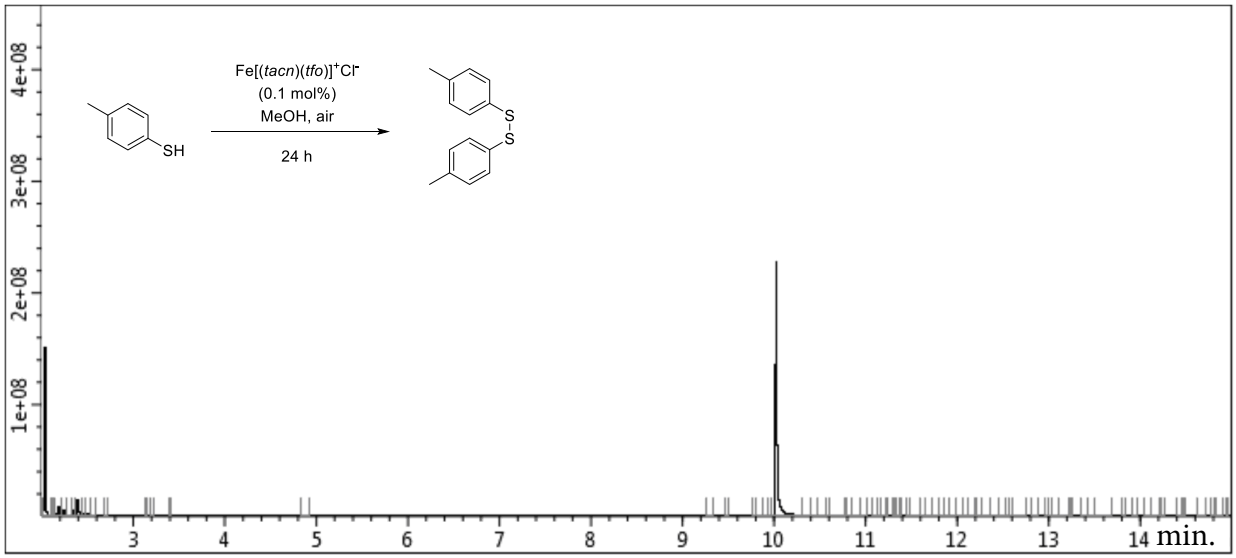
Reference – MeOH

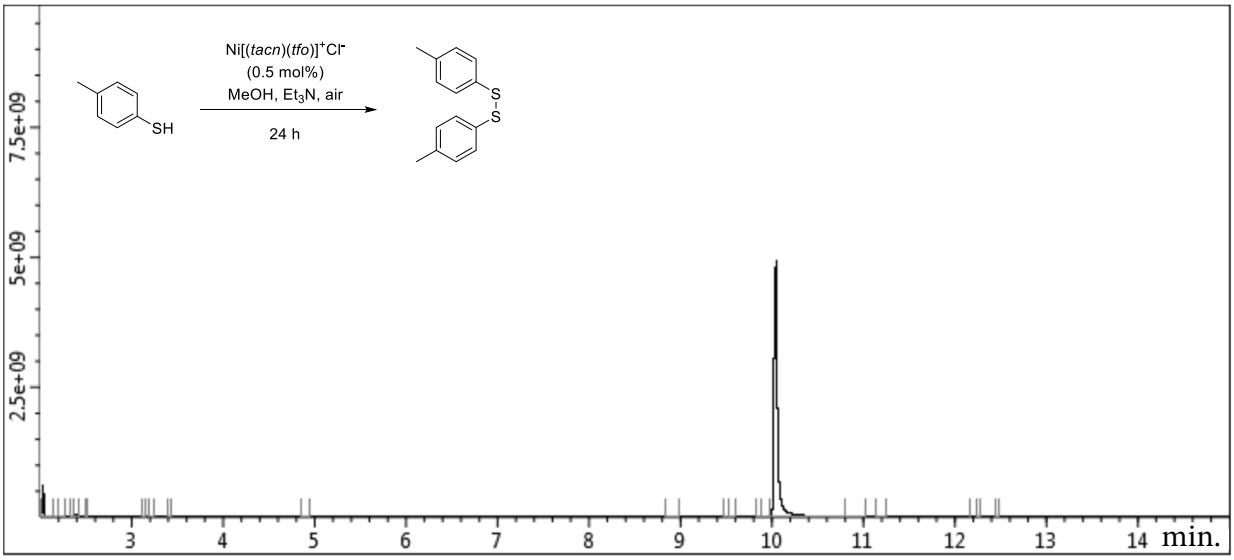


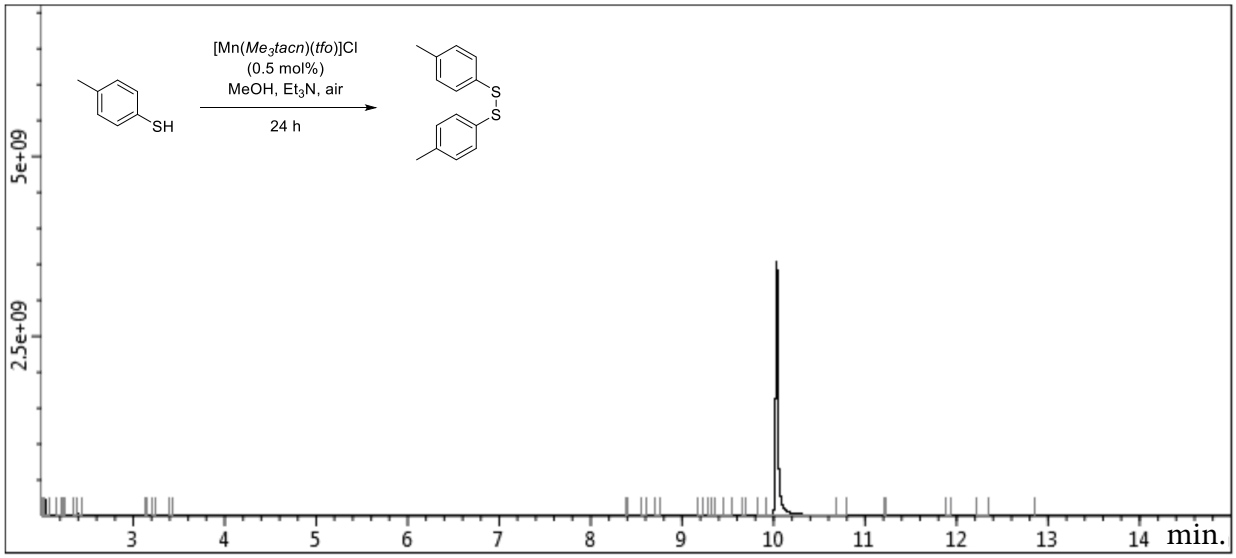
Reference – MeOH

5. Spectral data for aerobic oxidation reactions

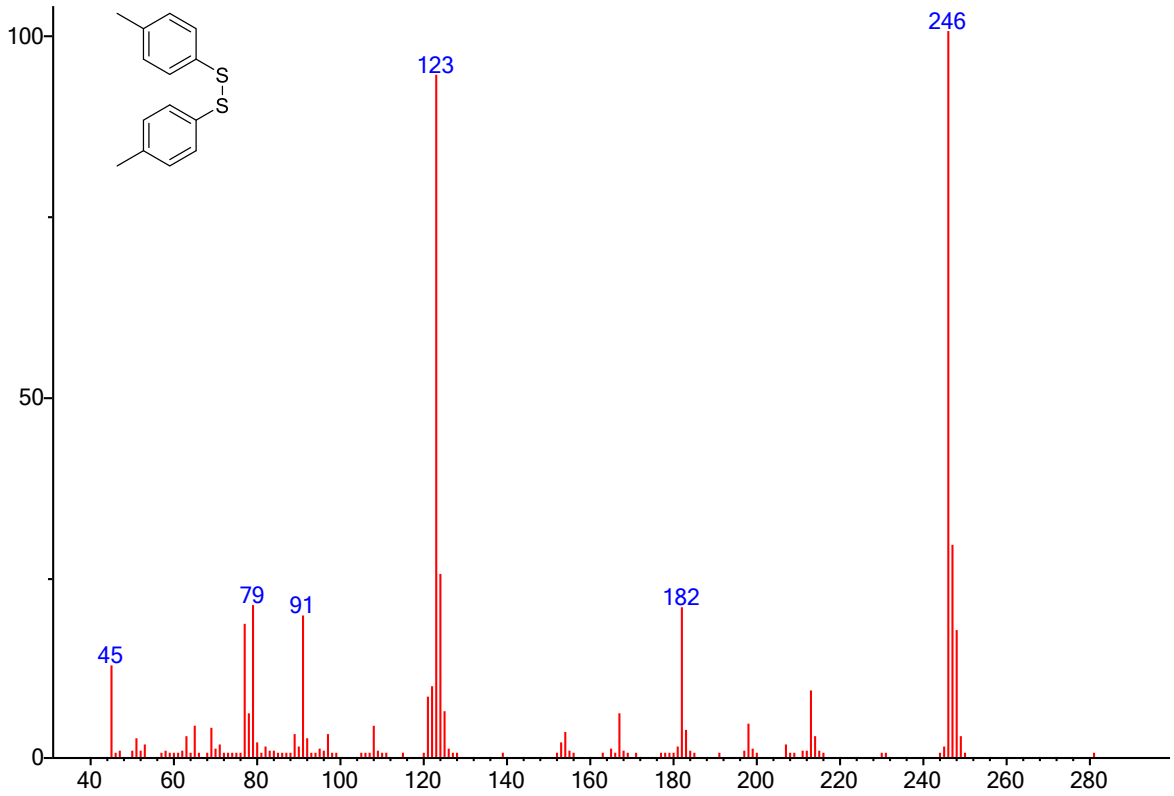
GC-MS analysis of aerobic oxidation reaction of *p*-thiocresol

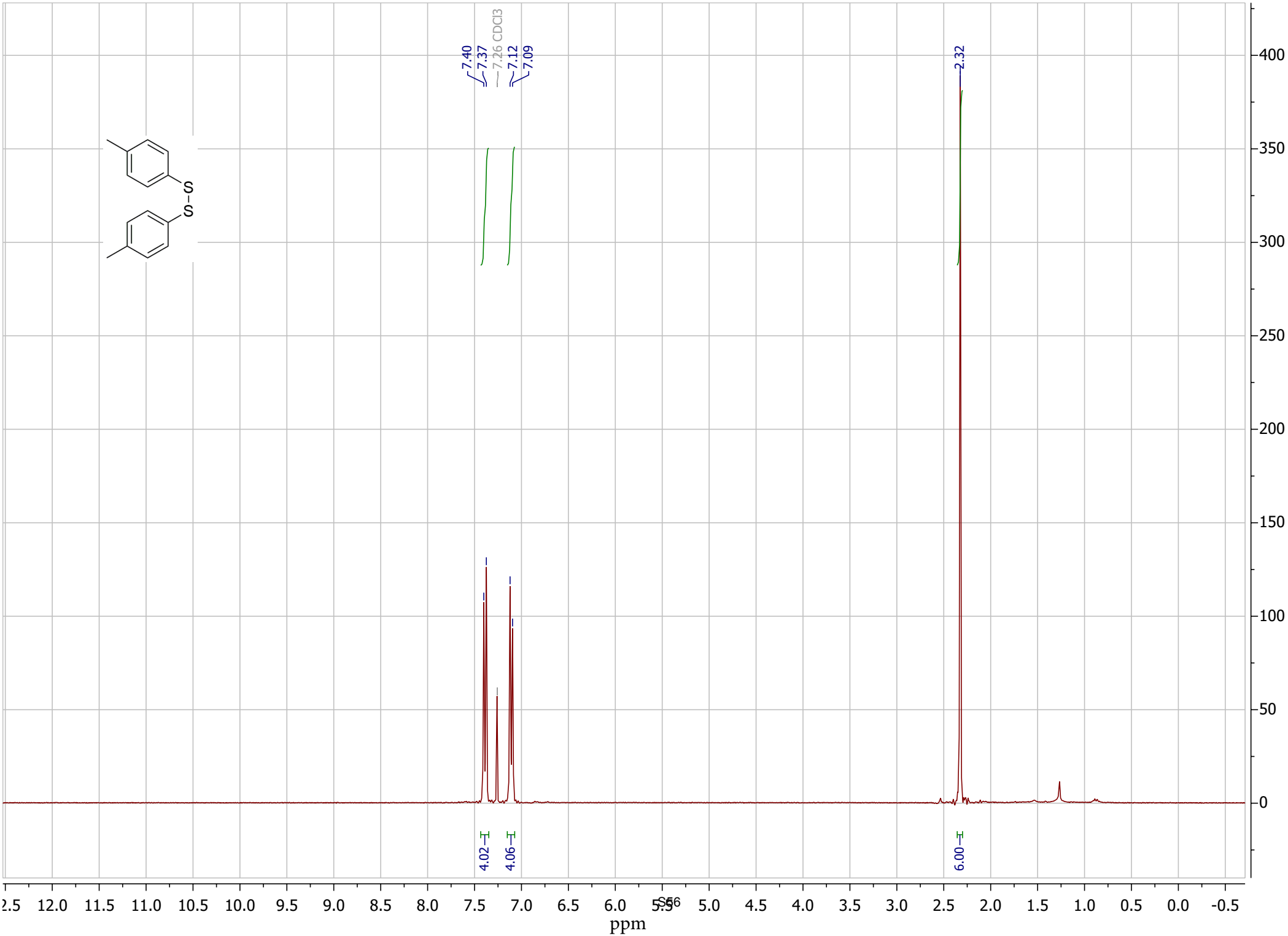




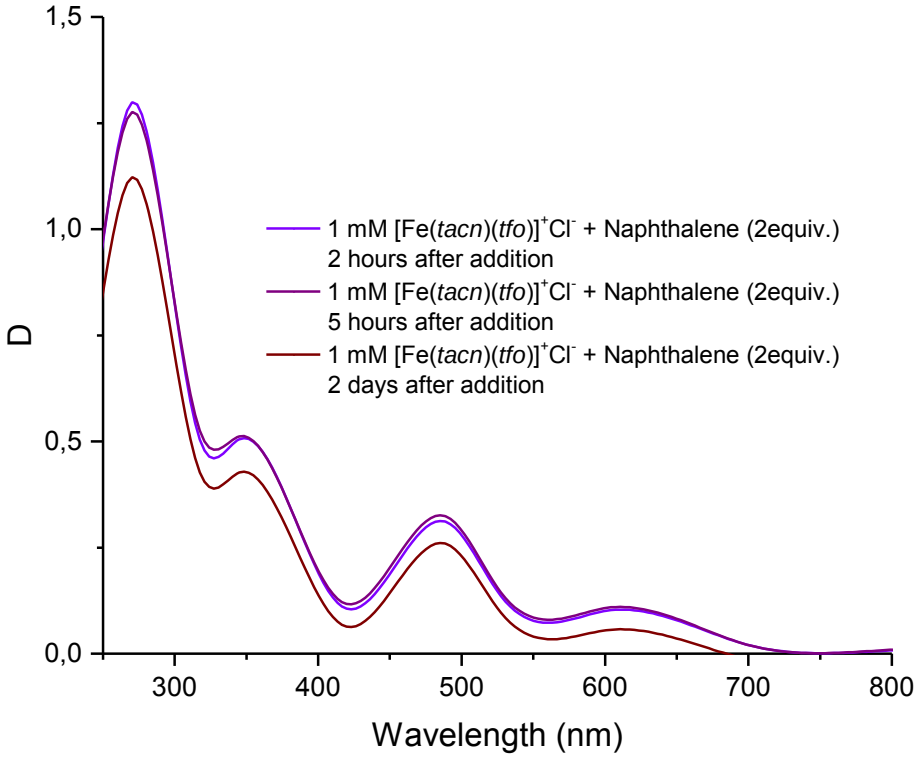


MS spectrum

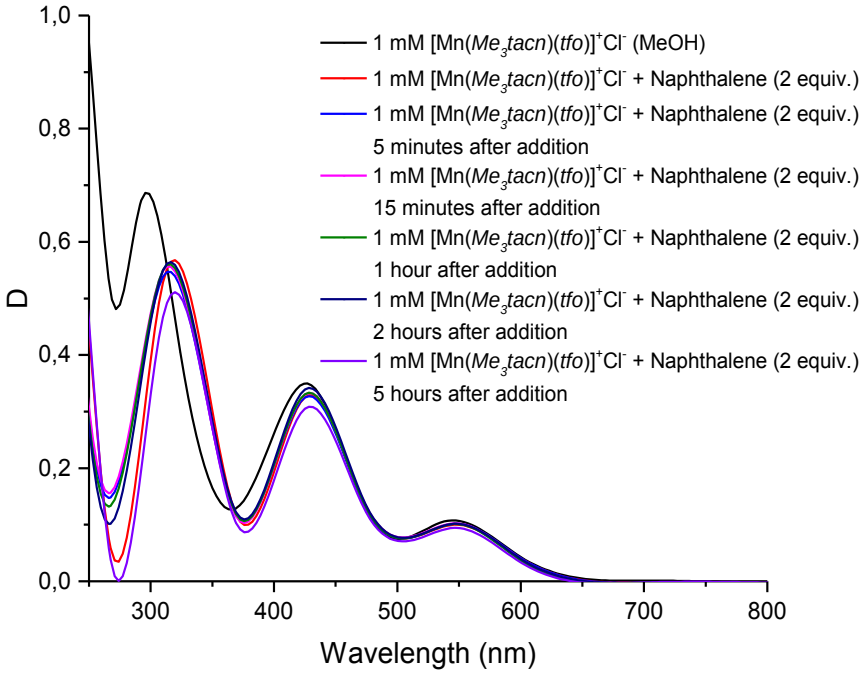

100
50
0
S
S
246
123
79
91
182
45
40
60
80
100
120
140
160
180
200
220
240
260
280


7.40
7.37
7.26 CDCl3
7.12
7.09
2.32
S
S
4.02
4.06
6.00
ppm

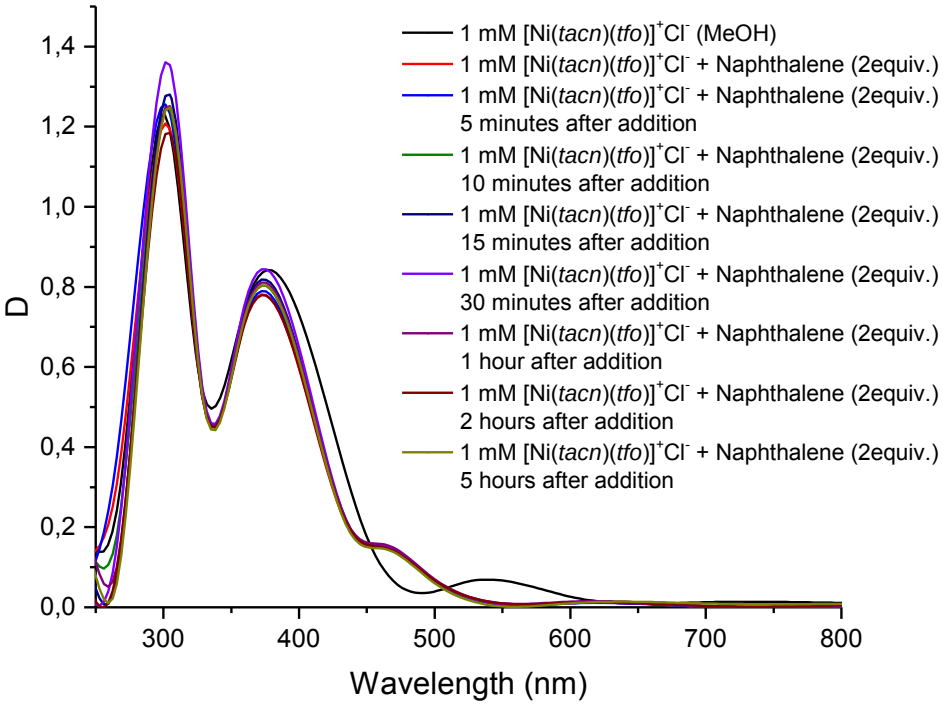
Reaction of tfo-complexes 2,3 and 5 with naphtalene (UV-Vis monitoring)



Reference – MeOH

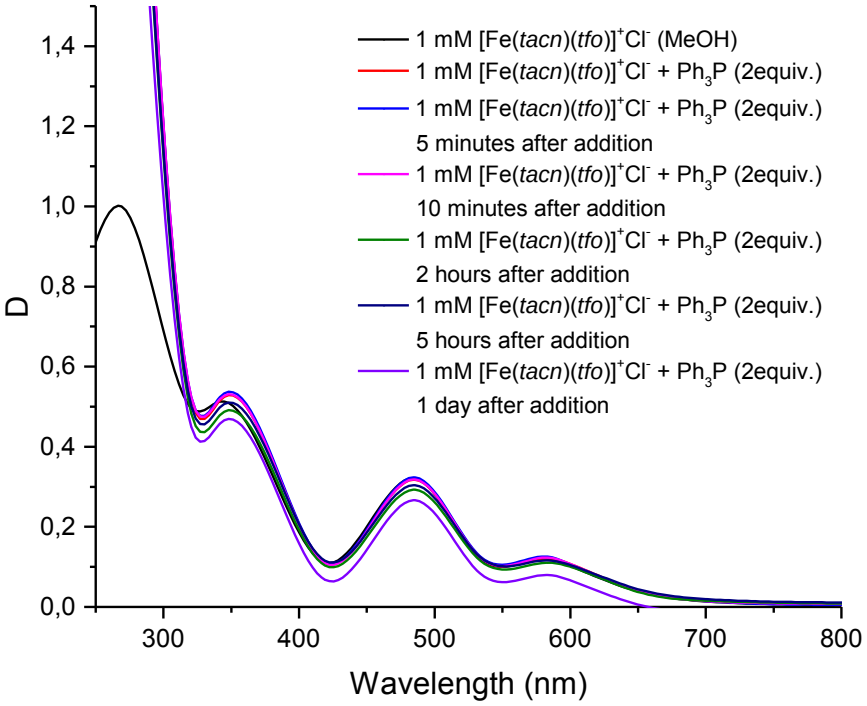


Reference – Naphthalene in MeOH

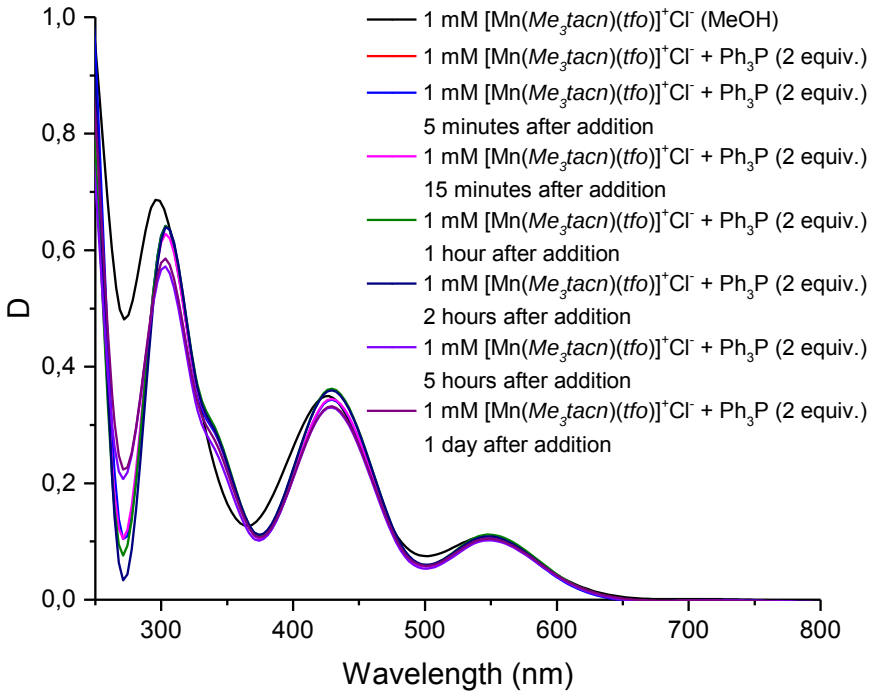


Reference – Naphthalene in MeOH

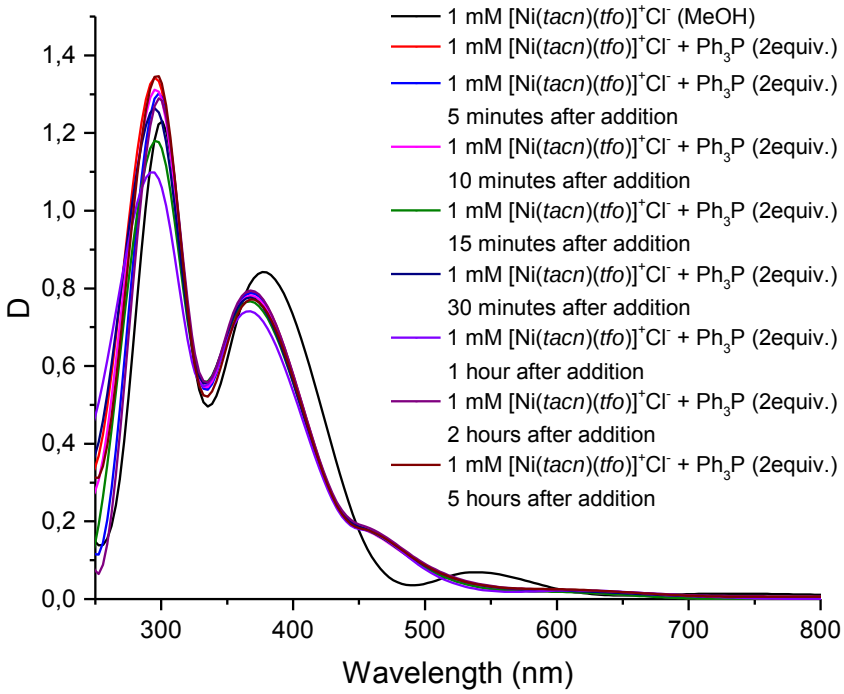
Reaction of tfo-complexes 2,3 and 5 with PPh_3 (UV-Vis monitoring)



Reference – MeOH

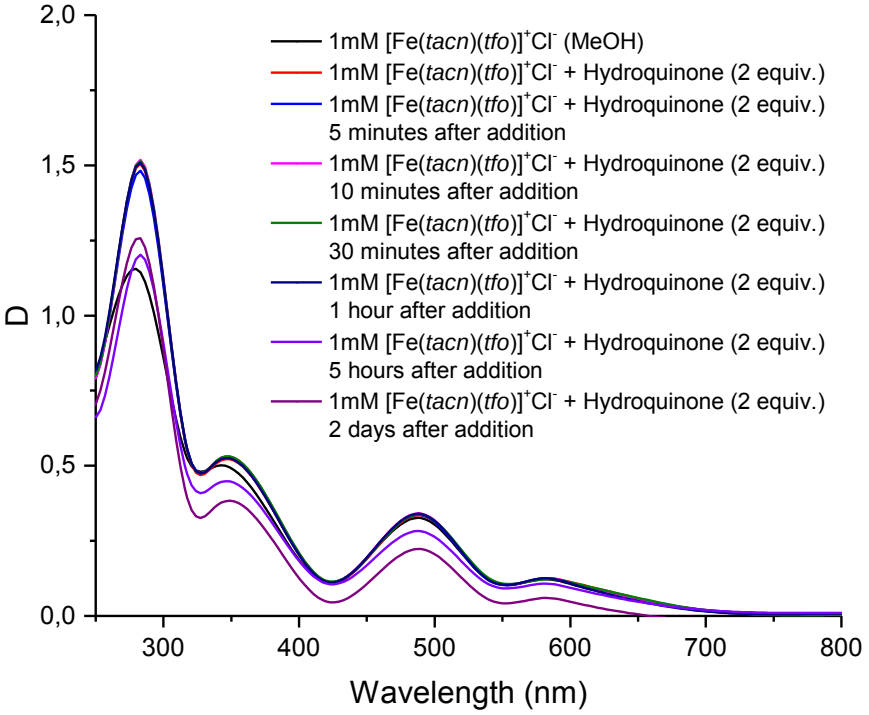


Reference – Ph_3P in MeOH

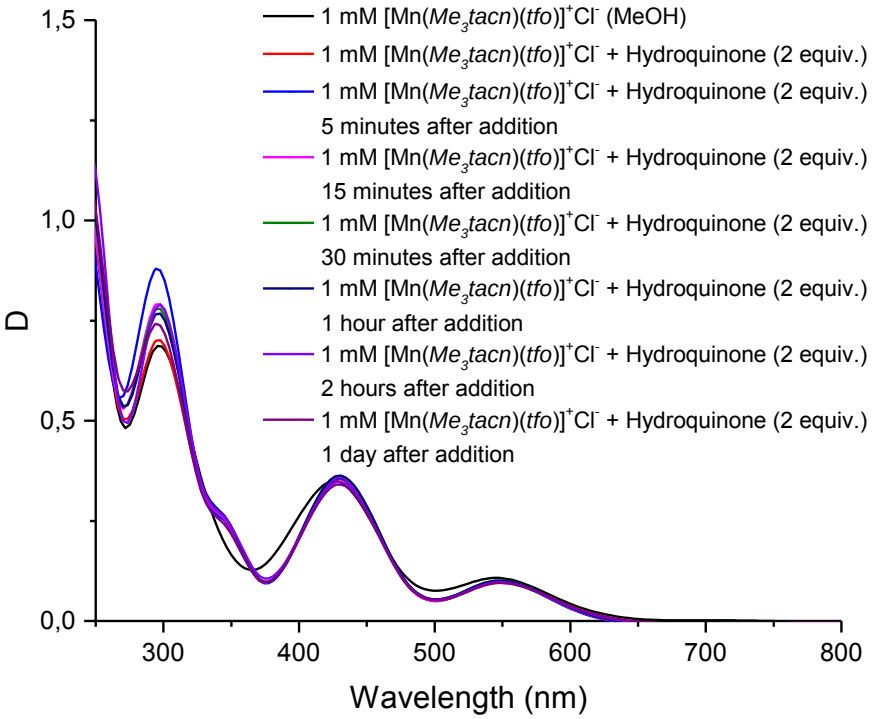


Reference – Ph_3P in MeOH

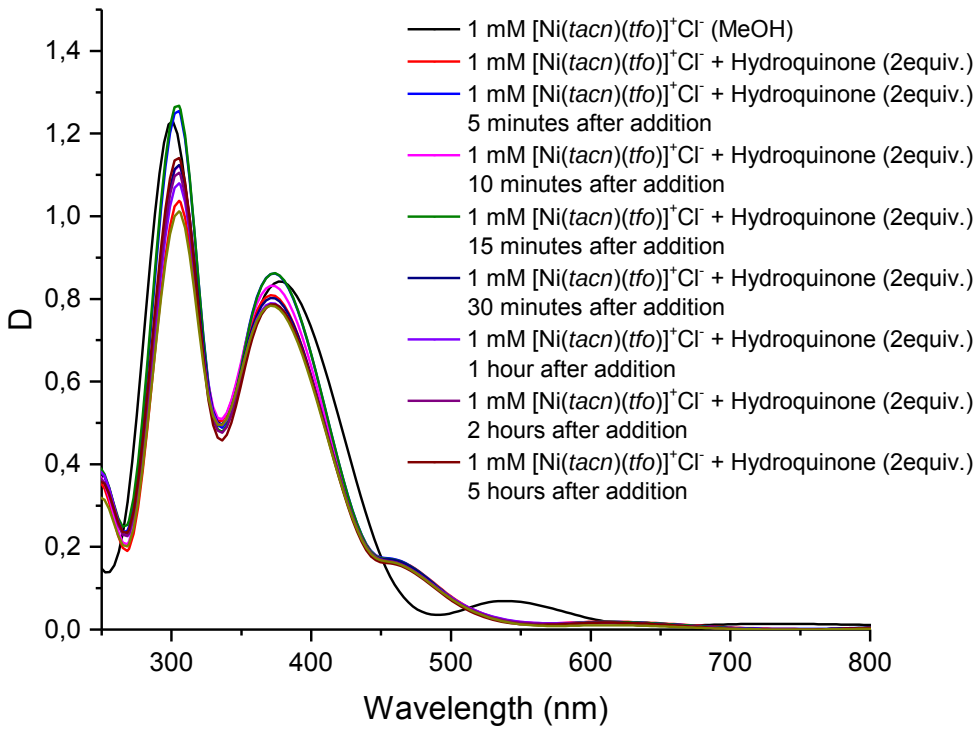
Reaction of tfo-complexes 2,3 and 5 with hydroquinone (UV-Vis monitoring)



Reference – MeOH

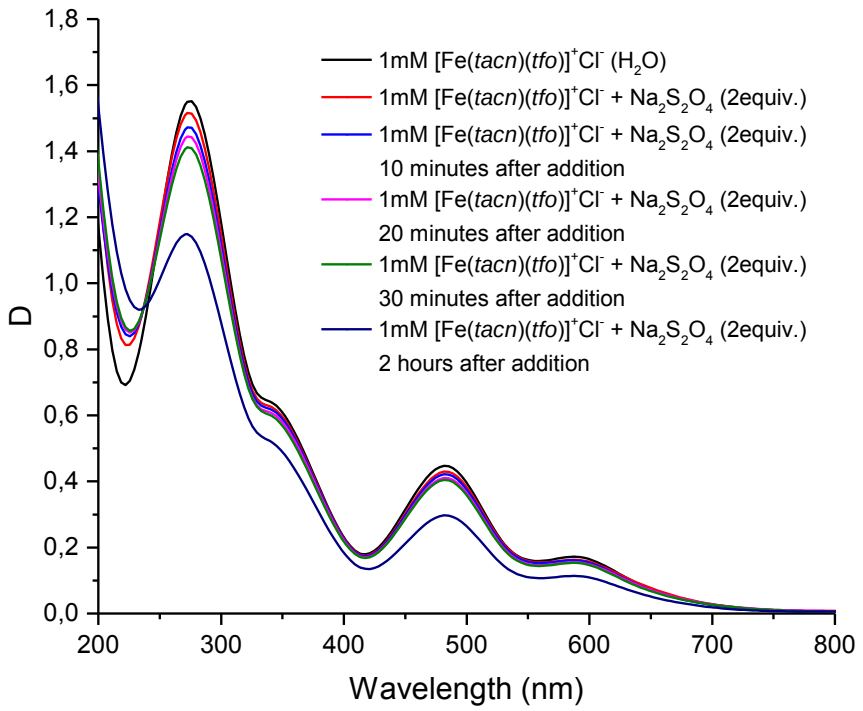


Reference – Hydroquinone in MeOH

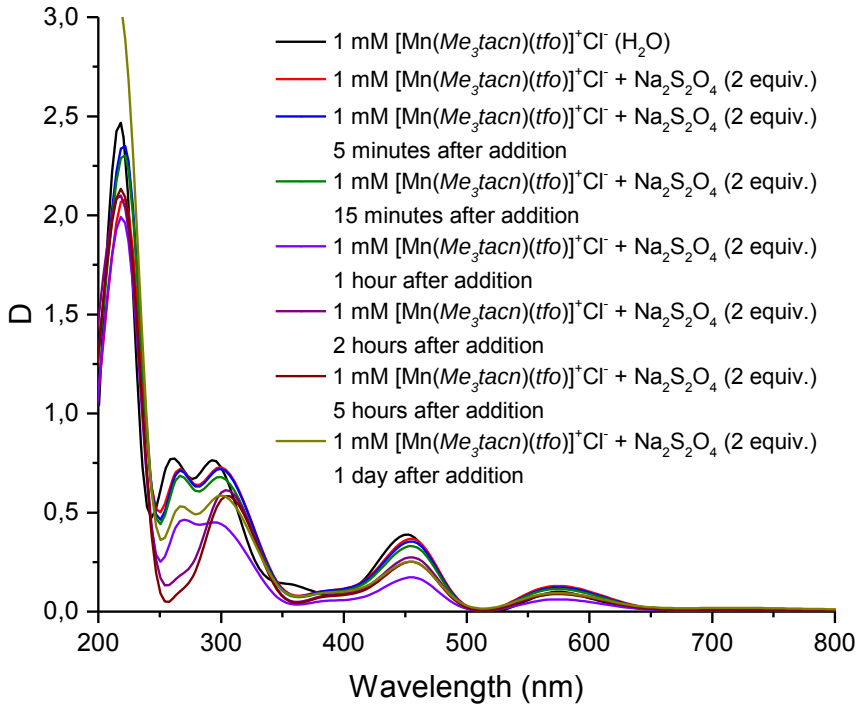


Reference – Hydroquinone in MeOH

Reaction of tfo-complexes 2,3 and 5 with sodium dithionite in air (UV-Vis monitoring)



Reference – H_2O



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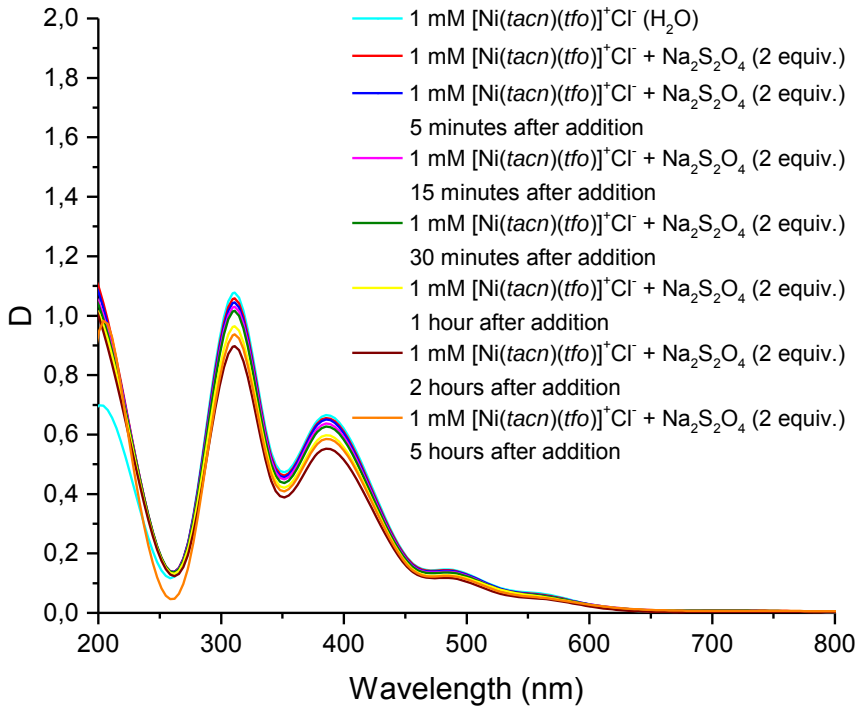
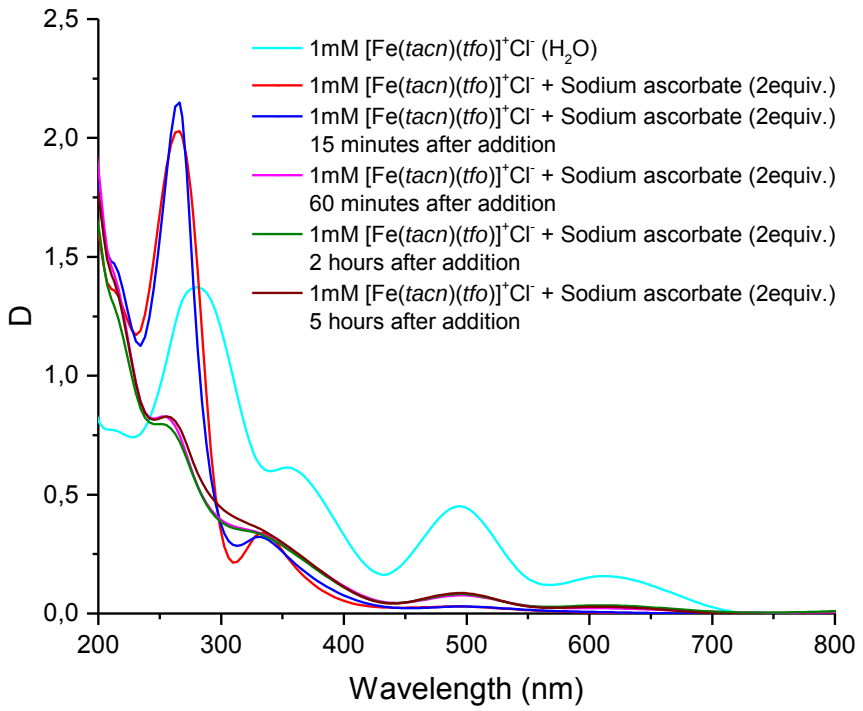
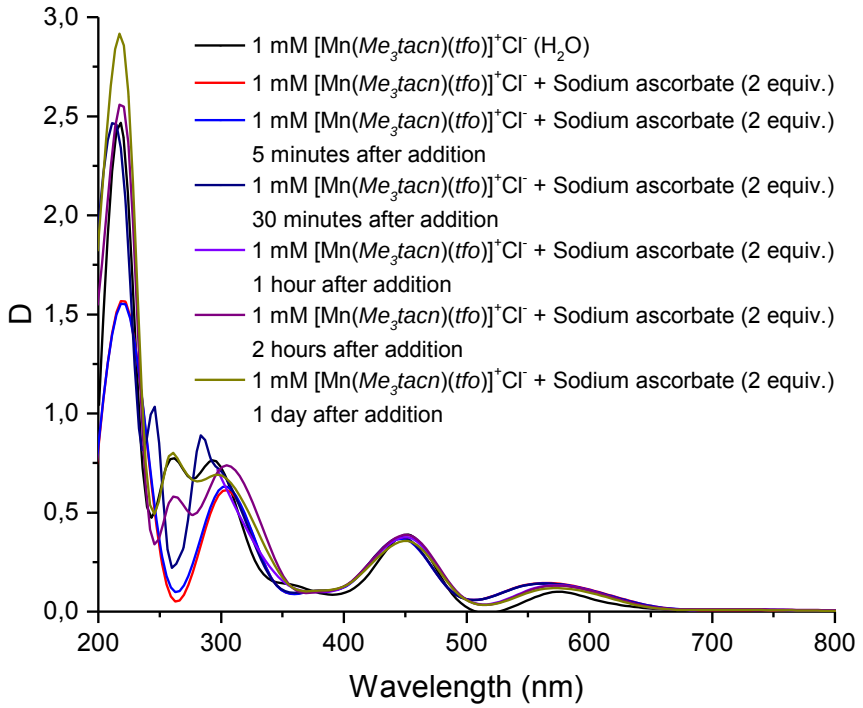


Reference – H_2O

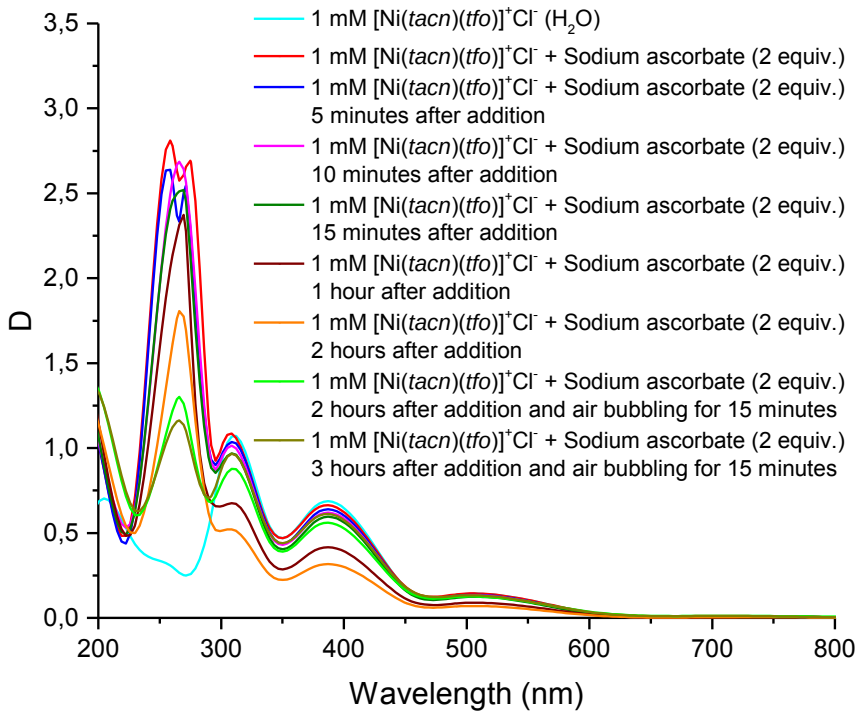
Reaction of tfo-complexes 2,3 and 5 with sodium ascorbate in air (UV-Vis monitoring)



Reference – H_2O

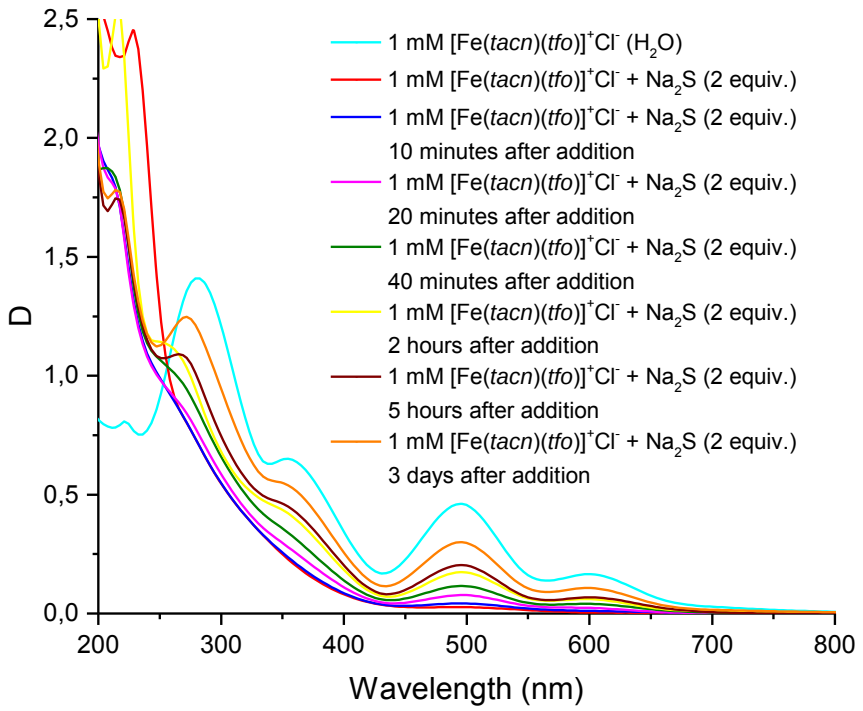


Reference – H_2O

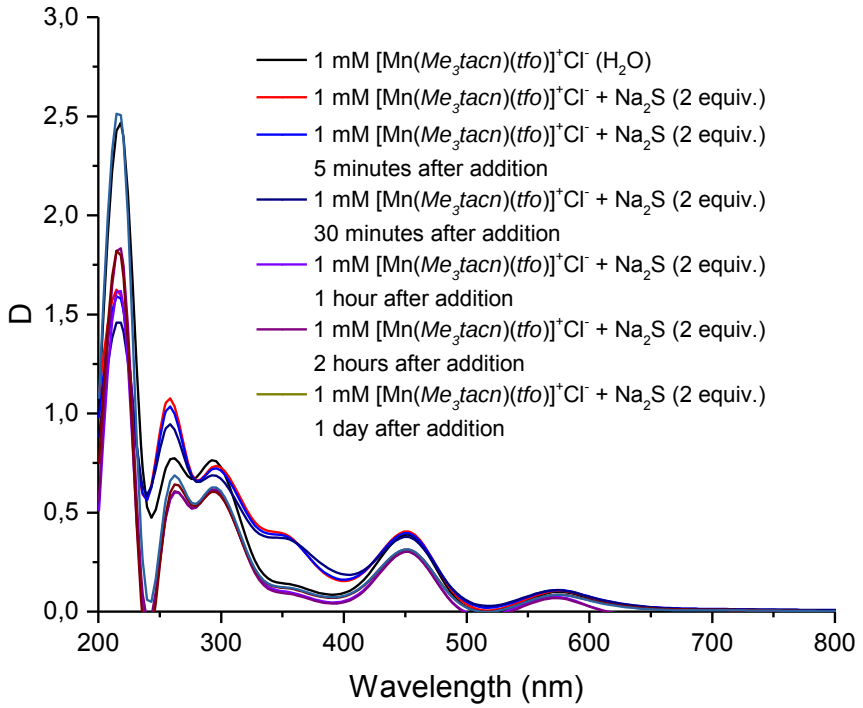


Reference – H_2O

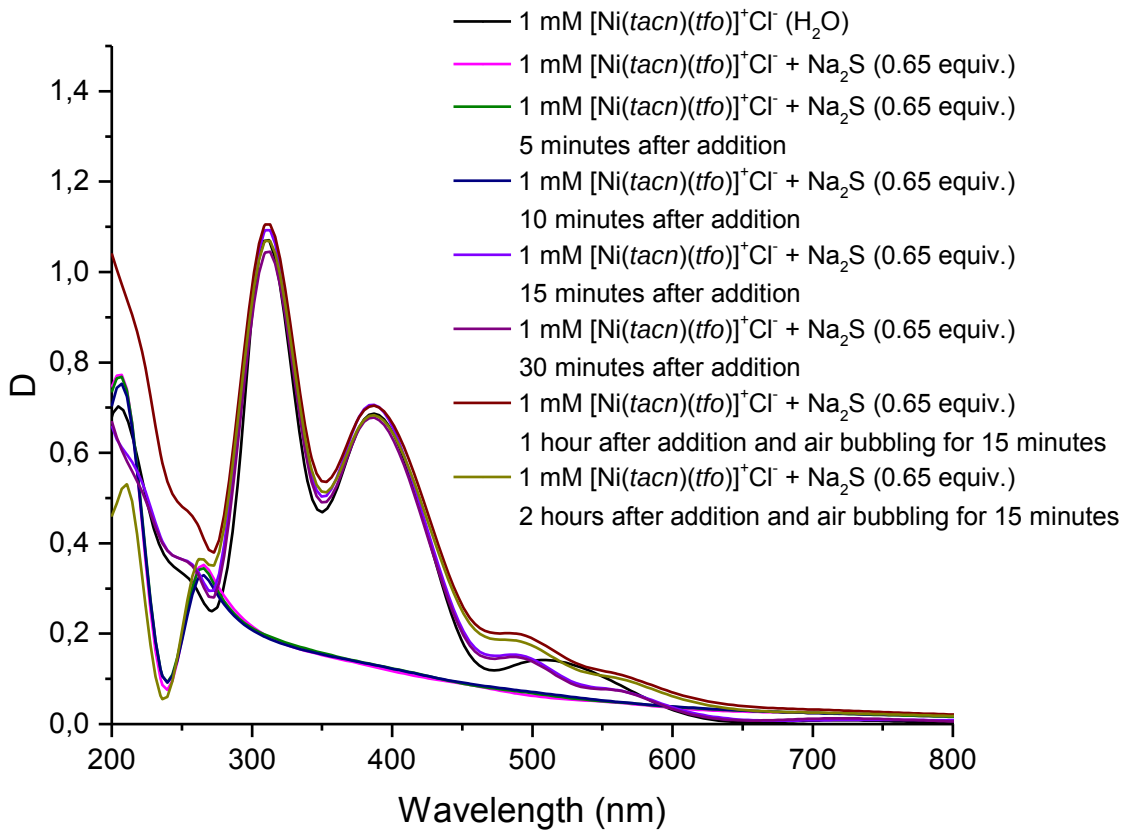
Reaction of tfo-complexes 2,3 and 5 with sodium sulfide in air (UV-Vis monitoring)



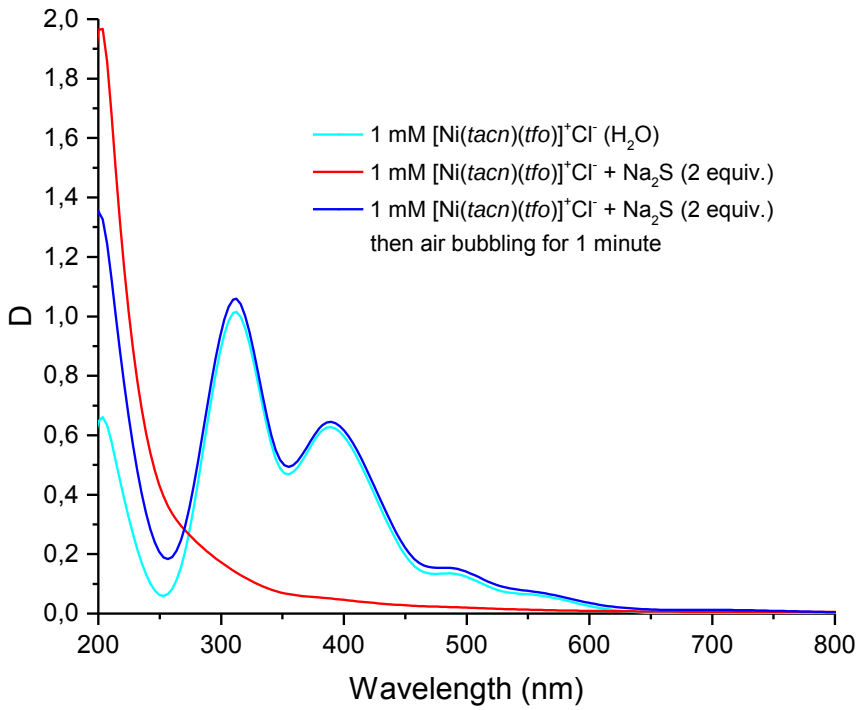
Reference – H_2O



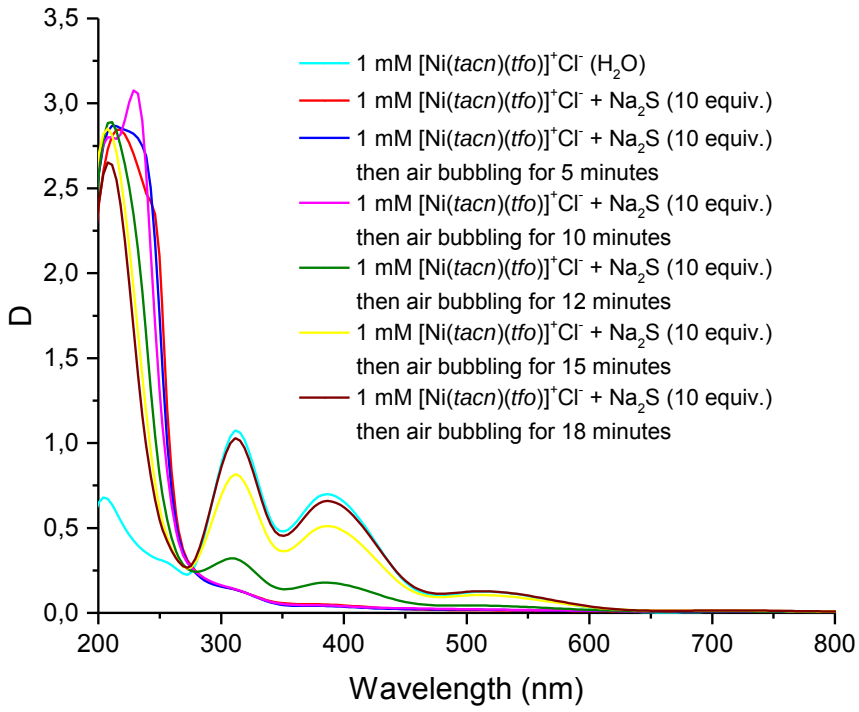
Reference – H_2O



Reference – H_2O

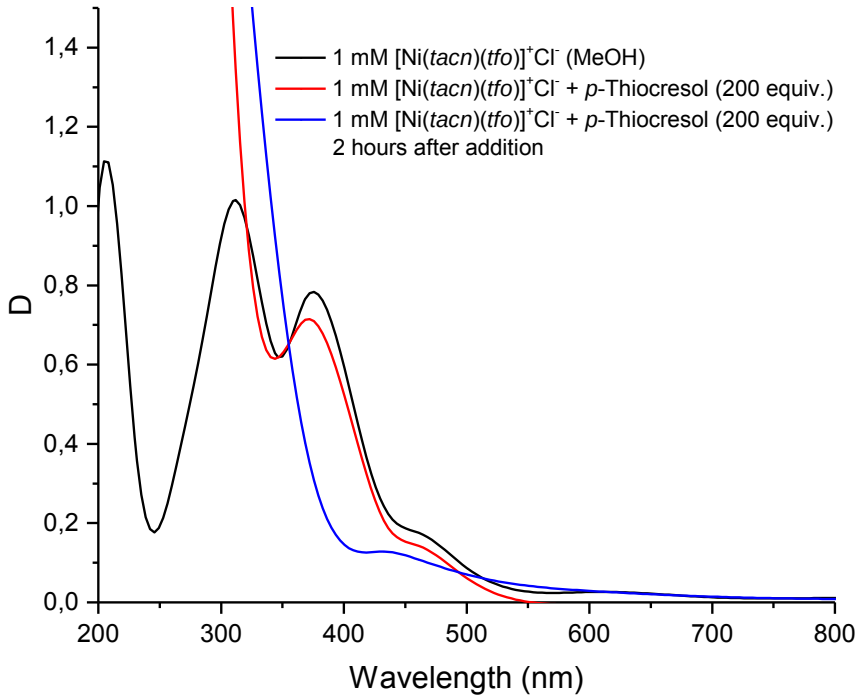


Reference – H_2O



Reference – H_2O

Reaction of nickel tfo-complex 3 with *p*-thiocresol in air (UV-Vis monitoring)



Reference – MeOH

6. Crystal data for 1-3 and 5

Table S1. Crystal data and structure refinement parameters for **tfoH$_3$·HCl**, **1-3** and **5**.

	tfoH$_3$·HCl	**1**	**2**	**3**	**5**
Empirical formula	$C_3H_{10}ClN_3O_3$	$C_{12}H_{12}FeN_6O_4$	$C_9H_{20}ClFeN_6O_3$	$C_{10}H_{25}ClN_6NiO_4$	$C_{13}H_{31}ClMnN_6O_4$
Formula weight	171.59	360.13	351.59	387.52	425.83
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$Cmc2_1$	$P2_1/c$	$Cmc2_1$	$P2_12_12_1$	$P2_1/c$
Z	4	8	4	4	4
a, Å	8.826(4)	12.1759(7)	10.3049(11)	8.9404(6)	10.0572(5)
b, Å	7.664(4)	14.4133(8)	9.5725(13)	11.4607(8)	11.4251(6)
c, Å	10.708(5)	17.3687(10)	14.6765(16)	15.3471(10)	16.7338(9)
β, °	90.00	104.872(2)	90.00	90.00	99.9070(10)
V, Å^3	724.3(6)	2946.0(3)	1447.7(3)	1572.51(18)	1894.12(17)
D_{calc} (g cm^{-1})	1.574	1.624	1.613	1.637	1.493
Linear absorption, μ (cm^{-1})	4.83	10.54	12.43	14.31	8.69
F(000)	360	1472	732	816	900
$2\theta_{max}$, °	52	58	56	58	58
Reflections measured	1845	24284	5467	13123	23226
Independent reflections	654	7828	1831	4166	5042
Observed reflections [I > 2σ(I)]	625	4946	1603	3760	4218
Parameters	53	415	108	200	231
R1	0.0486	0.0473	0.0458	0.0312	0.0293
wR2	0.1282	0.0975	0.1082	0.0649	0.0770
GOF	1.182	0.993	1.048	0.985	1.036
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e Å^{-3})	0.913/-0.535	0.408/-0.456	0.768/-0.748	0.398/-0.253	0.316/-0.463

In all the complexes synthesized, the coordination geometry around the metal ion is close to an ideal octahedron, as follows from the angles of distortion towards a trigonal prism in the range 49.41(4) – 58.49(9) (φ = 0° for an ideal trigonal prism, φ = 60° for an ideal octahedron). To better quantify this distortion, continuous symmetry measures were used[22] that measure how close is the shape of the coordination polyhedron to a reference shape, such as an ideal octahedron (OC) and an ideal trigonal prism. The lower the value of an appropriate symmetry measure, the better is the fit; for example, S(OC) would be zero for an ideal octahedron. For all the complexes synthesized, the symmetry measures S(OC) and S(TPR) evaluated from the X-ray

diffraction data confirm a very small deviation of the shape of the coordination polyhedron from an ideal octahedron hinted by the above distortion angles.

Table S2. Main geometric parameters and continuous symmetry measures[a] as obtained from X-ray diffraction at 120 K for for **1-3** and **5**.

	1	**2**	**3**	**5**
φ (°)	58.49(9)/52.23(8)	50.91(17)	51.54(10)	49.41(4)
h (Å)	2.1640(8)/2.2174(8)	2.3353(3)	2.3435(12)	2.4339(10)
S(OC)	0.722/ 0.740	0.172	0.100	0.295
S(TPR)	13.794/13.450	16.185	15.784	14.847

[a] φ is the distortion angle of the OC-TPR polyhedron, *h* is the height of this polyhedron; S(OC) and S(TPR) are octahedral and trigonal prismatic measures, respectively.

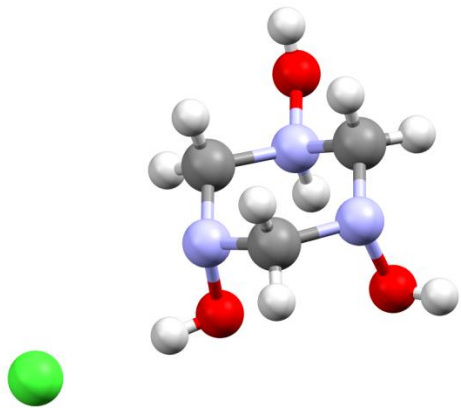


Figure S1. X-ray structure of **tfoH$_3$·HCl**.

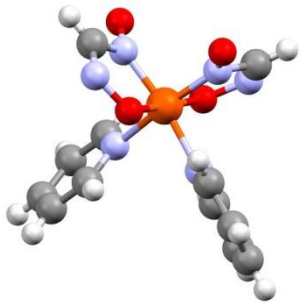


Figure S2. X-ray structure of complex **1**.

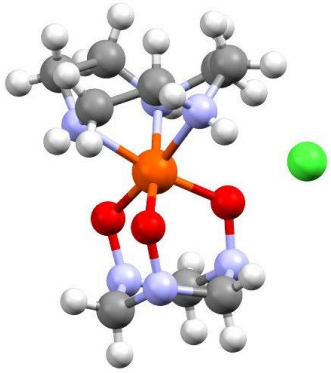


Figure S3. X-ray structure of complex **2**.

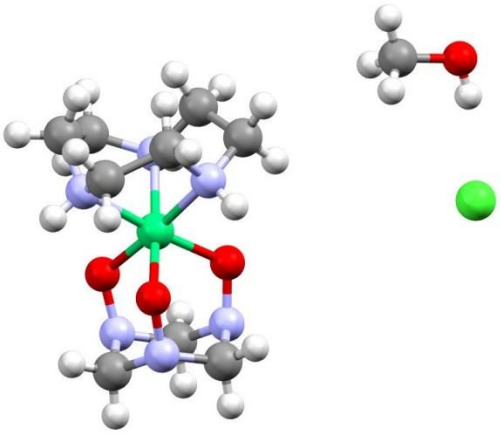


Figure S4. X-ray structure of complex **3**.

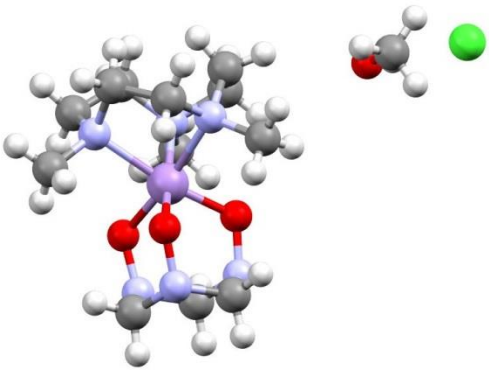
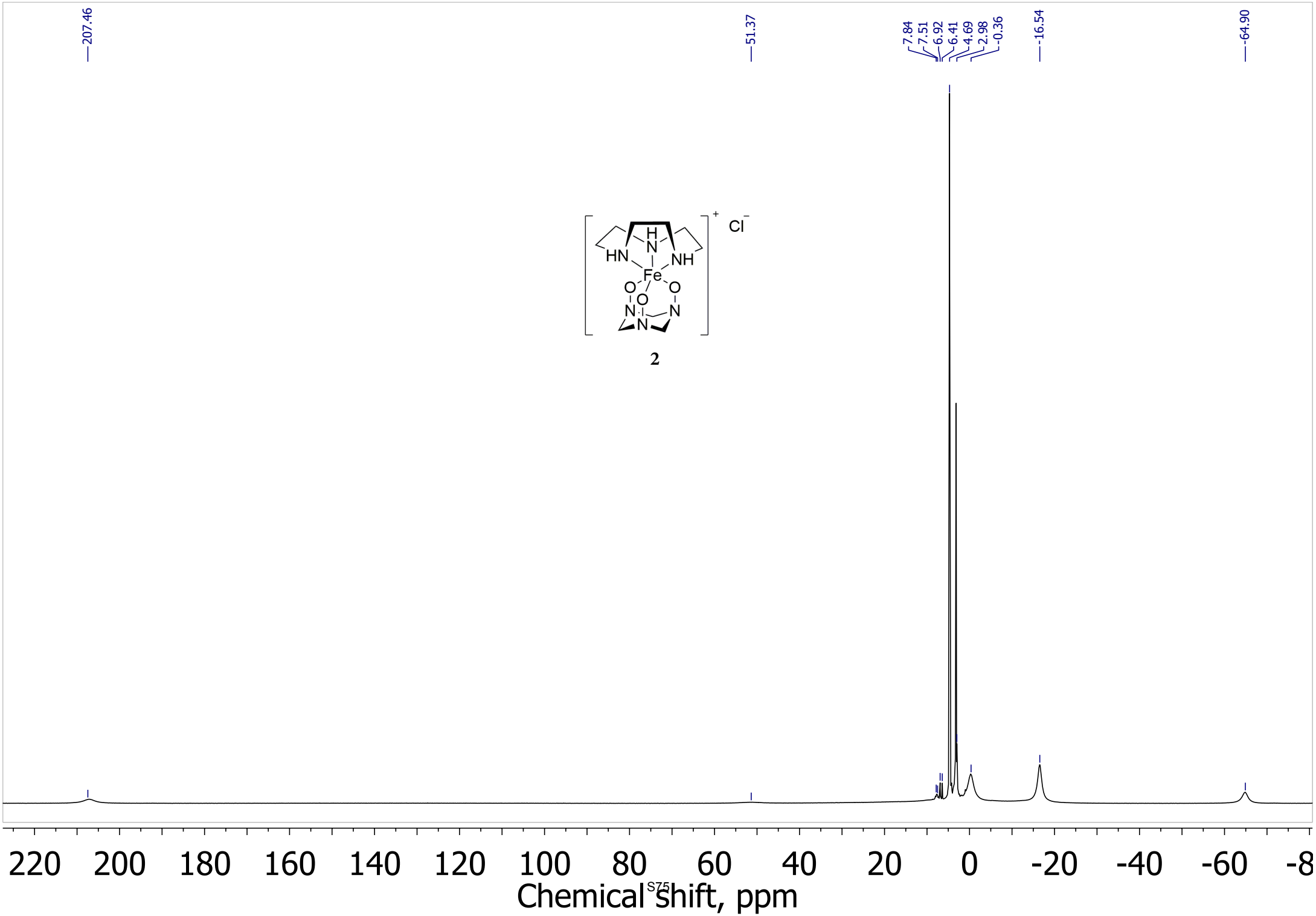


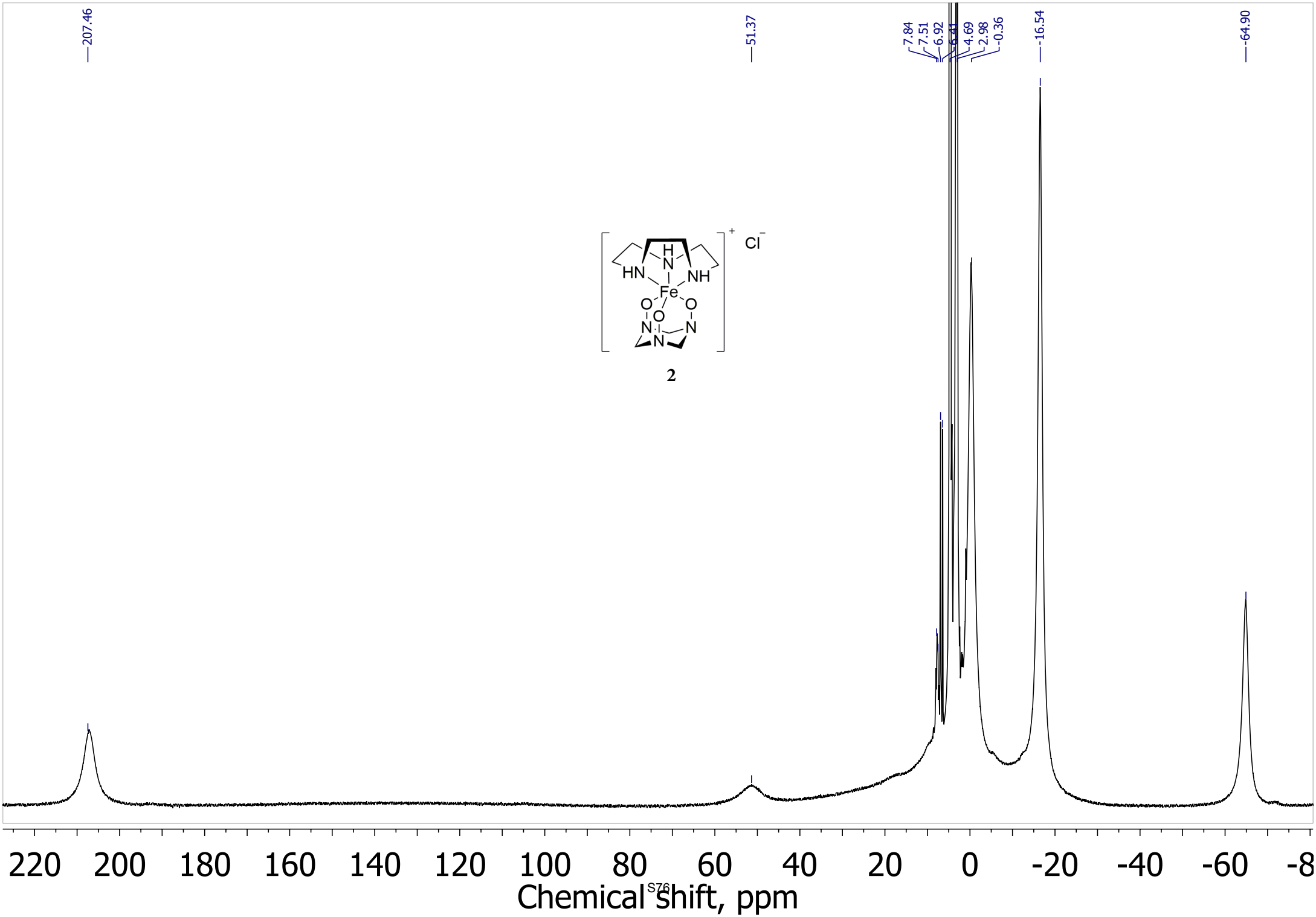
Figure S5. X-ray structure of complex **5**.

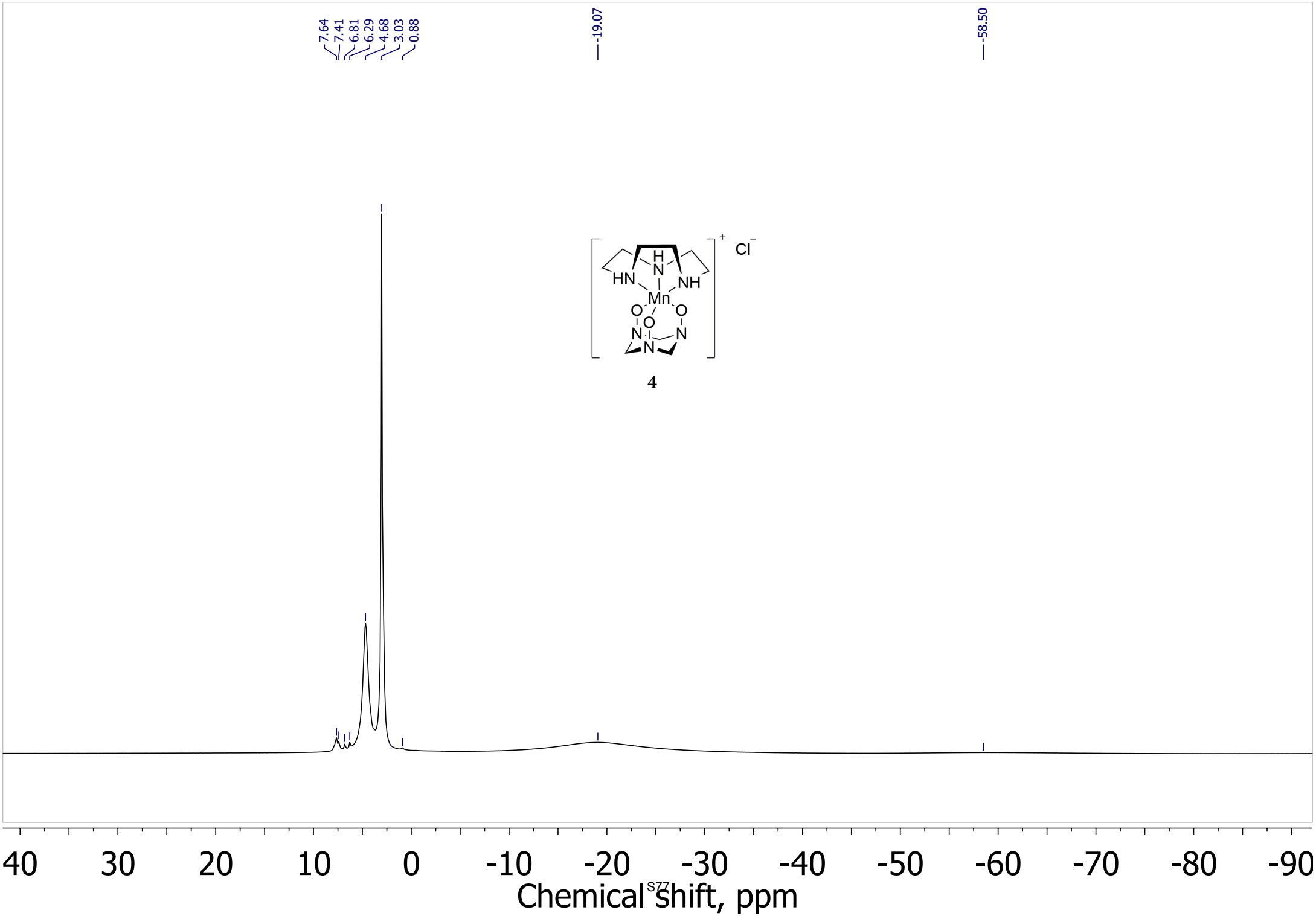
7. NMR spectroscopy and Evans method for 2 and 4

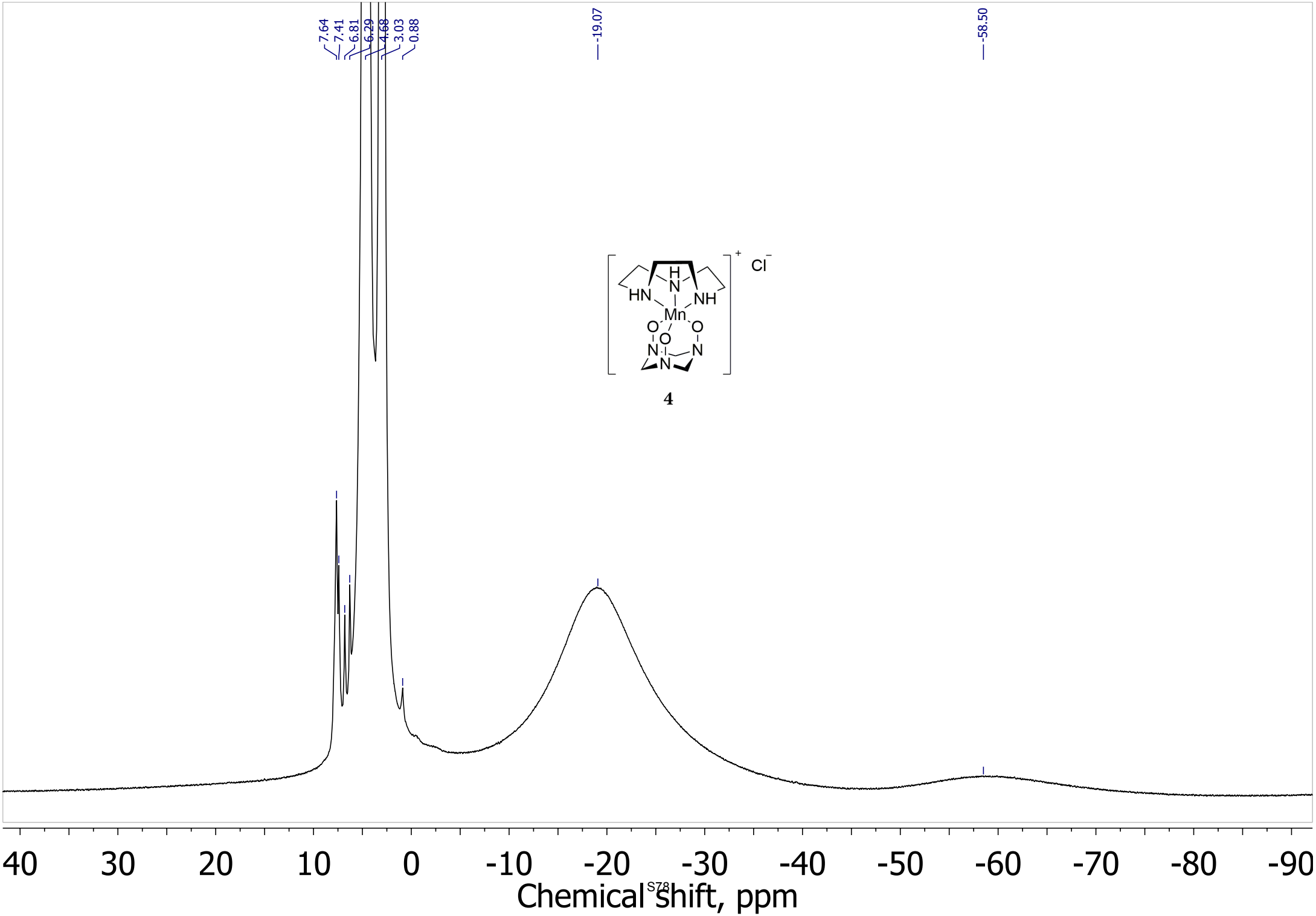
Table S3. Results of the Evans method for the paramagnetic iron (**2**) and manganese (**4**) complexes at 290 K (400 MHz, D_2O).

Compound	**Δδ, ppm**	**C (mg/ml)**	**χT, cm^3*mol*K^{-1}**
[Fe(*tacn*)(*tfo*)]Cl **(2)**	0.22	7.2	1.2
[Mn(*tacn*)(*tfo*)]Cl **(4)**	0.255	5.3	1.9


207.46
51.37
7.84
7.51
6.92
6.41
4.69
2.98
-0.36
-16.54
-64.90
Cl⁻
2
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-8
Chemical shift, ppm


207.46
51.37
7.84
7.51
6.92
6.41
4.69
2.98
-0.36
-16.54
-64.90
Cl⁻
2
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-8
Chemical shift, ppm


7.64
7.41
6.81
6.29
4.68
3.03
0.88
-19.07
-58.50
H
N
HN
NH
Mn
O
O
O
N
N
N
Cl
4
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
Chemical shift, ppm


7.64
7.41
6.81
6.29
4.68
3.03
0.88
-19.07
-58.50
H
N
HN
NH
Mn
O
O
O
N
N
N
Cl
4
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
Chemical shift, ppm

8. Electrochemical properties of complexes 2, 3 and 4

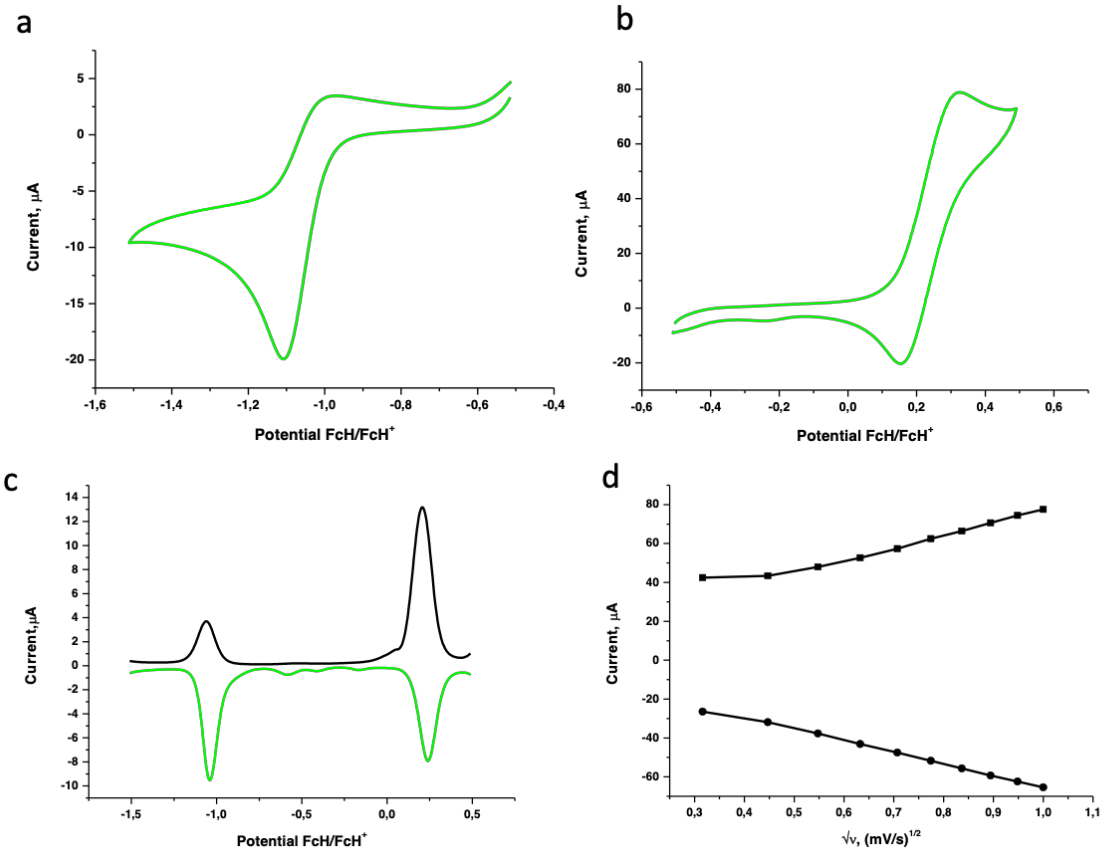


Figure S6. Electrochemical data for 1 mM dimethylformamide solution of the iron complex **2** with 0.1 M (n-$(C_4H_9)_4N)PF_6$ as a supporting electrolyte: (a) cyclic voltammogram for the first reduction process, (b) cyclic voltammogram for the first oxidation process, (c) differential pulse voltammograms, (d) dependence of peak current on square root of the scan rate. Conditions: scan rate 100 mV s^{-1} (for **a** and **b**), 298 K, platinum working and counter electrodes, Ag/AgCl reference electrode, the potentials are references to FcH/FcH^+ couple.

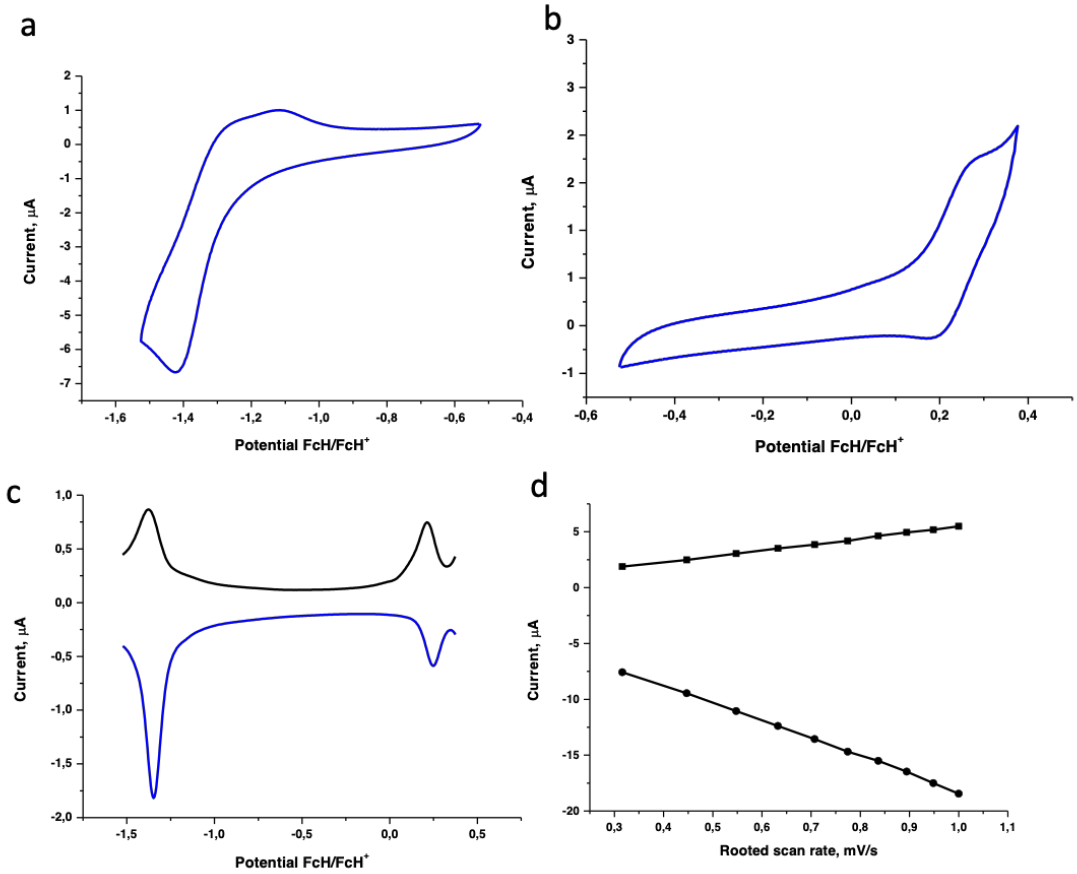


Figure S7. Electrochemical data for 1 mM dimethylformamide solution of the nickel complex **3** with 0.1 M (n-$(C_4H_9)_4N)PF_6$ as a supporting electrolyte: (a) cyclic voltammogram for the first reduction process, (b) cyclic voltammogram for the first oxidation process, (c) differential pulse voltammograms, (d) dependence of peak current on square root of the scan rate. Conditions: scan rate 100 mV s^{-1} (for **a** and **b**), 298 K, platinum working and counter electrodes, Ag/AgCl reference electrode, the potentials are references to FcH/FcH^+ couple.

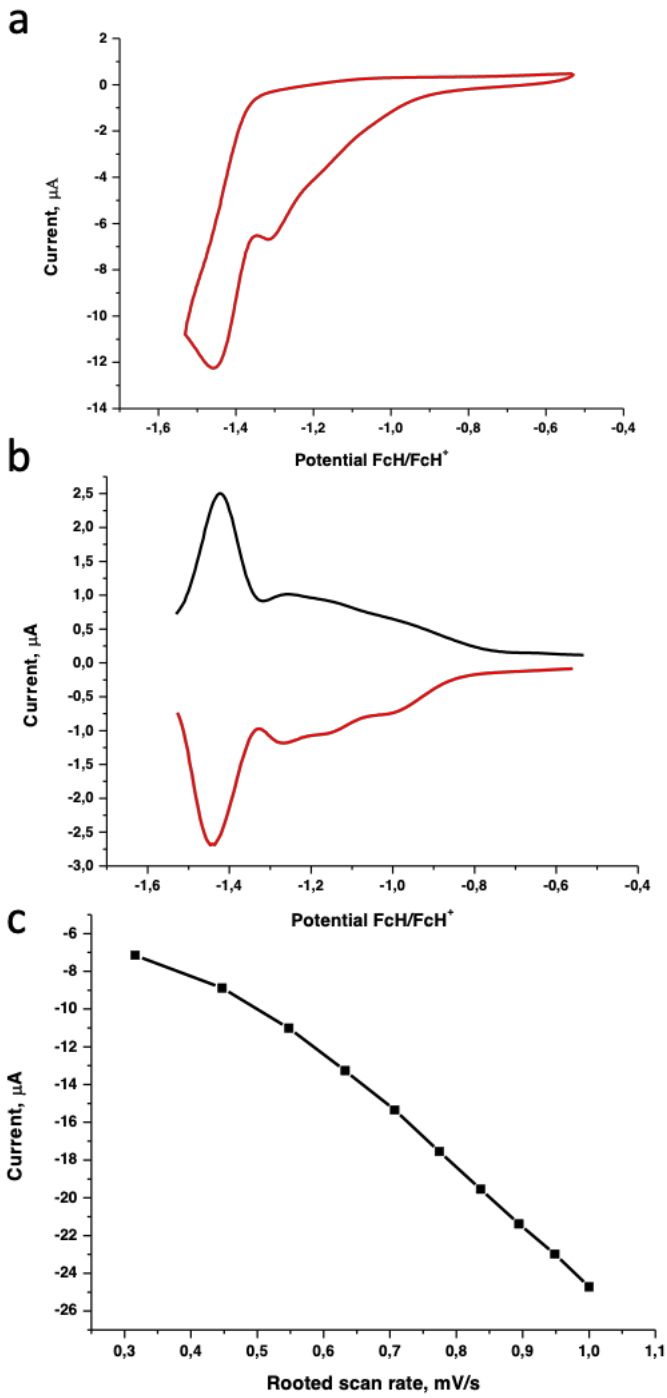
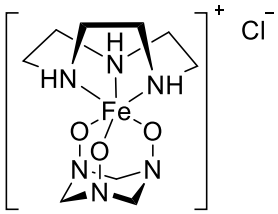


Figure S8. Electrochemical data for 1 mM dimethylformamide solution of the manganese complex **4** with 0.1 M (n-$(C_4H_9)_4N)PF_6$ as a supporting electrolyte: (a) cyclic voltammogram and (b) differential pulse voltammograms for the reduction process, (c) dependence of peak current on square root of the scan rate. Conditions: scan rate 100 mV s^{-1} (for **a**), 298 K, platinum working and counter electrodes, Ag/AgCl reference electrode, the potentials are references to FcH/FcH^+ couple.

9. XPS spectra of complexes 2, 3 and 5

The assignment of peaks of metals in XPS spectra was performed based on the available literature data for compounds with similar coordination geometry and metal-ligand distances.

XPS spectra of **2**.



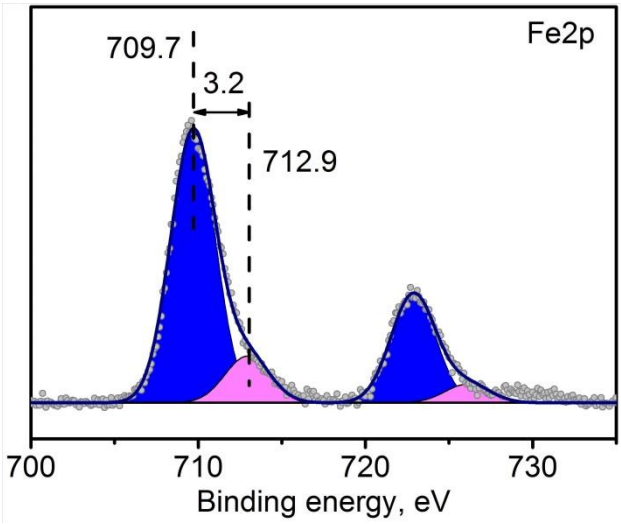


Figure S9. Curve fitted Fe2p XPS spectrum for complex **2** with deconvolution on individual components.

E_b(Fe2p) = 709.7 eV and 723 eV – formal oxidation state Fe^{+3} in Fe-O. 710.2 eV (lit.[23]) and 723.5 eV (lit.[23]). Possible reason of the presence of Fe^{+3} in XPS spectrum of **2** is photoreduction of the complex.[24]

E_b(Fe2p) = 712.9 eV and 727 eV (second doublet) - formal oxidation state Fe^{+4} in Fe-O. 713.3 eV (lit.[23]) and 727.2 eV (lit.[23]).

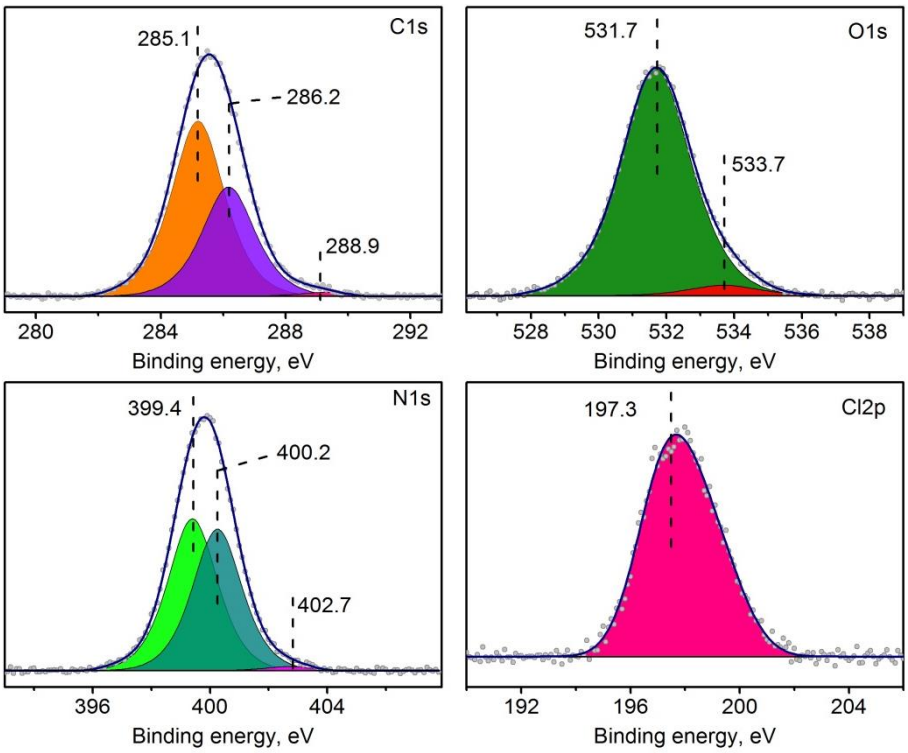


Figure S10. Curve fitted C1s, O1s, N1s and $Cl2p_{3/2}$ XPS spectra for complex **2** with deconvolution on individual components.

E_b(C1s) = 285.1 eV – carbon in $–CH_2$-CH_2- (*tacn* fragment).[7]

E_b(C1s) = 286.2 eV – carbon in CH_2-N (*tfo* and *tacn* fragments)[7] and carbon in CH_3-OH.[25]

E_b(C1s) = 288.9 eV – oxidized C.[26]

E_b(O1s) = 531.7 eV – oxygen in Fe-O.[23, 25]

E_b(O1s) = 533.7 eV – oxygen in CH_3-OH.[25]

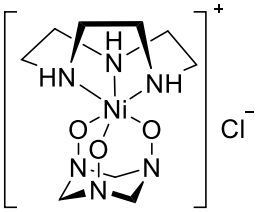
E_b(N1s) = 399.4 eV – nitrogen in -H_2C-N-H (*tacn* fragment).[27, 28]

E_b(N1s) = 400.2 eV – nitrogen in -O-N-CH_2- (*tfo* fragment).[29]

E_b(N1s) = 402.7 eV – N^+ (protonated *tfo* or *tacn* fragment).[28, 29]

$E_b(Cl2p_{3/2})$ = 197.3 eV – Cl^-.[30]

XPS spectra of **3**.



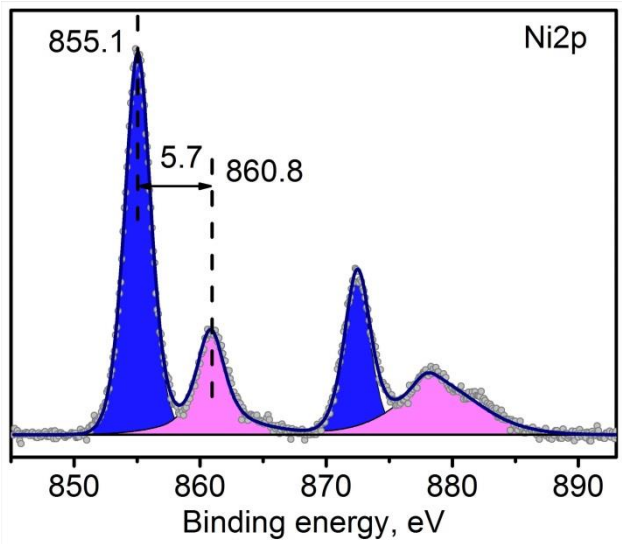


Figure S11. Curve fitted Ni2p XPS spectrum for complex **3** with deconvolution on individual components.

E_b(Ni2p) = 855.1, 860.8, 872, 878 eV – Ni^{+4} in Ni-O. In literature[26] for $KNiIO_6$: 855.4, 861.1, 873.0, 880.2 eV; Ni^{+4} has octahedral coordination, with a Ni-O bond length of 1.88 Å .[26]

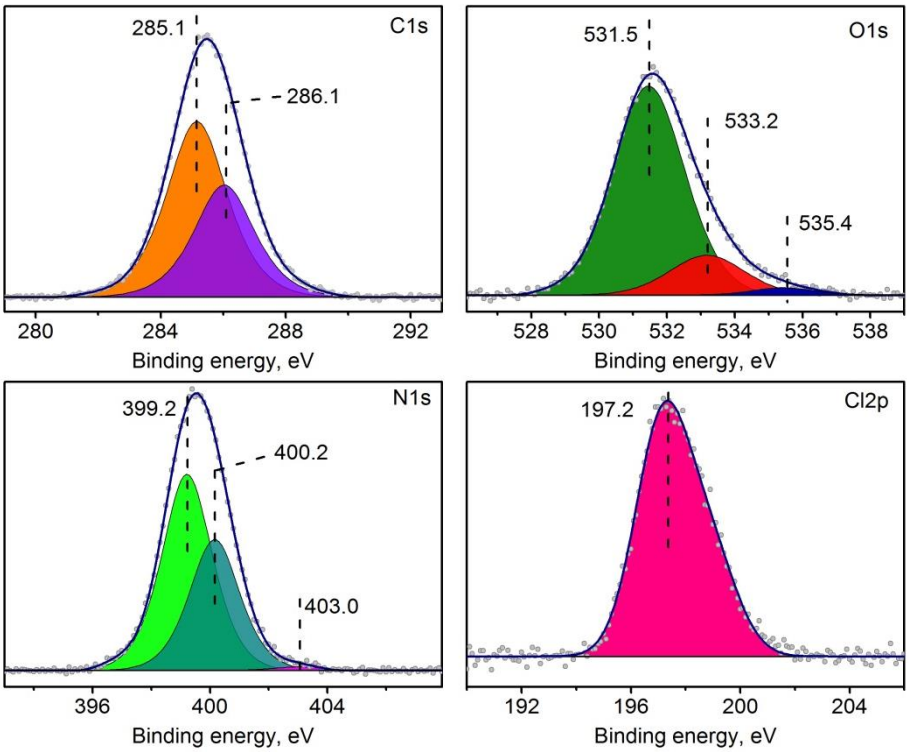


Figure S12. Curve fitted C1s, O1s, N1s and $Cl2p_{3/2}$ XPS spectra for complex **3** with deconvolution on individual components.

E_b(C1s) = 285.1 eV – carbon in $–CH_2$-CH_2- (*tacn* fragment).[7]

E_b(C1s) = 286.1 eV – carbon in CH_2-N (*tfo* and *tacn* fragments)[7] and carbon in CH_3-OH.[25]

E_b(O1s) = 531.5 eV – oxygen in Ni-O.[26]

E_b(O1s) = 533.2 eV – oxygen in CH_3-OH.[25]

E_b(O1s) = 535.4 eV – oxygen in H_2O.[31]

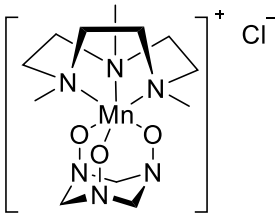
E_b(N1s) = 399.2 eV – nitrogen in -H_2C-N-H (*tacn* fragment).[27, 28]

E_b(N1s) = 400.2 eV – nitrogen in -O-N-CH_2- (*tfo* fragment).[29]

E_b(N1s) = 403.0 eV – N^+ (protonated *tfo* or *tacn* fragment).[28, 29]

$E_b(Cl2p_{3/2})$ = 197.2 eV – Cl^-.[30]

XPS spectra of **5**.



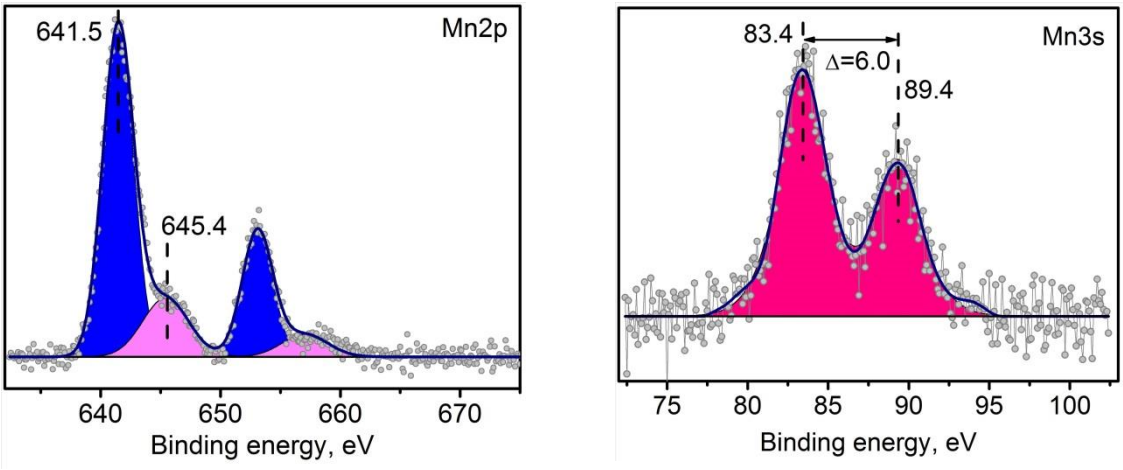


Figure S13. Curve fitted Mn2p and Mn3s XPS spectra for complex **5** with deconvolution on individual components.

E_b(Mn2p) = 641.5, 653 eV – Mn^{+4} in Mn-O. In literature[32] for **[$Mn^{II}_2Mn^{IV}_2(\mu_4$-Hedte$)_2$(thme$)_2$]**: 641.4, 653.2 eV – Mn^{+4} in Mn-O. Mn^{IV} has distorted octahedral coordination, with a Mn^{IV}-O bond lengths: 1.85 and 1.87 Å.[32] E_b(2p) of Mn^{+4} in a row of similar compounds is higher than E_b of Mn^{+2} and E_b of Mn^{+3}.[33]

E_b(Mn3s) = 83.4, 89.4 eV – Mn^{+4}, in Mn-O.[34] Serious doubt has been raised concerning the efficacy of using Mn3s for determining average oxidation states.[35]

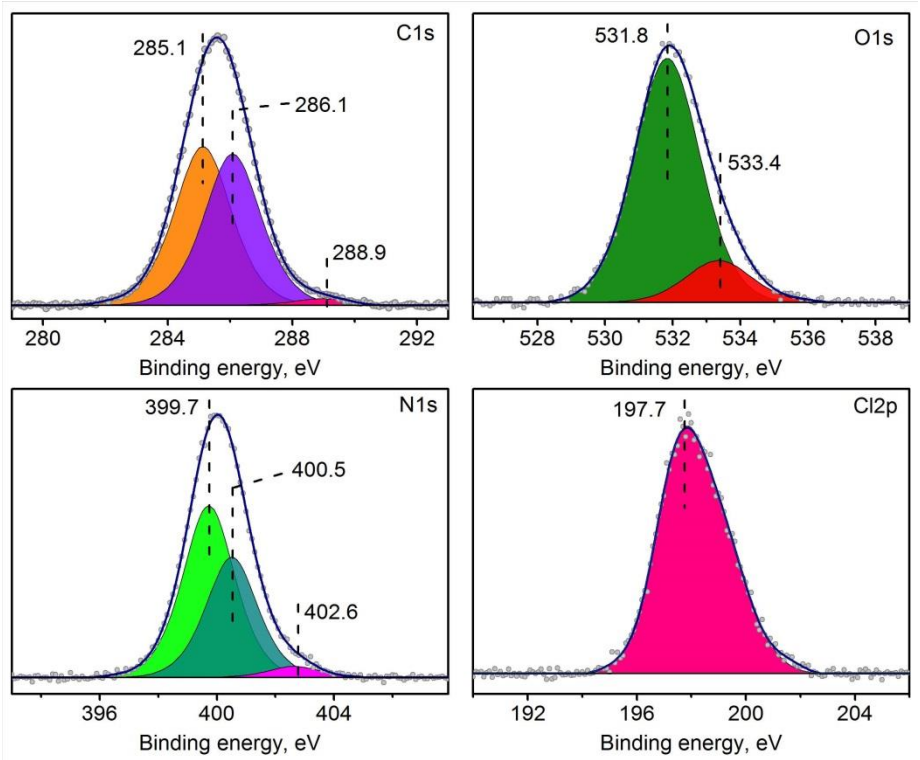


Figure S14. Curve fitted C1s, O1s, N1s and $Cl2p_{3/2}$ XPS spectra for complex **5** with deconvolution on individual components.

E_b(C1s) = 285.1 eV – carbon in $-CH_2-CH_2-$ (*Me_3tacn* fragment).[7]

E_b(C1s) = 286.1 eV – carbon in $-CH_2-N$ (*tfo* and *Me_3tacn* fragments),[7] carbon in $N-CH_3$ (*Me_3tacn* fragment)[7] and carbon in CH_3-OH.[25]

E_b(C1s) = 288.9 eV – oxidized C.[26]

E_b(O1s) = 531.8 eV – oxygen in Mn-O.[36]

E_b(O1s) = 533.4 eV – oxygen in CH_3-OH.[25]

E_b(N1s) = 399.7 eV – nitrogen in $-H_2C-N-CH_3$ (*Me_3tacn* fragment).[27, 28]

E_b(N1s) = 400.5 eV – nitrogen in $-O-N-CH_2-$ (*tfo* fragment).[29]

E_b(N1s) = 402.6 eV – N^+ (protonated *tfo* or *Me_3tacn* fragment).[28, 29]

$E_b(Cl2p_{3/2})$ = 197.7 eV – Cl^-.[30]

10. FT-IR spectroscopy studies with isotope-labeled [M(*tacn*)(*tfo*)]Cl complexes

Table S4. Frequencies of bands affected by $^{14}N/^{15}N$-substitution in [Fe(*tacn*)(*tfo*)]Cl (**2**).

#	**Band in FT-IR (KBr), cm^{-1} (intensity)**[a]			**Assignment**[37]
	[Fe(*tacn*)(*tfo*)]Cl	[Fe(*tacn*)($^{15}N_3$-*tfo*)]Cl	[Fe(*tacn*)(D_6-*tfo*)]Cl	
1	1167 (w)	1145 (w)	1127 (w)	C–N–C asymm, stretching
2	**972 (s)/949**[b]	**961 (s)/938**[b]	**959 (s)/902**[b]	**N–O stretching**
3	929 (s)	923 (s)	868 (s)	CH_2 rocking
4	746 (m)	729 (m)	734 (w)	N–C–N bending
5	632 (s)	622 (s)	590 (s)	N–C–N bending
6	460 (m)	455 (m)	453 (w)	C–N–C bending

[a] Intensities: s – strong, m – medium, w – weak. [b] Calculated frequencies of N–O stretching band, for animated frequency please watch corresponding .avi video file.

Table S5. Frequencies of bands affected by $^{14}N/^{15}N$-substitution in [Mn(*tacn*)(*tfo*)]Cl (**4**).

#	**Band in FT-IR (KBr), cm^{-1} (intensity)** [a]			**Assignment**[37]
	[Mn(*tacn*)(*tfo*)]Cl	[Mn(*tacn*)($^{15}N_3$-*tfo*)]Cl	[Mn(*tacn*)(D_6-*tfo*)]Cl	
1	1166 (w)	1147 (w)	1130 (m)	C–N–C asymm, stretching
2	**963 (s)/915**[b]	**956 (s)/901**[b]	**959 (s)/876**[b]	**N–O stretching**
3	932 (s)	924 (s)	868 (s)	CH_2 rocking
4	746 (w)	730 (w)	737 (w)	N–C–N bending
5	632 (s)	621 (s)	588 (s)	N–C–N bending
6	463 (m)	459 (m)	437 (w)	C–N–C bending

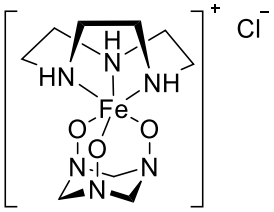
[a] Intensities: s – strong, m – medium, w – weak. [b] Calculated frequencies of N–O stretching band, for animated frequency please watch corresponding .avi video file.

Table S6. Frequencies of bands affected by $^{14}N/^{15}N$-substitution in [Ni(*tacn*)(*tfo*)]Cl (**3**).

#	**Band in FT-IR (KBr), cm^{-1} (intensity)** [a]			**Assignment**[37]
	[Ni(*tacn*)(*tfo*)]Cl	[Ni(*tacn*)($^{15}N_3$-*tfo*)]Cl	[NI(*tacn*)(D_6-*tfo*)]Cl	
1	1220 (m)	1203 (m)	1185 (m)	C–N–C asymm, stretching
2	**1015 (s)/1005**[b]	**1004 (s)/999**[b]	**955 (s)/930**[b]	**N–O stretching**
3	925 (s)	920 (s)	871 (s)	CH_2 rocking
4	762 (m)	741 (m)	743 (w)	N–C–N bending
5	625 (s)	615 (s)	582 (s)	N–C–N bending
6	445 (m)	441 (m)	428 (w)	C–N–C bending

[a] Intensities: s – strong, m – medium, w – weak. [b] Calculated frequencies of N–O stretching band, for animated frequency please watch corresponding .avi video file.

11. Mössbauer spectra of 2 in various conditions and DFT calculations of δ and ΔE_Q



Mössbauer spectra within temperature range from 90 K to 295 K have characteristic paramagnetic view and are well approximated by doublet (see Figure S15 and Figure S16). Given a distorted octahedral coordination geometry of [Fe(tacn)(tfo)]Cl, the observed hyperfine parameters of Mössbauer spectra are consistent with the values expected for Fe^{4+} ions with two unpaired electrons (S = 1).[38, 39] Large quadrupole splitting values $|\Delta E_Q| \approx 3$ mm/s point to relatively high value of electric field gradient. Such values are presumably arising from deformation (usually stretching along the axis of gradient) of the coordination octahedron. Mössbauer spectrum of complex **2** after 40 days reveals no signs of decomposition (Figure. S16).

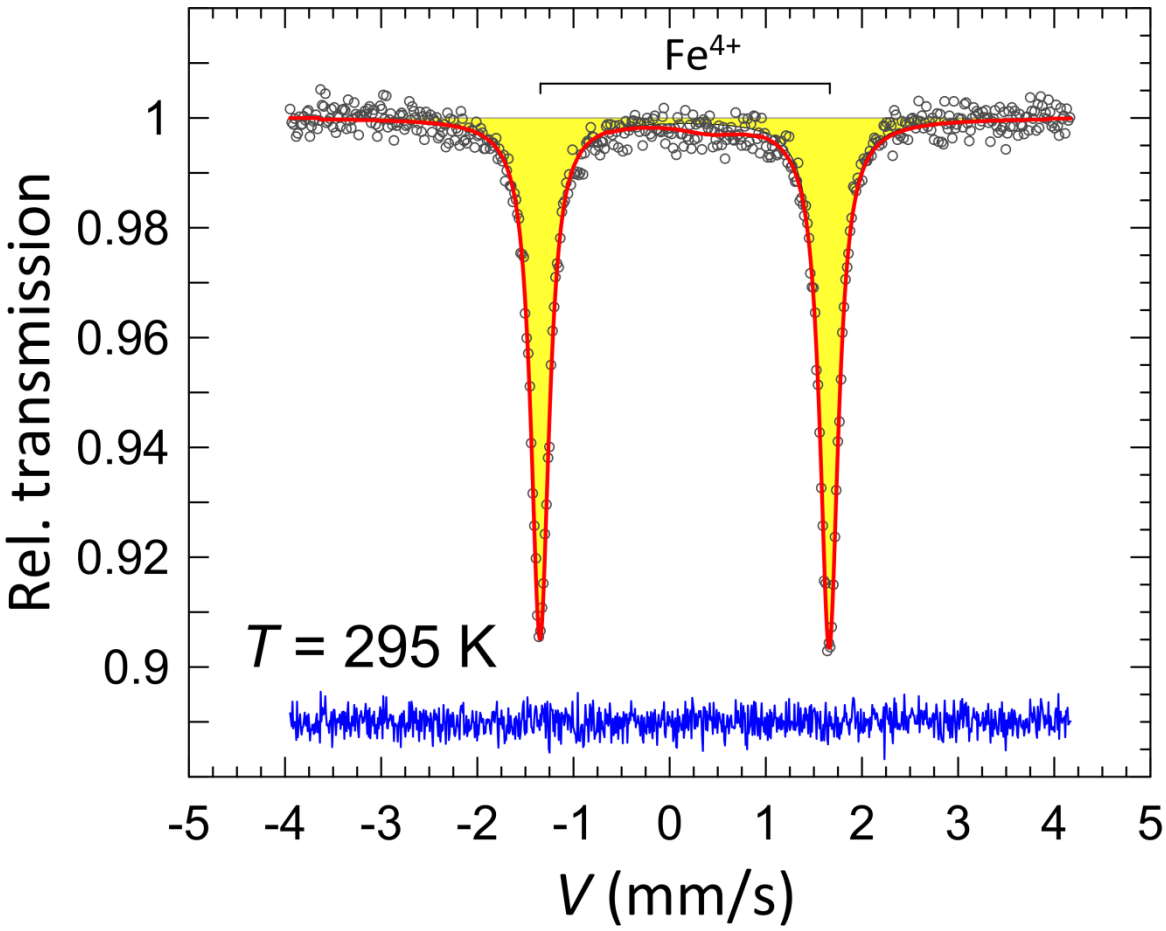


Figure S15. Mössbauer spectrum of complex **2** at T = 295 K.

Table S7. Hyperfine parameters of Mössbauer spectra of **2** at different temperatures.

Compound	T, (K)	δ, (mm/s)	$\|\Delta E_Q\|$, (mm/s)	Γ, (mm/s)
Complex **2** doublet Fe^{4+}	295	0.155(1)	3.007(1)	0.228(2)
	250	0.172(1)	3.010(1)	0.237(2)
	200	0.190(1)	3.010(1)	0.243(2)
	175	0.199(1)	3.010(1)	0.249(2)
	150	0.205(1)	3.009(1)	0.245(1)
	130	0.210(1)	3.010(1)	0.249(2)
	110	0.215(1)	3.008(1)	0.251(1)
	90	0.218(1)	3.007(1)	0.256(1)

T – temperature, δ – isomer shift, ΔE_Q – quadrupole splitting, Γ – full width at half-maximum of the signal.

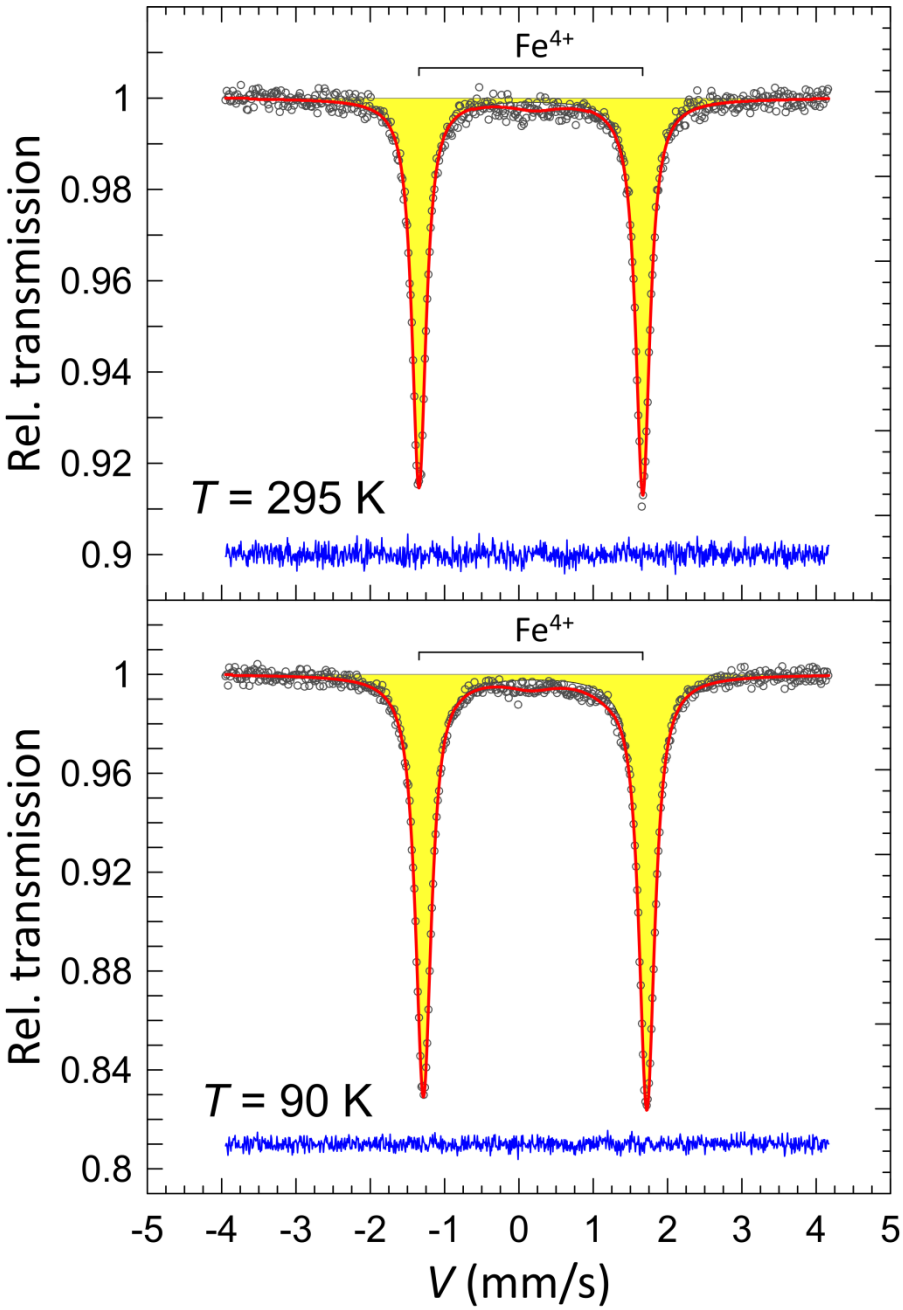


Figure S16. Mössbauer spectra of complex **2** at T = 295 K (after 40 days) and at T = 90 K.

DFT calculations of Mössbauer isomer shift (δ) and quadrupole splitting (ΔE_Q) were performed for several structures:

1) Neutral complex **2** (without methanol) with coordinates taken directly from X-ray diffraction analysis. Charge 0; multiplicity 3.

2) Cation derived from complex **2** (without methanol and Cl^-) with coordinates taken directly from X-ray diffraction analysis. Charge +1; multiplicity 3.

3) DFT optimized geometry of cation **2**.**2**.[19] Charge +1; multiplicity 3.

4) DFT optimized geometry of cation **2**.**1**. Charge +1; multiplicity 1.

5) DFT optimized geometry of cation **2**.**3**. Charge +1; multiplicity 5.

6) DFT optimized geometry of **FeTMCO**$^{2+}$ cation,[40] to verify our calculations. Charge +2; multiplicity 3.

Table S8. Calculated parameters of Mössbauer spectra.

#	Structure	δ	ΔE_Q
1	X-Ray neutral complex **2**	0.19 mm/s	-2.00 mm/s |3.007| mm/s (exp.)
	RHO = 23615.684 a.u.$^{-3}$		
	V_{zz} = -1.2342 V_{yy} = 0.6399 V_{xx} = 0.5944 (atomic units)		
2	X-Ray geometry of cation complex **2**	0.19 mm/s	-2.14 mm/s
	RHO = 23615.657		
	V_{zz} = -1.3257 V_{yy} = 0.6988 V_{xx} = 0.6270		
3	DFT optimized geometry of cation **2.2**	0.20 mm/s	-2.21 mm/s
	RHO = 23615.630		
	V_{zz} = -1.3629 V_{yy} = 0.7849 V_{xx} = 0.5780		
4	DFT optimized geometry of cation **2.1**	0.16 mm/s	-1.56 mm/s
	RHO = 23615.885		
	V_{zz} = -0.9428 V_{yy} = 0.6402 V_{xx} = 0.3026		
5	DFT optimized geometry of cation **2.3**	0.39 mm/s	-1.51 mm/s
	RHO = 23614.511		
	V_{zz} = -0.8726 V_{yy} =0.7266 V_{xx} = 0.1460		
6	DFT optimized geometry of **FeTMCO**$^{2+}$	0.13 mm/s 0.17 mm/s (exp.)[40] 0.19 mm/s (calc.)[41]	0.72 mm/s 1.24 mm/s (exp.)[40] 0.77 mm/s (calc.)[41]
	RHO = 23616.025		
	V_{zz} = 0.4428 V_{yy} = -0.2758 V_{xx} = -0.1670		

RHO – calculated contact electron density on Fe nucleus, a.u.$^{-3}$ V_{xx}, V_{yy}, V_{zz} - eigenvalues of the electric field gradient.

Worked-out example of ΔE_Q calculation for DFT optimized cation **2.2**:

$$\Delta E_Q = \frac{eQ_{(^{57}Fe)}V_{zz}}{2}\sqrt{\left(1+\frac{\eta^2}{3}\right)}$$

ΔE_Q – quadrupole splitting, V_{xx}, V_{yy}, V_{zz} - eigenvalues of the electric field gradient tensor $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$, $\eta = \frac{V_{xx}-V_{yy}}{V_{zz}}$ – asymmetry parameter, e – positron charge, $Q_{(^{57}Fe)}$ – nuclear quadrupole moment.[41-43]

$$V_{zz} \times \sqrt{\left(1+\frac{\eta^2}{3}\right)} = -1.3681 \text{ (atomic units)}$$

$$Q_{(^{57}Fe)} = 0.16 \times 10^{-28}(barn) = 2.5632 \times 10^{-48}\ (C \times m^2) = 0.5713 \times 10^{-8}(a.u.)$$

$$\Delta E_Q = -0.3991 \times 10^{-8}(hartree) = -10.6343 \times 10^{-8}\ (eV)$$

Conversion[44] of Doppler velocity into γ-energy increments:

$$\varepsilon_\gamma = \frac{vE_0}{c}$$

ε_γ- γ-energy increment, v - Doppler velocity, E_0 - the quantum energy of γ-photon, for ^{57}Fe $E_0 = 14.412497 \times 10^3$ eV, c - speed of light in vacuum.

if $v = 1\frac{mm}{s}$, then $\varepsilon_\gamma = 4.80766 \times 10^{-8}\ eV$

$$\Delta E_Q = \frac{-10.6343 \times 10^{-8}}{4.80766 \times 10^{-8}} = -2.2120\frac{mm}{s}$$

Reaction of *tfoH$_3$*·HCl, *tacn*·3HCl, anhydrous FeCl$_3$ and Et$_3$N in an inert atmosphere.

Caution: All actions have been taken without access of air. To a mixture of *tfoH$_3$*·HCl (110 mg, 0.65 mmol), *tacn*·3HCl (155 mg, 0.65 mmol), anhydrous FeCl$_3$ (100 mg, 0.65 mmol) under argon was added 5 mL of degassed methanol and Et$_3$N (0.8 mL, 5.9 mmol). The reaction mixture was stirred for 20 minutes at room temperature under argon and then was immediately evaporated to dryness in a vacuum (0.1 Torr, 25 °C, 1 hour). Mössbauer spectrum (a, Figure S17) and ESI-HRMS spectrum (Table S9) were recorded from resulted powder.

Then to the powder (200 mg) from the previous step was added 1 mL of methanol and Et$_3$N (0.25 mL, 1.84 mmol). The reaction mixture was stirred for 25 minutes at room temperature under air. Then reaction mixture was frozen in liquid nitrogen vapor and Mössbauer spectrum of resulting frozen solution was recorded (b, Figure S17).

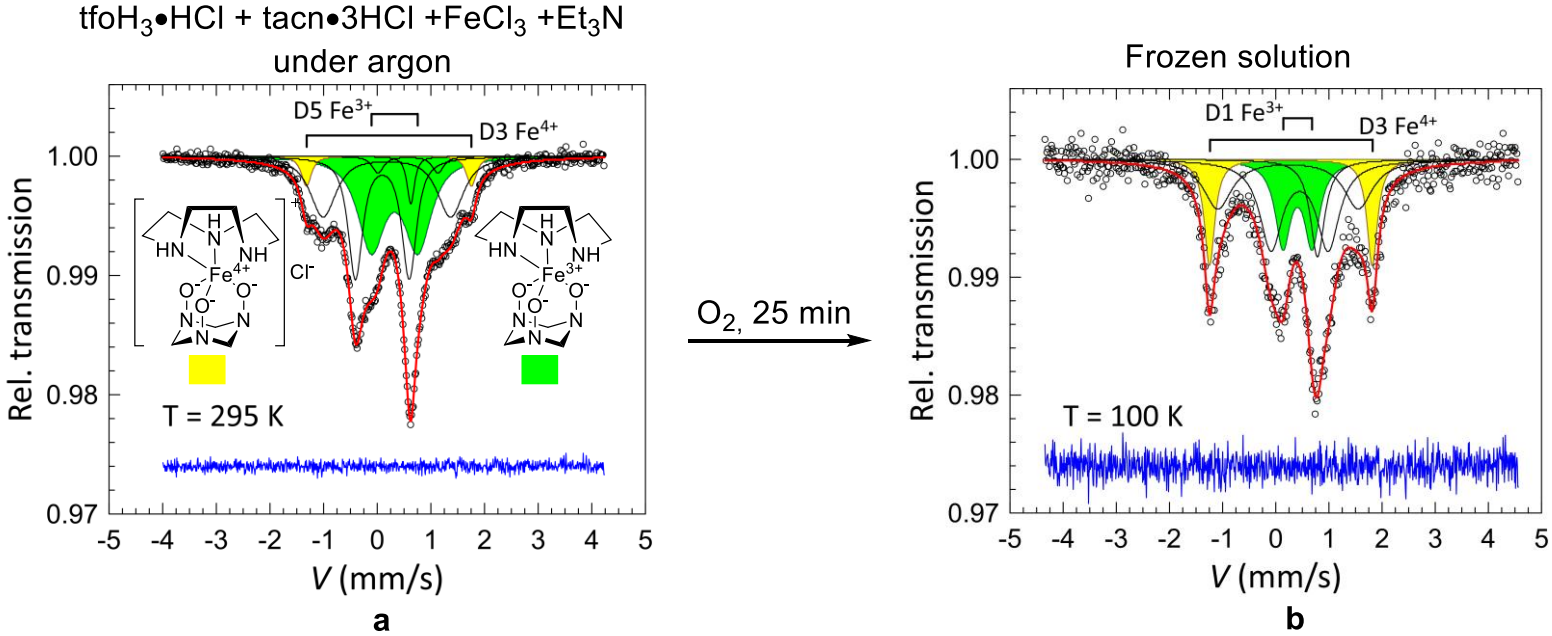


Figure S17. Mössbauer spectra of the reaction mixture: *tfoH$_3$*·HCl, *tacn*·3HCl, FeCl$_3$ and Et$_3$N in an inert atmosphere (a) and in frozen methanolic solution after air exposure (b). Yellow doublet – [Fe(*tacn*)(*tfo*)]Cl (**2**). Green doublet – [Fe(*tacn*)(*tfo*)] (reduced complex **2**).

Table S9. ESI-HRMS characterization after reaction of *tfoH*$_3$·HCl, *tacn*·3HCl, $FeCl_3$ and Et_3N in an inert atmosphere.

Compound	ESI-HRMS m/z: Calculated	ESI-HRMS m/z: Found	Δ ppm
[Fe(*tacn*)(*tfo*)]$^+$ **(2)** $[C_9H_{21}FeN_6O_3]^+$	317.1019	317.1019	0.0
[Fe(*tacn*)(*tfo*)]·H$^+$ (reduced complex **2)** $[C_9H_{22}FeN_6O_3]^+$	318.1097	318.1088	2.8

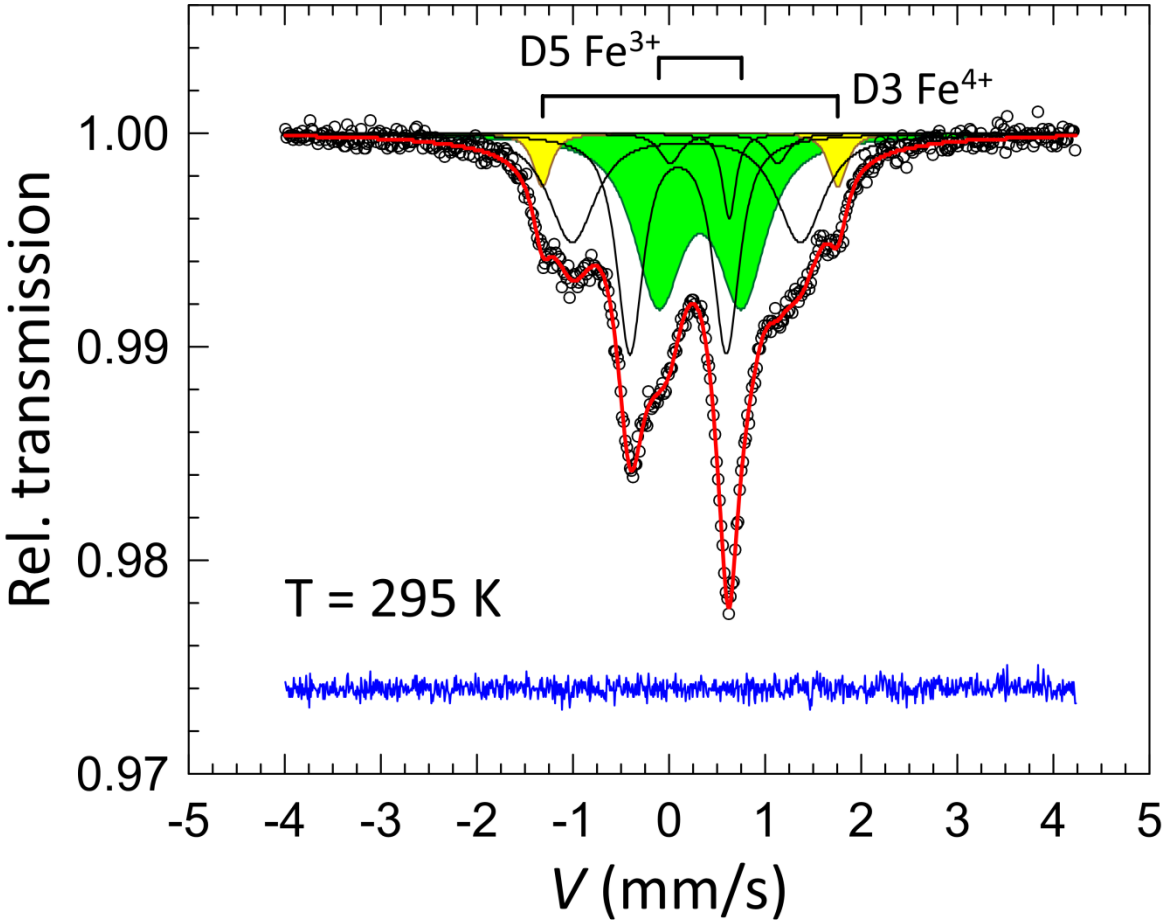


Figure S18. Mössbauer spectrum of the reaction mixture: *tfoH*$_3$·HCl, *tacn*·3HCl, $FeCl_3$ and Et_3N in an inert atmosphere at T = 295 K.

Table S10. Hyperfine parameters of Mössbauer spectrum of the reaction mixture: *tfoH*$_3$·HCl, *tacn*·3HCl, $FeCl_3$ and Et_3N in an inert atmosphere at T = 295 K.

Component	δ, (mm/s)	$\|\Delta E_Q\|$, (mm/s)	S rel, %	Γ, (mm/s)
Doublet 1	0.0945	1.0039	27.62	0.3255
Doublet 2	0.1791	2.3768	24.16	0.5804
Doublet 3	0.2185	3.0764	4.78	0.2273
Doublet 4	0.5723	1.1168	3.07	0.2641
Doublet 5	0.3236	0.8656	37.58	0.6022
Singlet 1	0.6253	0	2.79	0.1667

S rel, % - contribution of the component

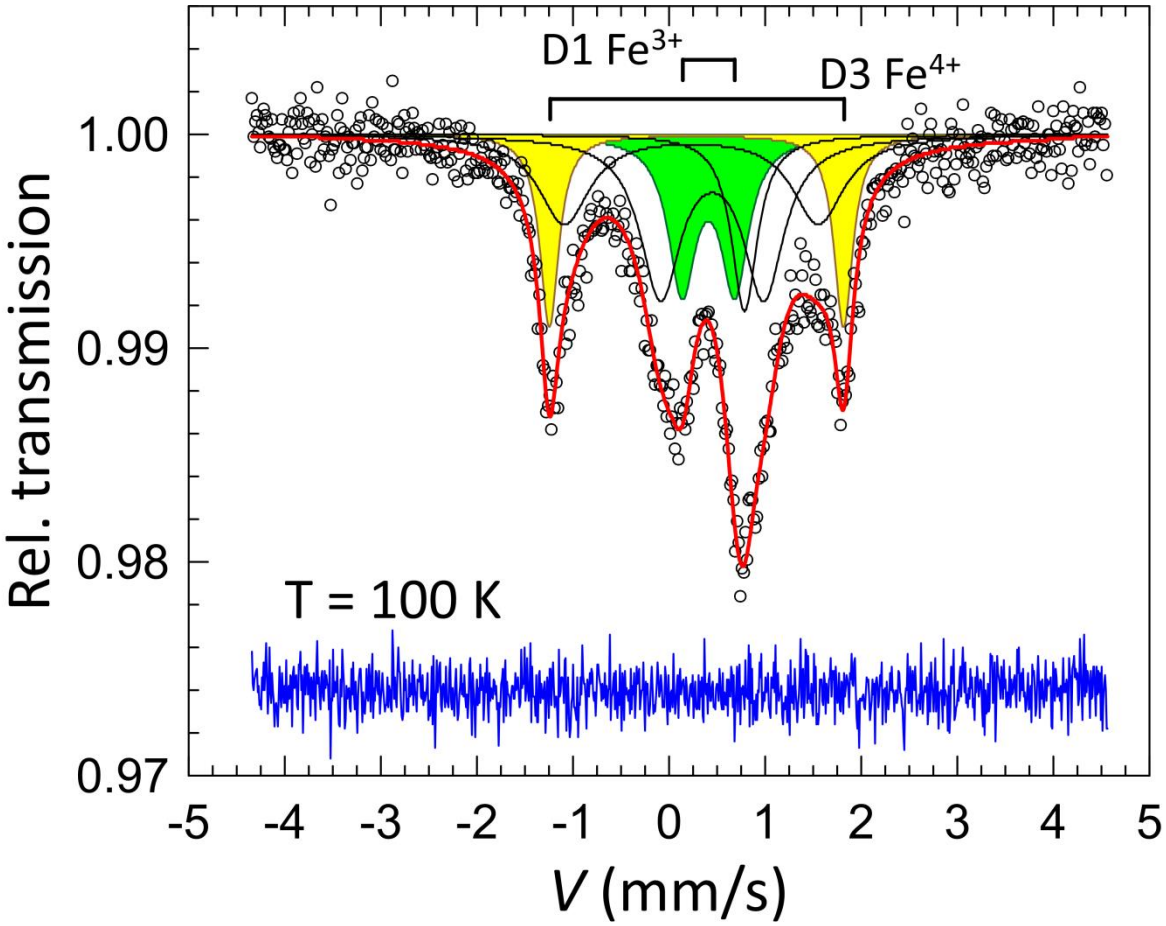


Figure S19. Mössbauer spectrum of the reaction mixture: *tfoH*$_3$·HCl, *tacn*·3HCl, $FeCl_3$ and Et_3N in frozen methanolic solution after air exposure. T = 100 K.

Table S11. Hyperfine parameters of Mössbauer spectrum of the reaction mixture: *tfoH*$_3$·HCl, *tacn*·3HCl, $FeCl_3$ and Et_3N in frozen methanolic solution after air exposure. T = 100 K.

Component	δ, (mm/s)	$\|\Delta E_Q\|$, (mm/s)	S rel, %	Γ, (mm/s)
Doublet 1	0.4112	0.5519	20.09	0.3554
Doublet 2	0.4470	1.0750	29.65	0.5120
Doublet 3	0.2855	3.0626	16.11	0.2367
Doublet 4	0.2336	2.6743	23.46	0.6845
Singlet 1	0.7830	0	10.70	0.3373

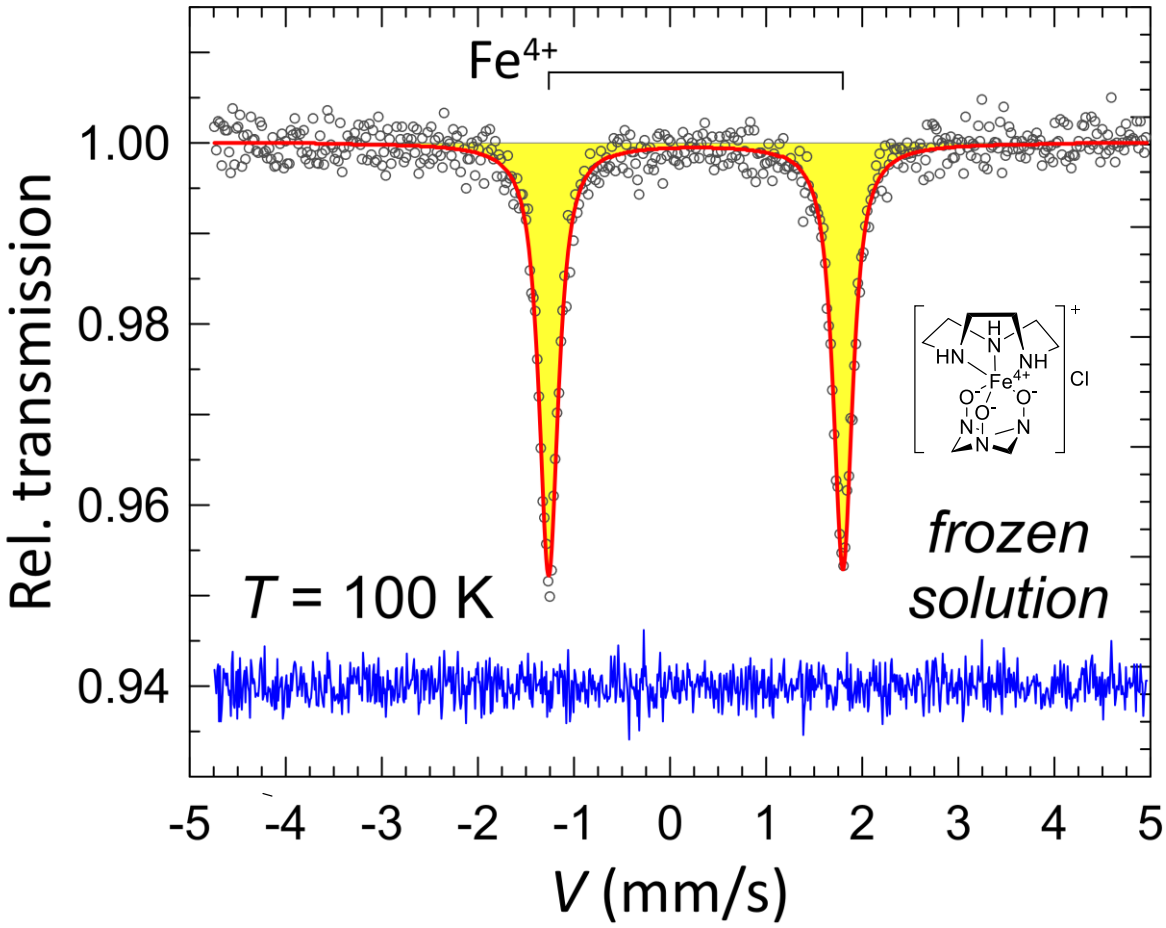


Figure S20. Mössbauer spectrum of pure complex **2** in frozen methanolic solution. T = 100 K.

Table S12. Hyperfine parameters of Mössbauer spectrum of pure complex **2** in frozen methanolic solution. T = 100 K.

Component	δ, (mm/s)	$\lvert\Delta E_Q\rvert$, (mm/s)	S rel, %	Γ, (mm/s)
Doublet 1	0.2676	3.0628	100.00	0.2420

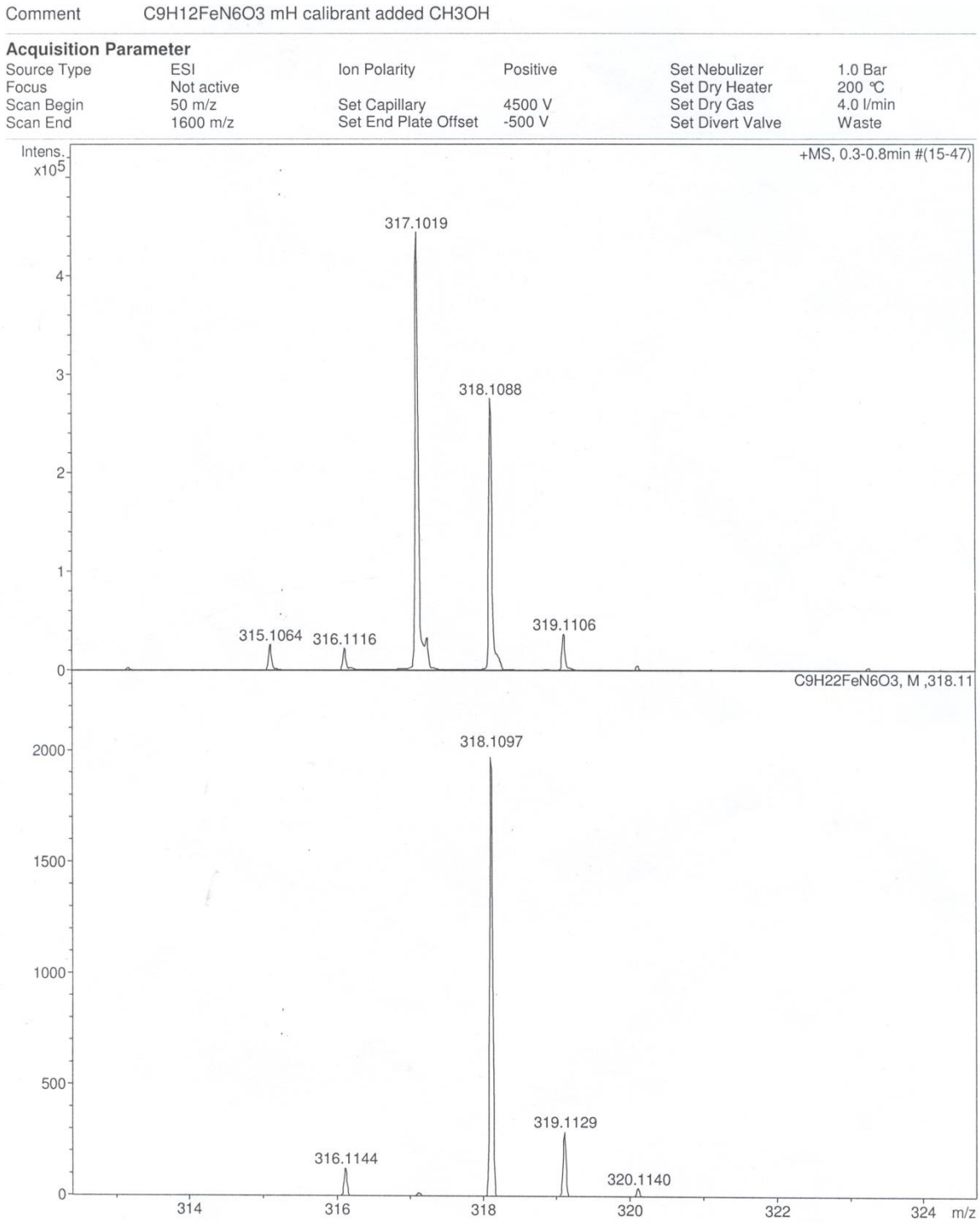


Figure S21. ESI-HRMS spectrum after reaction of *tfoH*$_3$·HCl, *tacn*·3HCl, $FeCl_3$ and Et_3N in an inert atmosphere.

Reaction of complex 2 with sodium ascorbate.

To a solution of **2** (75 mg, 0.21 mmol) in distilled water (5 ml) was added sodium ascorbate (168 mg, 0.85 mmol). The reaction mixture was stirred for 20 minutes at room temperature with closed cup and then was immediately evaporated to dryness in a vacuum (0.1 Torr, 35°C, 2 hours). Mössbauer spectrum and ESI-HRMS spectrum were recorded from resulted powder.

a **b** **c**

Figure S22. Color of the reaction of **2** with sodium ascorbate (a, b) and color comparison between reaction mixture (c, on the right) and aqueous solution of pure complex **2** (c, on the left).

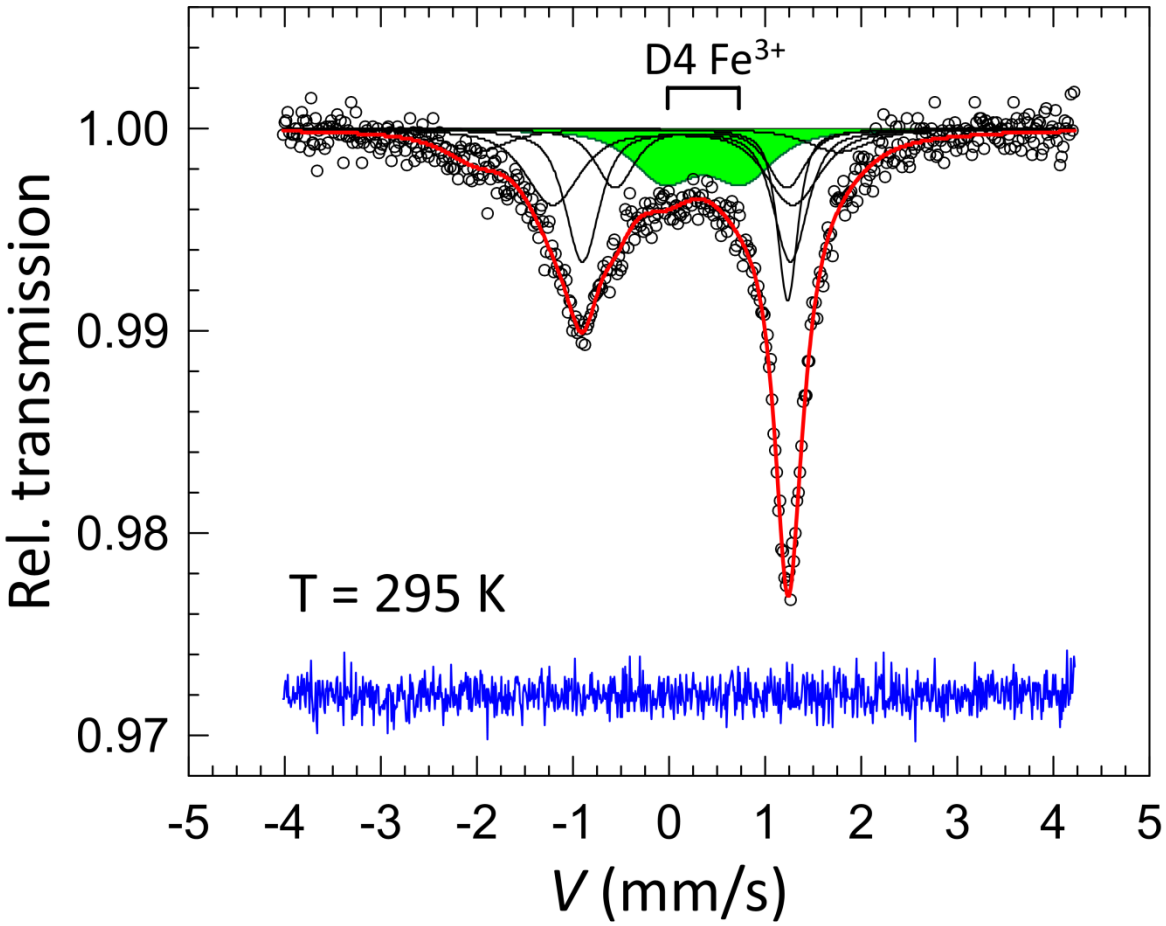


Figure S23. Mössbauer spectrum of the reaction of complex **2** with sodium ascorbate. T = 295 K.

Table S13. Hyperfine parameters of Mössbauer spectrum of the reaction of complex **2** with sodium ascorbate. T = 295 K.

Component	δ, (mm/s)	$\|\Delta E_Q\|$, (mm/s)	S rel, %	Γ, (mm/s)
Doublet 1	0.1804	2.1642	26.45	0.4215
Doublet 2	0.0373	2.5005	23,79	0.6744
Doublet 3	0.3321	1.7857	13.07	0.4683
Doublet 4	0.3557	0.8135	18.06	0.7760
Doublet 5	-0.1199	3.7711	8.35	0.7760
Singlet 1	1.2339	0	10.28	0.2507

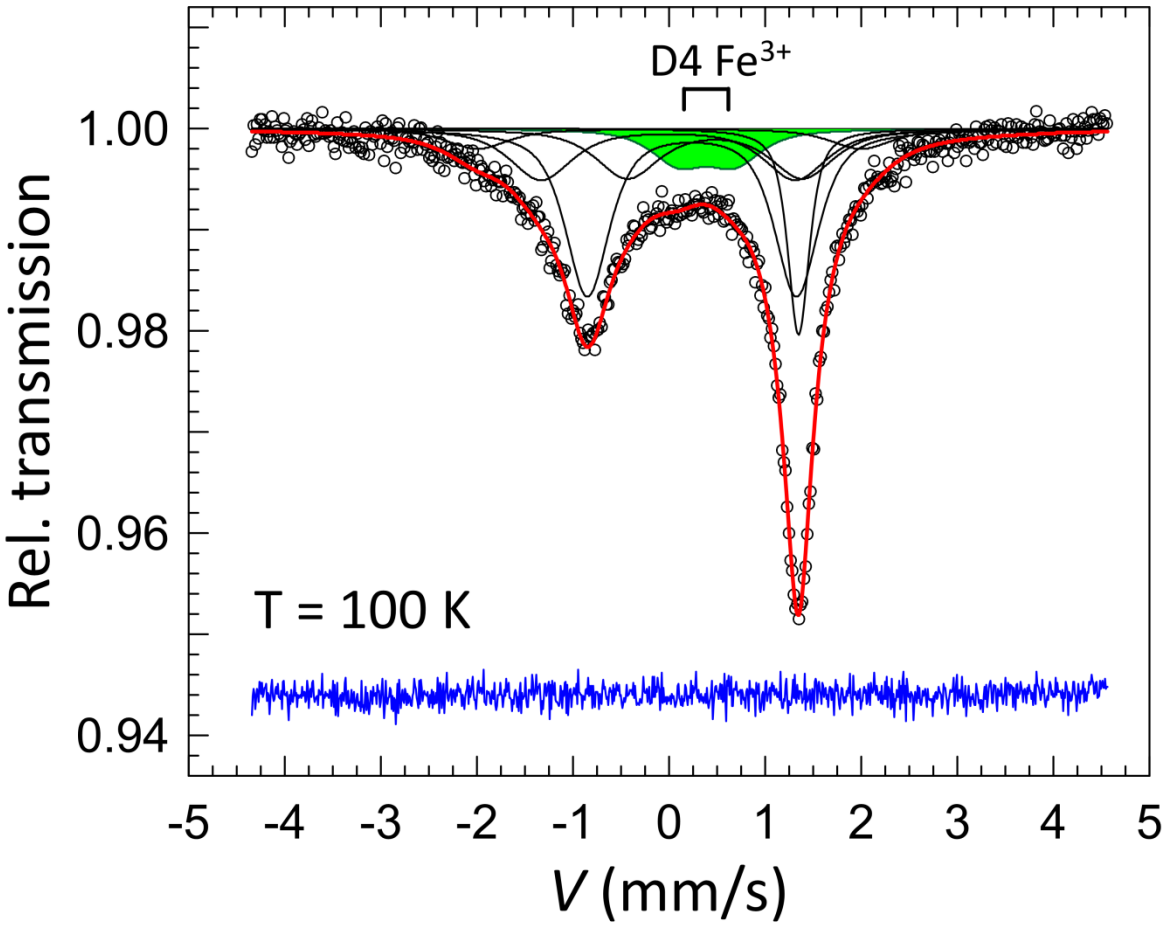


Figure S24. Mössbauer spectrum of the reaction of complex **2** with sodium ascorbate. T = 100 K.

Table S14. Hyperfine parameters of Mössbauer spectrum of the reaction of complex **2** with sodium ascorbate. T = 100 K.

Component	δ, (mm/s)	$\|\Delta E_Q\|$, (mm/s)	S rel, %	Γ, (mm/s)
Doublet 1	0.2385	2.1771	39.13	0.5478
Doublet 2	-0.0088	2.6477	16.71	0.7760
Doublet 3	0.4782	1.8237	16.05	0.7760
Doublet 4	0.3901	0.5851	9.58	0.6785
Doublet 5	0.0003	3.9971	6.60	0.7760
Singlet 1	1.3478	0	11.93	0.2677

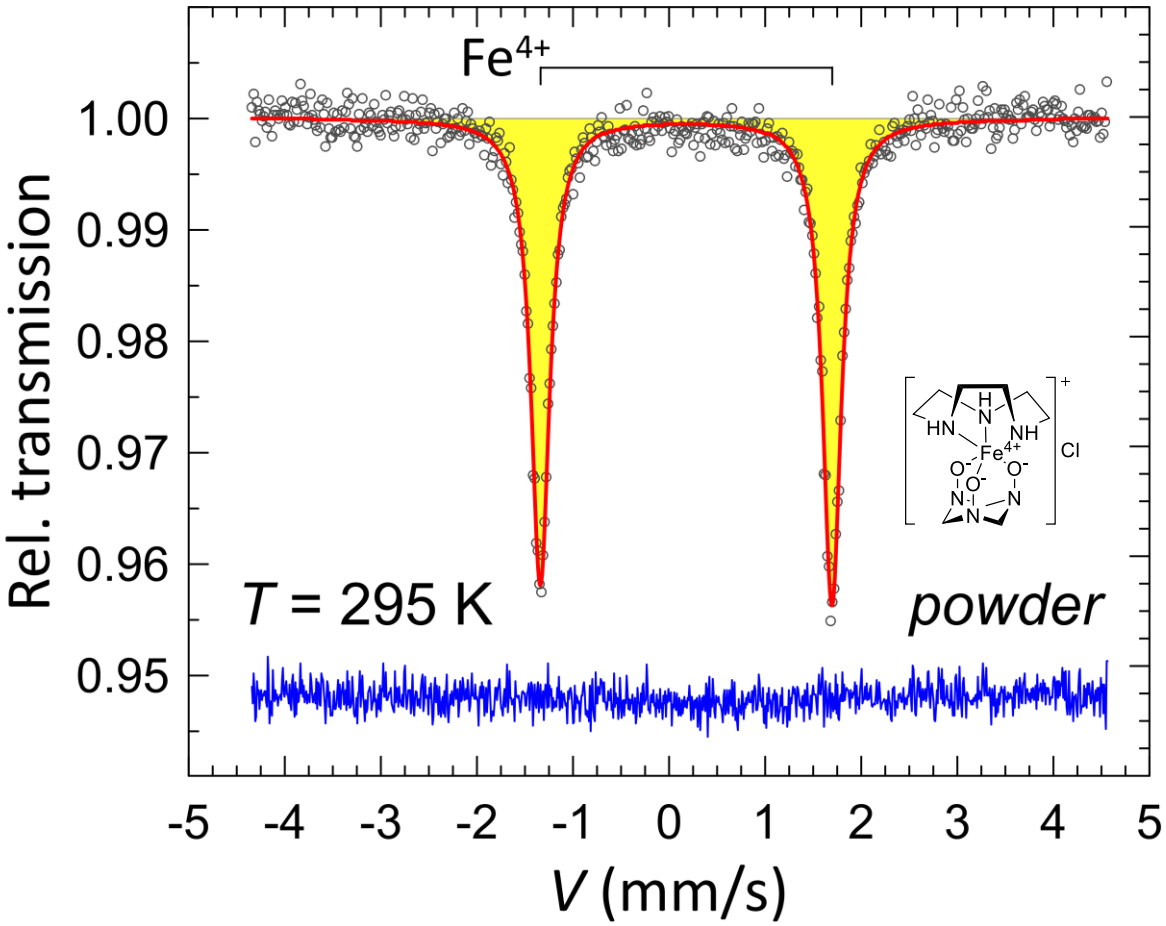


Figure S25. Mössbauer spectrum of pure complex **2** dissolved in water and evaporated to dryness after 20 min. T = 295 K.

Table S15. Hyperfine parameters of Mössbauer spectrum of pure complex **2** dissolved in water and evaporated to dryness after 20 min. T = 295 K.

Component	δ, (mm/s)	$\lvert\Delta E_Q\rvert$, (mm/s)	S rel, %	Γ, (mm/s)
Doublet 1	0.1774	3.0355	100.00	0.2358

Comment C9H22FeN6O3 calibrant added H2O

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

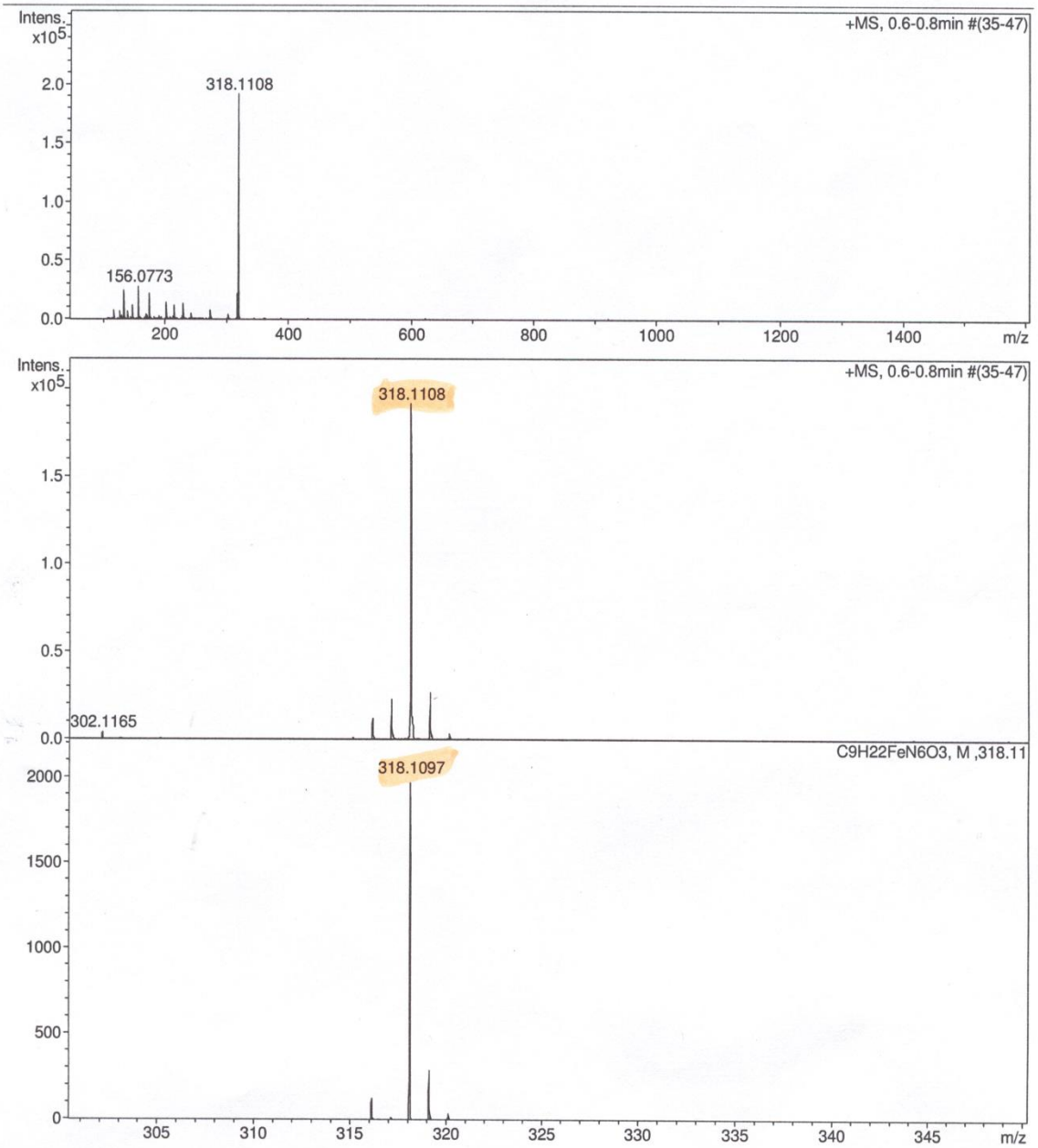


Figure S26. ESI-HRMS spectrum of the reaction of complex **2** with sodium ascorbate.

DFT calculations of Mössbauer isomer shift (δ) and quadrupole splitting (ΔE_Q) were performed for several possible structures of reduced complex **2** (**Fe(III) complex**):

1) DFT optimized geometry of reduced complex **2.4**. Charge 0; multiplicity 2.

2) DFT optimized geometry of reduced complex **2.5**. Charge 0; multiplicity 4.

3) DFT optimized geometry of reduced complex **2.6**. Charge 0; multiplicity 6.

Table S16. Calculated Mössbauer parameters for reduced complex **2**.

#	Structure	δ	ΔE_Q
1	Reduced complex **2.4**	0.36 mm/s	2.07 mm/s
	RHO = 23614.643 a.u.$^{-3}$		
	V_{zz} = 1.1098 V_{yy} = -1.1078 V_{xx} = -0.0020 (atomic units)		
2	Reduced complex **2.5**	0.50 mm/s	-2.38 mm/s
	RHO = 23613.827		
	V_{zz} = -1.4616 V_{yy} = 0.8581 V_{xx} = 0.6035		
3	Reduced complex **2.6**	0.57 mm/s	0.36 mm/s
	RHO = 23613.400		
	V_{zz} = 0.2197 V_{yy} = -0.1479 V_{xx} = -0.0718		

Table S17. Compairson of Mössbauer parameters for Fe(tacn)(tfo)]Cl and Fe(tacn)(tfo)]

Parameter	**[Fe(*tacn*)(*tfo*)]Cl (Fe(IV) complex)**	**[Fe(*tacn*)(*tfo*)] (Fe(III) complex)**
$\delta_{exp,}$ (mm/s)	0.16	0.32
$\lvert\Delta E_Q\rvert_{exp,}$ (mm/s)	3.00	0.87
$\delta_{calc,}$ (mm/s)	0.20	0.57
$\Delta E_{Q\ calc,}$ (mm/s)	-2.21	0.36

12. DFT calculations

12.1. Calculation of relative energies of anions A-C

Calculation of relative energies of anions **A-C** was performed with the Gaussian 16 Rev C.01 program.[15] Initially, preliminary calculations for structures **A-C** with overall multiplicity 1, 3 or 5 of each structure were performed to define one with the lowest total energy. BP86 DFT functional with GD3BJ empirical dispersion correction and jorge-adzp basis set[45-47] was used. Calculations were performed in methanol (SMD model). The approach of Martin and co-workers was followed.[48] Initial charge of Fe atom was set to +4, the charge of tfo ligand was set to -3. For better results, ***initial wavefunction*** was generated using division of the molecule into fragments.[49] Interpretation of metal oxidation state in DFT optimized structures was performed on the basis of Mulliken atom spin density.

First step of calculation job:

Keywords:[50]

 # BP86/Gen guess(only,fragment=3) pop=none SCF=XQC

A structure complex 1 mult 1 jorge-adzp

```
-2 1 -3 1 -3 1 4 1
 N(Fragment=2)     2.27276800   0.11159500   -1.23888200
 O(Fragment=2)     0.92838600   0.28219700   -1.35761700
 ….
```

Second step of calculation job:

 # opt BP86/Gen guess=read geom=checkpoint nosymm scrf=(smd,solvent=Methanol) SCF=XQC pressure=605 temperature=298.15

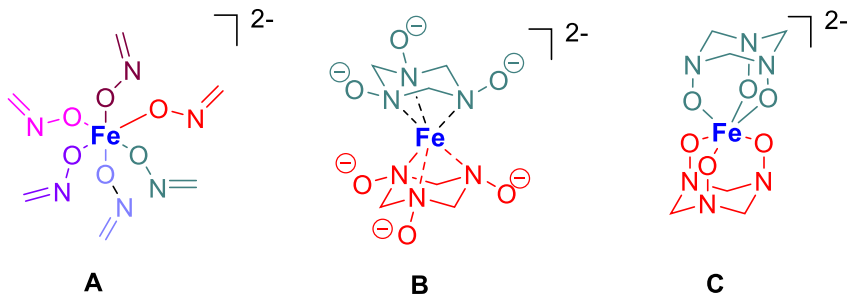


Figure S27. Fragmentation of structures **A-C**.

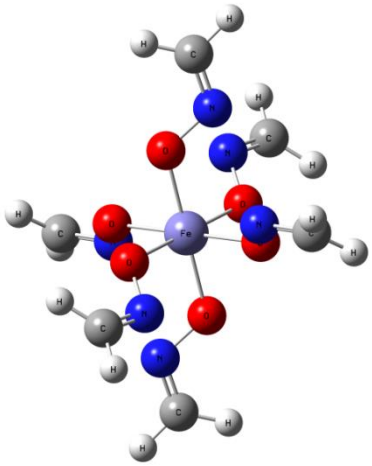
For the most stable structures **A-C**, DFT-D3 BP86/jorge-atzp[46, 51] level of theory was used for more precise geometry optimization and calculations of thermodynamics. Cartesian coordinates are given in angstroms; absolute energies for all substances are given in hartrees. Analysis of vibrational frequencies was performed for all optimized structures. All compounds were characterized by only real vibrational frequencies. Wavefunction stability, using *stable* keyword, was also checked for each molecule.

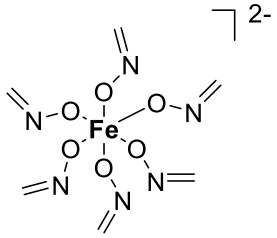
For calculations of optimized geometries, frequencies and thermodynamics, following keywords were used:

 # opt freq BP86/Gen scf=xqc nosymm scrf=(smd,solvent=Methanol) pressure=605 temperature=298.15 test

Table S18. Calculated relative energies of anions **A-C**.

Structure	$\Delta G°_{298,15\ K}$ Kcal/mol	ΔE_0 Kcal/mol
A	+36.9	+58.2
B	+75.8	+79.6
C	0.0	0.0



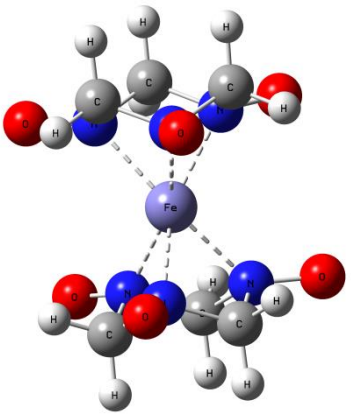


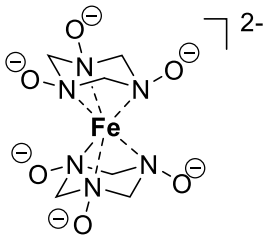
Structure A

Charge -2; multiplicity 3

O	-1.31196900	0.78479900	-1.22168500
O	1.27666700	0.65442900	-1.21687200
O	0.01795200	1.52903800	1.16672400
N	0.06325100	2.77497300	0.63939300
C	0.13347400	3.72227300	1.51217100
H	0.15540300	3.53430100	2.59568600
H	0.17073400	4.74527000	1.13046600
N	-2.37955100	1.46114900	-0.73642400
C	-3.15863100	1.94934500	-1.64136300
H	-2.97137000	1.82730300	-2.71834500
H	-4.03371400	2.50400100	-1.29454600
N	2.38931800	1.25223000	-0.72931000
C	3.22110800	1.64993000	-1.63147000
H	3.04321600	1.51440000	-2.70837900
H	4.13376900	2.13833000	-1.28177700
Fe	-0.05413700	0.00364800	0.00413000
O	-1.38507100	-0.64703400	1.22511900
O	1.20355700	-0.77749100	1.22997400
O	-0.12639200	-1.52164200	-1.15850600
N	-2.49736100	-1.24543700	0.73747400
N	2.27124300	-1.45377300	0.74477200
N	-0.17113200	-2.76766200	-0.63129400
C	-3.32924100	-1.64314100	1.63954800
C	3.05027800	-1.94190200	1.64977800
C	-0.24154100	-3.71485900	-1.50416500
H	-3.15170100	-1.50716800	2.71646000
H	-4.24161100	-2.13203400	1.28978100
H	2.86291600	-1.81987700	2.72674400
H	3.92543900	-2.49648900	1.30304400
H	-0.26401500	-3.52675200	-2.58764400
H	-0.27832800	-4.73792100	-1.12258300

DFT-D3 UBP86/ jorge-atzp, solvent methanol, SMD model		
Total electronic energy=	-2280.093094	E_0
Sum of electronic and zero-point Energies=	-2279.896379	$E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2279.871567	$E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2279.870623	$E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2279.945747	$E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.196715	
Mulliken atom spin density for Fe atom: 1.87		



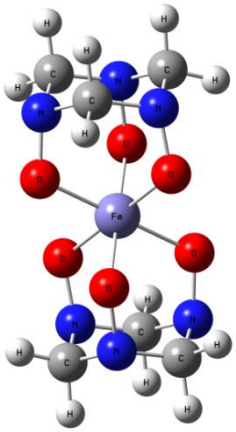


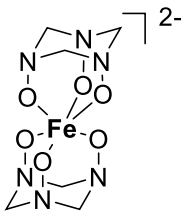
Structure B

Charge -2; multiplicity 3

N	-1.49773000	1.41493300	-0.08825800
O	-1.45716400	2.76501200	-0.16785600
N	-1.66941500	-0.51146800	1.17538000
O	-1.79837800	-1.11443300	2.37951400
N	-1.62292000	-0.64586800	-1.13246500
O	-1.71123800	-1.37879200	-2.26631700
C	-2.12724600	0.90022700	1.15321700
H	-3.23227400	0.99948000	1.15115800
H	-1.68174300	1.42120400	2.00784700
C	-2.25427200	-1.28161100	0.04996700
H	-3.36262400	-1.23737200	0.02433700
H	-1.89832800	-2.31551500	0.11849700
C	-2.07836400	0.75857500	-1.28708400
H	-3.18225200	0.85369900	-1.34170500
H	-1.59811900	1.17961800	-2.17742000
Fe	-0.01344200	-0.01863800	0.01370700
O	1.48316100	-2.13126300	1.82276400
O	1.79194400	2.41011500	0.86244300
O	1.61490600	-0.68713100	-2.60158600
N	1.49779600	-1.12547200	0.91764400
N	1.65029300	1.13206900	0.44108300
N	1.56175700	-0.40551700	-1.28012800
C	2.13876000	0.11912600	1.41046600
C	2.03726400	-1.51054000	-0.40989100
C	2.20608400	0.87926500	-0.91062600
H	3.24550000	0.05230300	1.44738300
H	1.72097300	0.35526800	2.39537200
H	3.14125700	-1.62045400	-0.41410400
H	1.54397100	-2.43585400	-0.72780700
H	3.31423800	0.82679800	-0.92104600
H	1.83705300	1.65778800	-1.58741900

DFT-D3 UBP86/ jorge-atzp, solvent methanol, SMD model		
Total electronic energy=	-2280.059277	E_0
Sum of electronic and zero-point Energies=	-2279.844502	$E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2279.826835	$E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2279.825891	$E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2279.883761	$E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.214775	
Mulliken atom spin density for Fe atom: 2.06		





Structure C

Charge -2; multiplicity 3

N	2.47855900	1.47748300	-0.00475400
O	1.06650000	1.62422000	-0.00524400
N	2.51063700	-0.67767000	-1.23019600
O	1.10278900	-0.78782800	-1.37559300
N	2.51295300	-0.66053600	1.24970900
O	1.10528400	-0.76548900	1.40038100
C	2.90769800	0.73886600	-1.20274700
H	4.00878500	0.77650500	-1.24096600
H	2.48818200	1.23562000	-2.08736400
C	2.94206300	-1.33461200	0.01397700
H	4.04426200	-1.35640300	0.01333400
H	2.55095700	-2.36032900	0.02132500
C	2.91068100	0.75521800	1.20200300
H	4.01188100	0.79307100	1.23659200
H	2.49389800	1.26418200	2.08096100
Fe	-0.00010000	0.00576000	0.00672000
O	-1.06669400	-1.61270700	-0.00480900
O	-1.10288300	0.79883500	-1.37596600
O	-1.10559100	0.77750400	1.40001500
N	-2.47875500	-1.46597800	-0.00446000
N	-2.51074500	0.68875900	-1.23062600
N	-2.51324500	0.67246400	1.24928600
C	-2.90782200	-0.72775900	-1.20272600
C	-2.91095100	-0.74331500	1.20203000
C	-2.94226400	1.34612100	0.01329600
H	-4.00890700	-0.76540200	-1.24099500
H	-2.48826100	-1.22481500	-2.08715300
H	-4.01215300	-0.78117000	1.23657200
H	-2.49420800	-1.25198000	2.08117900
H	-4.04446300	1.36790900	0.01255800
H	-2.55116100	2.37184100	0.02033300

DFT-D3 UBP86/ jorge-atzp, solvent methanol, SMD model		
Total electronic energy=	-2280.186061	E_0
Sum of electronic and zero-point Energies=	-2279.967521	$E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2279.951921	$E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2279.950977	$E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2280.004666	$E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.218540	
Mulliken atom spin density for Fe atom: 2.10		

12.2. Calculation of various characteristics of cations derived from complexes 2, 3-5

BP86 DFT functional with GD3BJ empirical dispersion correction and jorgetzp basis set[52, 53] was used for geometry optimization and calculations of thermodynamics. Cartesian coordinates are given in angstroms; absolute energies for all substances are given in hartrees. Analysis of vibrational frequencies was performed for all optimized structures. All compounds were characterized by only real vibrational frequencies. Wavefunction stability, using *stable* keyword, was also checked for each molecule.

Calculations were performed in methanol (SMD model). The approach of Martin and co-workers was followed.[48] Data from X-ray diffraction experiments for complexes **2**, **3-5** (without chlorine anion and solvent) were used as starting points for geometry optimizations.

Initial charge of Mn, Ni or Fe atom was set to +4, the charge of tfo ligand was set to -3. For better results, ***initial wavefunction*** was generated using division of the molecule into fragments.[49] Interpretation of metal oxidation state in DFT optimized structures was performed on the basis of Mulliken atom spin density.

For calculations of optimized geometries, frequencies and thermodynamics, following keywords were used:

 # opt freq UBP86/Gen nosymm EmpiricalDispersion=GD3BJ pressure=605 temperature=298.15 scf=xqc scrf=(smd,solvent=Methanol)

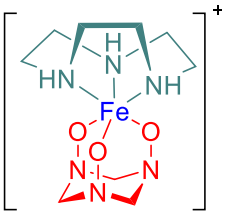


Figure S28. Fragmentation of **cation 2**.

For calculation of vibrational frequencies of isotope labeled compounds corresponding input file with optimized geometry was modified as in example:

….

N(Iso=15) -2.33653 -0.78886 -1.1811

….

Keywords for MO orbitals analysis (single point calculation, performed on optimized structure):

 # SP UBP86/Gen scrf=(smd,solvent=Methanol) nosymm EmpiricalDispersion=GD3BJ scf=xqc guess=always pressure=605 test pop=(Biorthogonalize,SaveBiorth)

Keywords for NBO orbitals analysis for **cation 3.1** (single point calculation, performed on optimized structure):

 # SP BP86/Gen scrf=(smd,solvent=Methanol) EmpiricalDispersion=GD3BJ scf=xqc pressure=605 nosymm pop=(nboread) test

$NBO RESONANCE $END

Complex 2

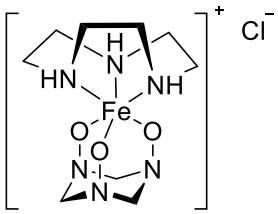
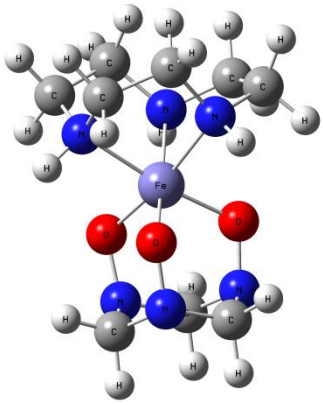


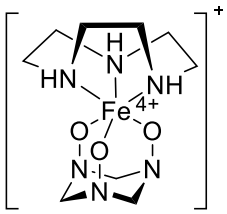
Table S19. Calculated relative energies of cations **2.1 – 2.3**.

cation	$\Delta G°_{298,15\ K}$ Kcal/mol	ΔE_0 Kcal/mol
2.1	+9.0	+9.0
2.2	0.0	0.0
2.3	+18.0	+20.7

Table S20. Selected X-Ray structural parameters of **complex 2**.

Fe-O bond distances in **complex 2**, Å
1.86, 1.86, 1.86
Fe-N bond distances in **complex 2**, Å
2.07, 2.07, 2.05





Cation 2.1

Cation 2.1 was calculated with unrestricted formalism and *stable = opt* additional first step due to RHF-UHF wavefunction instability (broken-symmetry solution was found).

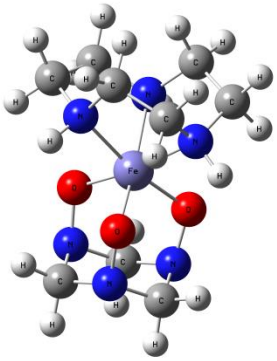
Charge 1; multiplicity 1

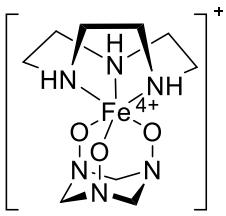
Fe	-0.02881300	-0.05147400	0.06056300
O	1.03246000	-0.82625600	1.37250000
O	0.91712400	1.55087400	0.02253300
N	2.40991800	-0.70911000	1.16228300
N	2.30730400	1.42564800	-0.04813900
N	-1.28152100	-1.66321200	0.10258200
H	-0.69770700	-2.50599000	0.10847700
N	-1.45958300	0.74737900	-1.20292200
H	-0.96373300	0.94467100	-2.07740600
C	2.79460800	-1.37489600	-0.09342100
H	2.40786900	-2.39955800	-0.08353600
H	3.89254000	-1.37553200	-0.14713700
C	2.81168600	0.70669700	1.13288500
H	2.43360500	1.20057400	2.03456400
H	3.90996800	0.74170300	1.10311500
C	-2.06129500	-1.65334100	-1.16283700
H	-1.37629500	-2.00602900	-1.94644300
H	-2.91257000	-2.35145300	-1.10919000
C	-2.54483400	-0.24616600	-1.48004300
H	-3.41889100	0.01582700	-0.87306000
C	-1.94647800	2.03641000	-0.62959800
H	-1.35162800	2.84380100	-1.07265400
H	-2.99378100	2.19371200	-0.92415500
O	0.89781800	-0.79722500	-1.36640200
N	2.29023500	-0.68779100	-1.29357400
C	2.69437500	0.72730000	-1.28431000
H	2.22878200	1.23363100	-2.13675400
H	3.78999000	0.76418800	-1.36280700
N	-1.34618600	0.74666300	1.42931200
H	-0.81275000	0.89197300	2.29272200
C	-2.04204800	-1.62113300	1.38036300
H	-1.35731600	-1.99307500	2.15563900
H	-2.91627100	-2.29111700	1.34296600
C	-2.47084200	-0.19770600	1.70448000
H	-3.33301400	0.10784700	1.10074700
C	-1.78161800	2.06950900	0.91132100
H	-1.00071700	2.78924300	1.18194000
H	-2.71542400	2.38008300	1.40414200
H	-2.85429200	-0.18105600	-2.53335900
H	-2.77607000	-0.12438600	2.75868900

DFT-D3 UBP86/ jorgeTZP, solvent methanol, SMD model		
Total electronic energy=	-2173.984578	E_0
Sum of electronic and zero-point Energies=	-2173.652156	$E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2173.635048	$E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2173.634104	$E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2173.688954	$E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.332422	

Table S21. Selected structural parameters of **cation 2.1**.

Fe-O bond distances in **cation 2.1**, Å
1.86, 1.86, 1.86
Fe-N bond distances in **cation 2.1**, Å
2.04, 2.06, 2.07





Cation 2.2

Raman frequencies were also calculated for optimized **cation 2.2**, using *freq=Raman* keyword.

Charge 1; multiplicity 3

Fe	0.04092000	-0.05409100	0.01227000
O	-0.95210800	-0.90634400	-1.30977000
O	-0.91434600	1.54350800	-0.10251300
N	-2.33653000	-0.78886100	-1.18110900
N	-2.30286400	1.41150200	-0.09843500
N	1.30881700	-1.66875400	0.10459800
H	0.73261500	-2.51325400	0.17957800
N	1.41913100	0.82510500	1.29116900
H	0.92123700	1.02275700	2.16511000
C	-2.78654400	-1.38547800	0.08761600
H	-2.39543000	-2.40625400	0.15764000
H	-3.88561700	-1.39063600	0.08372500
C	-2.74542300	0.62285200	-1.25963200
H	-2.32178300	1.06388200	-2.16850200
H	-3.84366700	0.65297900	-1.28906500
C	2.11269500	-1.54683300	1.34938300
H	1.45663200	-1.87152400	2.16958200
H	2.98727400	-2.21711400	1.32322700
C	2.55177700	-0.10614200	1.57404800
H	3.38963800	0.16173900	0.91999500
C	1.82957100	2.11253400	0.67537500
H	1.05760100	2.84688800	0.93271300
H	2.78103500	2.45457100	1.11035200
O	-0.96323000	-0.72253900	1.42629700
N	-2.34603400	-0.62465000	1.26862600
C	-2.75457400	0.78497100	1.15416600
H	-2.33781500	1.34344100	1.99945200
H	-3.85294300	0.81870100	1.17090600
N	1.43208200	0.67432000	-1.35495900
H	0.91116000	0.82427800	-2.22411700
C	2.04126700	-1.72417900	-1.18721200
H	1.33071400	-2.12396100	-1.92425800
H	2.89865500	-2.41447900	-1.12697600
C	2.50738400	-0.33647700	-1.60487300
H	3.40070200	-0.03774000	-1.04450800
C	1.93507900	1.99191300	-0.86794600
H	1.32187200	2.77385500	-1.33123100
H	2.97026900	2.13507200	-1.20925700
H	2.89942000	0.02461300	2.60943900
H	2.78236400	-0.33805900	-2.66971600

DFT-D3 UBP86/ jorgeTZP, solvent methanol, SMD model		
Total electronic energy=	-2173.998968	E_0
Sum of electronic and zero-point Energies=	-2173.665742	$E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2173.648910	$E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2173.647965	$E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2173.703308	$E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.333226	

Table S22. Selected structural parameters of **cation 2.2**.

Fe-O bond distances in **cation 2.2**, Å
1.86, 1.86, 1.86
Fe-N bond distances in **cation 2.2**, Å
2.08, 2.08, 2.06
Mulliken atom spin density
Fe: 1.79

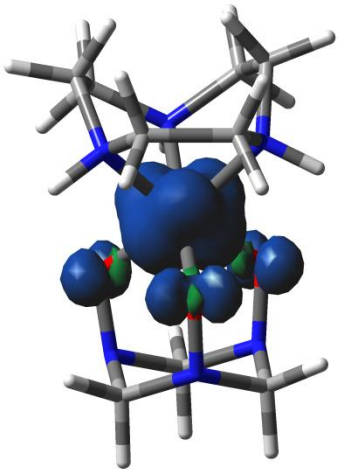


Figure S29. Spin density of **cation 2.2**.

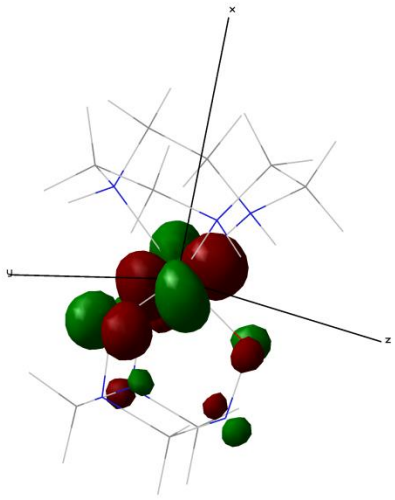


Figure S30. SOMO 83 of **cation 2.2** with strong dxy Fe AO contribution.

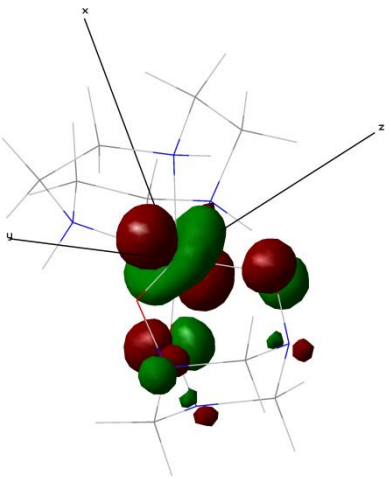
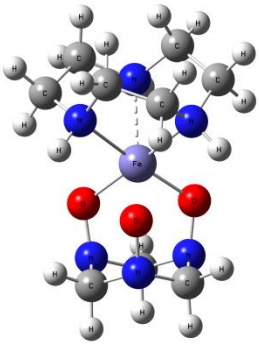
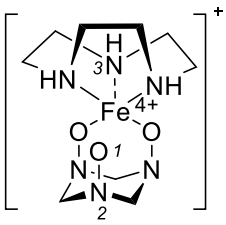


Figure S31. SOMO 84 of **cation 2.2** with strong dx^2-y^2 Fe AO contribution.





Cation 2.3

Charge 1; multiplicity 5

Fe	0.03025800	0.00572600	-0.21613700
O	-1.10566600	-1.11835900	-1.19331600
O	-1.03442700	1.54553400	-0.41184300
N	-2.46707400	-0.94669500	-1.02799200
N	-2.40626100	1.39960300	-0.35344200
N	1.22948800	-1.65109900	0.36056400
H	0.55733800	-2.40152500	0.54574500
N	1.38155700	1.03350100	1.08651100
H	0.77804600	1.38572500	1.83636100
C	-2.88077200	-1.31360200	0.34852300
H	-2.47536200	-2.30431400	0.57931200
H	-3.97978500	-1.33040000	0.35870200
C	-2.88228600	0.42711200	-1.35005400
H	-2.48327100	0.69924500	-2.33331400
H	-3.97986500	0.45512800	-1.34946100
C	1.92027400	-1.32135200	1.63327500
H	1.17610300	-1.46617600	2.42804300
H	2.75992300	-2.01205800	1.81775800
C	2.41407900	0.12234200	1.64958200
H	3.33140600	0.23375800	1.06029600
C	1.91397600	2.16042300	0.29549000
H	1.06202700	2.81907500	0.07675900
H	2.65696500	2.74284700	0.86557500
O	-1.05344000	-0.45574900	1.60056400
N	-2.42008200	-0.35811400	1.35682300
C	-2.83038300	1.00271500	1.01091500
H	-2.39093600	1.70331800	1.72861400
H	-3.92784100	1.05639300	1.03578500
N	1.91666500	0.35937400	-1.44736500
H	1.54735300	0.46029800	-2.39522100
C	2.05520800	-2.03901200	-0.80464900
H	1.35798500	-2.44980200	-1.54991400
H	2.77597100	-2.83113200	-0.53938300
C	2.79685700	-0.83733600	-1.38428400
H	3.67172300	-0.59678800	-0.76731100
C	2.54240900	1.63682000	-1.01423200
H	2.41154700	2.39437700	-1.79791800
H	3.62332900	1.48118900	-0.88993400
H	2.66271700	0.41742000	2.68009500
H	3.17321500	-1.09382700	-2.38603100

DFT-D3 UBP86/ jorgeTZP, solvent methanol, SMD model		
Total electronic energy=	-2173.966047	E_0
Sum of electronic and zero-point Energies=	-2173.635830	$E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2173.618001	$E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2173.617057	$E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2173.674602	$E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.330217	

Table S23. Selected structural parameters of **cation 2.3**.

Fe-O bond distances in **cation 2.3**, Å
1.87, 1.88, 2.16 - (Fe-O*1*)
Fe-N bond distances in **cation 2.3**, Å
2.13, 2.14, 2.28 - (Fe-N*3*)
Mulliken atom spin density
Fe: 3.34; O*1*: 0.26; N*2*: 0.16; N*3*: 0.11

Complex 3

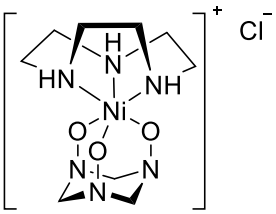
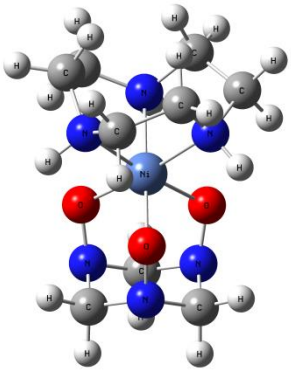


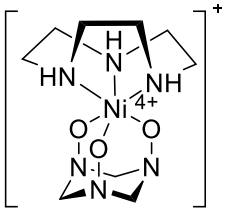
Table S24. Calculated relative energies of cations **3.1 – 3.3**.

cation	$\Delta G°_{298,15\ K}$ Kcal/mol	ΔE_0 Kcal/mol
3.1	0.0	0.0
3.2	+19.2	+22.6
3.3	+36.3	+41.3

Table S25. Selected X-Ray structural parameters of **complex 3**.

Ni-O bond distances in **complex 3**, Å
1.91, 1.91, 1.92
Ni-N bond distances in **complex 3**, Å
2.02, 2.03, 2.04





Cation 3.1

Charge 1; multiplicity 1

Ni	0.09618800	0.00034900	-0.00774800
N	-2.30658500	1.38739300	0.18077500
O	-0.96325700	1.57829700	0.20494700
N	-2.30729300	-0.84900700	1.10277200
O	-0.96387900	-0.97002600	1.25404500
N	-2.31066900	-0.52922500	-1.29520000
O	-0.96795600	-0.60482900	-1.47723700
N	1.38015500	0.59227600	1.45602900
H	0.80915200	1.06245200	2.16448700
N	1.37978200	-1.56415200	-0.22927500
H	0.81012900	-2.41347900	-0.17151200
N	1.37972800	0.97186800	-1.25459600
H	0.80866500	1.34805700	-2.01706500
C	-2.76776400	0.53710400	1.29271000
H	-3.86551500	0.54384900	1.30922700
H	-2.35299100	0.92372500	2.22960000
C	-2.77265500	-1.38481800	-0.18893900
H	-3.87050600	-1.39779800	-0.18904600
H	-2.36246800	-2.39136000	-0.32345500
C	-2.77083300	0.85874900	-1.11314400
H	-3.86855400	0.86986100	-1.12469000
H	-2.35836000	1.47719500	-1.91738000
C	1.92978400	-0.66760300	2.00914000
H	1.11486400	-1.15274200	2.56334500
H	2.75898800	-0.47583200	2.71027600
C	2.40027300	-1.55420100	0.85939900
H	3.34559900	-1.17923300	0.44507100
H	2.58578300	-2.57600800	1.21905200
C	1.92280700	-1.41547700	-1.59970800
H	1.10350200	-1.65035500	-2.29263900
H	2.74895000	-2.12092700	-1.78846900
C	2.39643300	0.02218300	-1.79429300
H	3.34287000	0.19106100	-1.26322700
H	2.58003500	0.22156100	-2.85933200
C	1.92680100	2.08298900	-0.44168100
H	1.11088400	2.80513800	-0.30208200
H	2.75617700	2.59442600	-0.95777700
C	2.39565900	1.53578600	0.90408600
H	3.34457000	0.99485700	0.79108200
H	2.57394600	2.36089500	1.60771300

DFT-D3 BP86/ jorgeTZP, solvent methanol, SMD model		
Total electronic energy=	-2418.612598	E_0
Sum of electronic and zero-point Energies=	-2418.278400	$E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2418.262093	$E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2418.261148	$E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2418.313294	$E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.334198	

Table S26. Selected structural parameters of **cation 3.1**.

Ni-O bond distances in **cation 3.1**, Å
1.91, 1.91, 1.91
Ni-N bond distances in **cation 3.1**, Å
2.04, 2.04, 2.04

Table S27. Fragment of NBO analysis for **cation 3.1**.

Summary of Natural Population Analysis:

		Natural Population				
		Natural	----------			
Atom	No	Charge	Core	Valence	Rydberg	Total
Ni	1	0.60237	17.99613	9.39185	0.00965	27.39763
N	2	-0.06276	1.99952	5.03134	0.03190	7.06276
O	3	-0.45338	1.99977	6.43765	0.01597	8.45338
N	4	-0.06284	1.99952	5.03143	0.03189	7.06284
O	5	-0.45358	1.99977	6.43785	0.01596	8.45358
N	6	-0.06284	1.99952	5.03142	0.03190	7.06284
O	7	-0.45323	1.99977	6.43750	0.01596	8.45323
N	8	-0.52725	1.99935	5.50591	0.02200	7.52725
H	9	0.42651	0.00000	0.56744	0.00606	0.57349
N	10	-0.52731	1.99935	5.50596	0.02200	7.52731
H	11	0.42645	0.00000	0.56750	0.00605	0.57355
N	12	-0.52732	1.99935	5.50597	0.02199	7.52732
H	13	0.42645	0.00000	0.56750	0.00605	0.57355
C	14	-0.14629	1.99931	4.12695	0.02004	6.14629
H	15	0.23692	0.00000	0.75917	0.00391	0.76308
H	16	0.23523	0.00000	0.76029	0.00448	0.76477
C	17	-0.14630	1.99931	4.12696	0.02004	6.14630
H	18	0.23697	0.00000	0.75912	0.00391	0.76303
H	19	0.23519	0.00000	0.76033	0.00448	0.76481
C	20	-0.14632	1.99931	4.12697	0.02004	6.14632
H	21	0.23689	0.00000	0.75920	0.00391	0.76311
H	22	0.23525	0.00000	0.76027	0.00448	0.76475
C	23	-0.24195	1.99935	4.22588	0.01672	6.24195
H	24	0.23404	0.00000	0.76226	0.00370	0.76596
H	25	0.22544	0.00000	0.76990	0.00466	0.77456
C	26	-0.25467	1.99934	4.23797	0.01736	6.25467
H	27	0.22217	0.00000	0.77405	0.00378	0.77783
H	28	0.23860	0.00000	0.75727	0.00413	0.76140
C	29	-0.24183	1.99935	4.22576	0.01672	6.24183
H	30	0.23405	0.00000	0.76226	0.00370	0.76595
H	31	0.22538	0.00000	0.76996	0.00466	0.77462
C	32	-0.25437	1.99934	4.23767	0.01736	6.25437
H	33	0.22212	0.00000	0.77409	0.00379	0.77788
H	34	0.23860	0.00000	0.75728	0.00413	0.76140
C	35	-0.24192	1.99935	4.22586	0.01671	6.24192
H	36	0.23387	0.00000	0.76243	0.00370	0.76613
H	37	0.22543	0.00000	0.76991	0.00466	0.77457
C	38	-0.25442	1.99934	4.23773	0.01736	6.25442
H	39	0.22200	0.00000	0.77420	0.00380	0.77800
H	40	0.23864	0.00000	0.75724	0.00413	0.76136

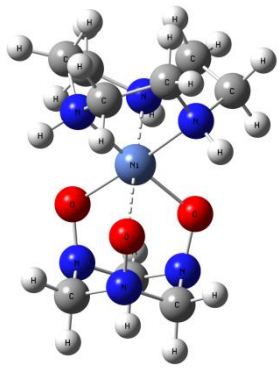
NATURAL BOND ORBITAL ANALYSIS:

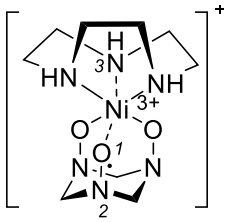
```
                    Occupancies      Lewis Structure    Low   High
          Occ.    ------------------ ----------------   occ   occ
  Cycle   Thresh.   Lewis   Non-Lewis     CR  BD  3C  LP    (L)   (NL)   Dev
  ==============================================================================
    76. (1.71640) LP ( 1) N   2          s( 23.39%)p 3.27( 76.54%)d 0.00(  0.07%)
                                          f 0.00(  0.01%)
                                  0.0005  0.4836  0.0002  0.0054 -0.0001
                                 -0.3302 -0.0247 -0.0028  0.8018  0.0316
                                  0.0098  0.1080  0.0043  0.0013  0.0157
                                 -0.0020  0.0021 -0.0002 -0.0049  0.0010

    79. (1.71643) LP ( 1) N   4          s( 23.38%)p 3.27( 76.54%)d 0.00(  0.07%)
                                          f 0.00(  0.01%)
                                  0.0005  0.4835  0.0002  0.0054 -0.0001
                                 -0.3307 -0.0247 -0.0028 -0.4936 -0.0194
                                 -0.0060  0.6409  0.0252  0.0078 -0.0096
                                  0.0012  0.0126 -0.0016  0.0177 -0.0035
                                  0.0042 -0.0008 -0.0078  0.0016 -0.0013
                                  0.0018  0.0020  0.0026 -0.0060  0.0003
                                 -0.0018
```

82. (1.71636) LP (1) N 6 s(23.37%)p 3.28(76.56%)d 0.00(0.07%)
f 0.00(0.01%)
0.0005 0.4834 0.0002 0.0054 -0.0001
-0.3329 -0.0248 -0.0028 -0.3073 -0.0121
-0.0038 -0.7474 -0.0294 -0.0091 -0.0061
0.0008 -0.0147 0.0018 -0.0128 0.0026
-0.0001 0.0000 -0.0150 0.0030 0.0025
0.0040 0.0017 -0.0023 0.0044 0.0020
-0.0010
874. (0.28385) BD*(1)Ni 1 - O 5
(78.45%) 0.8857*Ni 1 s(16.36%)p 2.74(44.77%)d 2.37(38.85%)
f 0.00(0.02%)g 0.00(0.00%)
0.0000 -0.0000 0.0001 0.4038 -0.0246
0.0022 -0.0007 0.0000 -0.0000 -0.0000
-0.0003 -0.4098 -0.0317 -0.0025 0.0000
-0.0000 -0.0002 -0.3164 -0.0095 0.0028
0.0000 0.0000 0.0002 0.4223 0.0124
-0.0036 -0.0000 0.3076 0.0161 0.0007
-0.4035 -0.0202 0.0005 -0.3484 -0.0020
-0.0009 0.0395 0.0168 -0.0007 0.0845
-0.0091 0.0001 -0.0041 -0.0013 -0.0038
-0.0014 -0.0020 -0.0012 0.0031 0.0007
0.0086 0.0031 -0.0004 0.0010 -0.0042
-0.0015 -0.0004 -0.0000 0.0000 0.0000
0.0002 0.0001 -0.0004 -0.0001 0.0000
(21.55%) -0.4642* O 5 s(8.16%)p11.25(91.77%)d 0.01(0.07%)
f 0.00(0.00%)
-0.0000 0.2849 -0.0194 0.0010 0.0003
0.3601 0.0016 0.0004 0.5406 0.0061
-0.0021 -0.7040 -0.0087 0.0020 0.0017
-0.0009 -0.0023 0.0013 -0.0229 0.0050
-0.0044 -0.0021 0.0095 -0.0004 0.0032
0.0003 0.0016 -0.0023 -0.0020 0.0005
0.0033
875. (0.28385) BD*(1)Ni 1 - O 7
(78.45%) 0.8857*Ni 1 s(16.35%)p 2.74(44.78%)d 2.38(38.85%)
f 0.00(0.02%)g 0.00(0.00%)
0.0000 -0.0000 0.0001 0.4036 -0.0247
0.0022 -0.0007 0.0000 -0.0000 -0.0000
-0.0003 -0.4110 -0.0317 -0.0025 0.0000
-0.0000 -0.0001 -0.2069 -0.0059 0.0017
0.0000 -0.0000 -0.0002 -0.4845 -0.0143
0.0043 0.0000 0.1954 0.0094 -0.0007
0.4692 0.0240 0.0004 0.2535 0.0014
0.0002 0.1220 0.0174 -0.0001 0.2238
-0.0083 0.0011 0.0024 0.0005 -0.0058
-0.0029 -0.0023 -0.0013 -0.0053 -0.0017
-0.0071 -0.0020 -0.0020 -0.0002 -0.0032
-0.0010 -0.0002 0.0001 0.0002 0.0003
0.0002 -0.0000 0.0004 0.0000 0.0000
(21.55%) -0.4643* O 7 s(8.15%)p11.27(91.78%)d 0.01(0.07%)
f 0.00(0.00%)
-0.0000 0.2848 -0.0194 0.0010 0.0003
0.3623 0.0017 0.0004 0.3387 0.0045
-0.0007 0.8196 0.0096 -0.0028 0.0011
-0.0007 0.0027 -0.0015 0.0167 -0.0037
0.0010 -0.0032 0.0188 -0.0023 -0.0018
0.0010 0.0018 0.0041 0.0015 0.0011
0.0024
880. (0.06299) BD*(1) N 2 - C 14
(40.36%) 0.6353* N 2 s(26.92%)p 2.71(72.94%)d 0.01(0.14%)
f 0.00(0.00%)
0.0002 -0.5187 0.0097 0.0026 -0.0001
0.2463 -0.0149 -0.0015 0.5003 0.0152
-0.0064 -0.6462 0.0168 0.0010 -0.0122
0.0023 0.0022 0.0035 0.0298 0.0010
0.0173 -0.0003 -0.0048 -0.0008 0.0008
0.0013 0.0040 0.0007 -0.0027 -0.0028
0.0021
(59.64%) -0.7723* C 14 s(24.56%)p 3.07(75.37%)d 0.00(0.07%)
f 0.00(0.01%)
-0.0002 -0.4953 -0.0161 -0.0002 -0.0004

-0.2760 0.0021 0.0010 -0.4919 -0.0414
0.0001 0.6586 0.0031 -0.0023 -0.0033
-0.0052 0.0136 0.0018 0.0138 0.0084
0.0044 0.0012 -0.0126 -0.0021 -0.0004
-0.0017 -0.0036 0.0001 -0.0034 0.0050
-0.0027
881. (0.06256) BD*(1) N 2 - C 20
(40.36%) 0.6353* N 2 s(26.98%)p 2.70(72.87%)d 0.01(0.14%)
f 0.00(0.00%)
0.0002 -0.5193 0.0097 0.0026 -0.0001
0.2483 -0.0149 -0.0015 0.3130 0.0191
-0.0059 0.7539 -0.0122 -0.0026 -0.0114
0.0032 -0.0055 -0.0028 -0.0279 -0.0004
0.0094 -0.0005 -0.0185 -0.0011 0.0017
0.0024 0.0035 0.0016 0.0027 -0.0018
0.0019
(59.64%) -0.7723* C 20 s(24.60%)p 3.06(75.33%)d 0.00(0.07%)
f 0.00(0.01%)
-0.0002 -0.4957 -0.0163 -0.0003 -0.0004
-0.2781 0.0021 0.0011 -0.3018 -0.0392
-0.0006 -0.7636 -0.0140 0.0022 0.0004
-0.0045 -0.0140 -0.0032 -0.0075 -0.0067
0.0015 -0.0009 -0.0175 -0.0056 -0.0017
-0.0006 -0.0026 -0.0024 0.0021 0.0059
-0.0023
883. (0.06254) BD*(1) N 4 - C 14
(40.36%) 0.6353* N 4 s(26.98%)p 2.70(72.87%)d 0.01(0.14%)
f 0.00(0.00%)
0.0002 -0.5194 0.0097 0.0026 -0.0001
0.2456 -0.0148 -0.0015 -0.8101 0.0011
0.0052 -0.1065 0.0227 -0.0038 0.0103
0.0008 -0.0071 0.0041 0.0042 -0.0009
0.0300 0.0006 0.0172 0.0008 0.0014
-0.0004 0.0039 0.0020 -0.0007 -0.0040
0.0003
(59.64%) -0.7723* C 14 s(24.59%)p 3.06(75.34%)d 0.00(0.07%)
f 0.00(0.01%)
-0.0002 -0.4956 -0.0163 -0.0003 -0.0004
-0.2761 0.0021 0.0011 0.8129 0.0317
-0.0016 0.1206 -0.0270 -0.0016 0.0119
0.0050 0.0073 -0.0024 -0.0088 -0.0013
0.0156 0.0060 0.0068 0.0063 -0.0016
-0.0057 -0.0034 -0.0025 0.0017 0.0019
0.0007
884. (0.06298) BD*(1) N 4 - C 17
(40.36%) 0.6353* N 4 s(26.92%)p 2.71(72.94%)d 0.01(0.14%)
f 0.00(0.00%)
-0.0002 0.5188 -0.0097 -0.0026 0.0001
-0.2485 0.0150 0.0015 -0.3085 0.0221
-0.0024 -0.7561 -0.0047 0.0061 -0.0042
0.0042 0.0118 -0.0002 0.0110 0.0012
-0.0011 0.0001 0.0329 0.0004 -0.0003
-0.0040 -0.0043 -0.0013 -0.0008 0.0007
-0.0006
(59.64%) -0.7723* C 17 s(24.56%)p 3.07(75.37%)d 0.00(0.07%)
f 0.00(0.01%)
0.0002 0.4953 0.0161 0.0002 0.0004
0.2787 -0.0021 -0.0010 0.3232 -0.0181
-0.0019 0.7549 0.0374 -0.0013 0.0102
-0.0010 0.0097 0.0055 0.0144 0.0052
-0.0049 0.0016 0.0116 0.0068 -0.0008
0.0014 0.0042 0.0015 -0.0032 -0.0052
0.0005
886. (0.06256) BD*(1) N 6 - C 17
(40.36%) 0.6353* N 6 s(26.98%)p 2.70(72.88%)d 0.01(0.14%)
f 0.00(0.00%)
0.0002 -0.5193 0.0097 0.0026 -0.0001
0.2466 -0.0149 -0.0015 0.4963 -0.0201
0.0007 -0.6487 -0.0104 0.0065 0.0010
-0.0040 0.0125 -0.0013 0.0238 0.0013
0.0058 0.0003 -0.0248 0.0002 0.0025
0.0034 0.0038 0.0007 -0.0021 -0.0011
0.0007
(59.64%) -0.7723* C 17 s(24.60%)p 3.06(75.33%)d 0.00(0.07%)

f 0.00(0.01%)
-0.0002 -0.4957 -0.0163 -0.0003 -0.0004
-0.2770 0.0021 0.0011 -0.5098 0.0075
0.0022 0.6441 0.0409 -0.0006 -0.0123
-0.0004 0.0066 0.0055 0.0163 0.0079
0.0091 0.0002 -0.0044 -0.0038 -0.0033
-0.0029 -0.0030 -0.0003 -0.0038 0.0041
-0.0007
887. (0.06296) BD*(1) N 6 - C 20
(40.36%) 0.6353* N 6 s(26.93%)p 2.71(72.92%)d 0.01(0.14%)
f 0.00(0.00%)
0.0002 -0.5189 0.0097 0.0026 -0.0001
0.2455 -0.0149 -0.0015 -0.8099 0.0070
0.0041 -0.1109 -0.0215 0.0051 0.0079
0.0019 0.0094 -0.0037 -0.0188 0.0003
0.0269 0.0008 0.0117 0.0011 0.0014
0.0002 0.0043 -0.0000 0.0020 -0.0036
0.0006
(59.64%) -0.7723* C 20 s(24.57%)p 3.07(75.36%)d 0.00(0.07%)
f 0.00(0.01%)
-0.0002 -0.4954 -0.0161 -0.0002 -0.0004
-0.2756 0.0022 0.0010 0.8163 0.0234
-0.0021 0.0977 0.0343 0.0011 0.0134
0.0042 -0.0040 0.0036 0.0006 -0.0032
0.0169 0.0058 0.0091 0.0058 -0.0010
-0.0061 -0.0043 0.0009 0.0002 0.0016
0.0001
Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis
Threshold for printing: 0.50 kcal/mol
E(2) E(j)-E(i) F(i,j)
Donor NBO (i) Acceptor NBO (j) kcal/mol a.u. a.u.
==========
within unit 1
76. LP (1) N 2 /873. BD*(1)Ni 1 - O 3 4.78 0.63 0.049
76. LP (1) N 2 /883. BD*(1) N 4 - C 14 6.62 0.54 0.057
76. LP (1) N 2 /887. BD*(1) N 6 - C 20 6.66 0.54 0.057
79. LP (1) N 4 /874. BD*(1)Ni 1 - O 5 4.77 0.63 0.049
79. LP (1) N 4 /880. BD*(1) N 2 - C 14 6.65 0.54 0.057
79. LP (1) N 4 /886. BD*(1) N 6 - C 17 6.62 0.54 0.057
82. LP (1) N 6 /875. BD*(1)Ni 1 - O 7 4.78 0.63 0.049
82. LP (1) N 6 /881. BD*(1) N 2 - C 20 6.63 0.54 0.057
82. LP (1) N 6 /884. BD*(1) N 4 - C 17 6.66 0.54 0.057





Cation 3.2

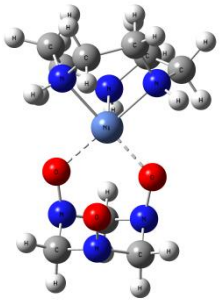
Charge 1; multiplicity 3

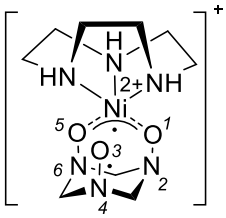
Ni	0.14110700	0.04432700	-0.05123100
N	-2.33555200	1.35296900	0.24076800
O	-0.98862300	1.52192000	0.34873000
N	-2.46370500	-0.88782400	1.13159200
O	-1.20830400	-1.16596100	1.47207100
N	-2.33942700	-0.57081600	-1.25271200
O	-0.99297900	-0.72214900	-1.37872500
N	1.40086500	0.62582800	1.41141300
H	0.82906600	1.10618600	2.11253900
N	1.39834800	-1.52171400	-0.26365400
H	0.81725100	-2.36436800	-0.21787900
N	1.47510800	1.01556700	-1.31525600
H	0.93045700	1.40287300	-2.09008500
C	-2.87857300	0.50646400	1.32844900
H	-3.97427900	0.56232900	1.29020500
H	-2.48790600	0.86296100	2.28614800
C	-2.89149000	-1.41626300	-0.16918400
H	-3.98686900	-1.38081900	-0.23029400
H	-2.51135800	-2.43584500	-0.28272500
C	-2.74420100	0.83285300	-1.07332100
H	-3.83856400	0.88656700	-1.14066400
H	-2.26969100	1.43768500	-1.85330700
C	1.92863100	-0.63941100	1.98120000
H	1.09995700	-1.11205500	2.52534700
H	2.74949400	-0.45105100	2.69313600
C	2.40358800	-1.53414400	0.84144400
H	3.36206500	-1.17621200	0.44240600
H	2.56324900	-2.56029000	1.20091700
C	1.96688000	-1.38651200	-1.62612700
H	1.15286900	-1.60341800	-2.33164400
H	2.77804600	-2.11264900	-1.80061600
C	2.47759900	0.03931500	-1.82197800
H	3.41756400	0.19151200	-1.27453000
H	2.68681900	0.22006000	-2.88595400
C	2.01275200	2.11047900	-0.47755500
H	1.20374900	2.84383800	-0.35575300
H	2.86561500	2.61384700	-0.96389100
C	2.44109700	1.55364000	0.87789100
H	3.38316700	0.99743200	0.78307800
H	2.61861800	2.37585000	1.58500600

DFT-D3 UBP86/ jorgeTZP, solvent methanol, SMD model		
Total electronic energy=	-2418.576569	E_0
Sum of electronic and zero-point Energies=	-2418.244586	$E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2418.227210	$E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2418.226265	$E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2418.282657	$E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.331983	

Table S28. Selected structural parameters of **cation 3.2**.

Ni-O bond distances in **cation 3.2**, Å
1.91, 1.91, 2.37 - (Ni-O*1*)
Ni-N bond distances in **cation 3.2**, Å
2.02, 2.02, 2.08 - (Ni-N*3*)
Mulliken atom spin density
Ni: 0.86; O*1*: 0.34; N*2*: 0.36; N*3*: 0.17





Cation 3.3

Charge 1; multiplicity 5

Ni	0.28479900	0.07228400	0.00115800
N	-2.29065100	-0.80811400	-1.06156800
O	-1.08784400	-0.25632600	-1.38158300
N	-3.35401900	1.20217700	-0.27070700
O	-2.48924000	2.15882700	-0.47133900
N	-2.30953000	-0.30324400	1.29388600
O	-1.10608200	0.32718100	1.38127900
N	1.60282400	0.63545000	-1.49174900
H	1.07204900	0.80982500	-2.34906500
N	1.61489500	1.05181000	1.25131200
H	1.10331800	1.72997200	1.82206100
N	1.51767800	-1.53324100	0.23803800
H	0.96276600	-2.34514900	0.52253600
C	-3.39580800	0.12908700	-1.29483000
H	-4.34457900	-0.41448800	-1.20090400
H	-3.28427700	0.58609200	-2.28264800
C	-3.41275400	0.64531900	1.10358400
H	-4.36207800	0.10895900	1.22784400
H	-3.31359100	1.46864900	1.81733100
C	-2.34066900	-1.37626900	0.29211500
H	-3.27939900	-1.93330000	0.40348000
H	-1.47193200	-2.02738600	0.44009100
C	2.18209700	1.90824800	-1.00319000
H	1.38314100	2.66186300	-1.06122000
H	3.02109500	2.24673700	-1.63550000
C	2.65252200	1.74619300	0.44164900
H	3.57711200	1.15426200	0.47870500
H	2.88311100	2.73181700	0.87061800
C	2.11888400	-0.03503800	2.12543700
H	1.29066100	-0.31429100	2.79209200
H	2.96505300	0.30035400	2.74952600
C	2.54408400	-1.23363100	1.27935000
H	3.49853400	-1.03024600	0.77533100
H	2.69877600	-2.10979000	1.92464400
C	2.06029000	-1.77147200	-1.12382800
H	1.23003700	-2.15994600	-1.73064600
H	2.86304900	-2.52815400	-1.11040100
C	2.58275700	-0.46326000	-1.71512400
H	3.53486700	-0.18286100	-1.24396700
H	2.78047300	-0.59504400	-2.78859600

DFT-D3 UBP86/ jorgeTZP, solvent methanol, SMD model		
Total electronic energy=	-2418.546810	E_0
Sum of electronic and zero-point Energies=	-2418.215633	$E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2418.197772	$E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2418.196828	$E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2418.255497	$E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.331177	

Table S29. Selected structural parameters of **cation 3.3**.

Ni-O bond distances in **cation 3.3**, Å
1.98, 1.98, 3.50 - (Ni-O*3*)
Ni-N bond distances in **cation 3.3**, Å
2.04, 2.07, 2.07
Mulliken atom spin density
Ni: 1.56; O*3*: 0.46; N*4*: 0.39;
O*1*: 0.33; N*2*: 0.29; O*5*: 0.33 N*6*: 0.30 $\sum$ O1 − N6: 2.1

Complex 5

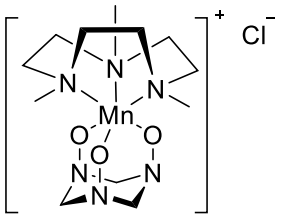


Table SI30. Calculated relative energies of cations **5.1** and **5.2**.

cation	$\Delta G°_{298,15\ K}$ Kcal/mol	ΔE_0 Kcal/mol
5.1	+18.8	+18.4
5.2	0.0	0.0
5.1* ROMN15	+28.0	+28.3
5.2* ROMN15	0.0	0.0

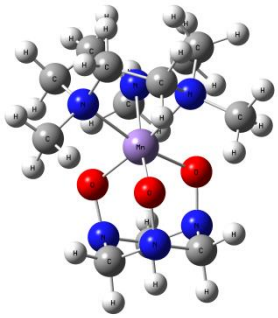
Table S31. Selected X-Ray structural parameters of **complex 5**.

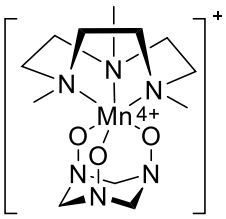
Mn-O bond distances in **complex 5**, Å
1.88, 1.88, 1.88
Mn-N bond distances in **complex 5**, Å
2.15, 2.16, 2.16

Due to spin contamination problem for cation **5.1**, both cations were also calculated with DFT-D3 ROMN15/ Def2TZVP level of theory. *Stable* keyword was not used.

Keywords:

 # opt freq ROMN15/Def2TZVP nosymm scrf=(smd,solvent=Methanol) pressure=605 temperature=298.15 test





Cation 5.1

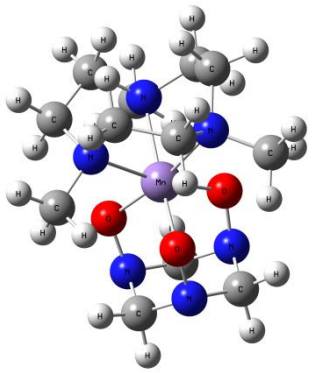
Charge 1; multiplicity 2

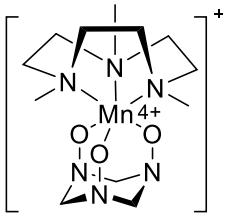
Mn	-0.06152300	0.03965500	-0.01049300
O	-1.04805700	1.17907400	1.04247400
O	-1.02952500	0.31238200	-1.54999700
O	-1.02045800	-1.49530500	0.50363700
N	-2.45112300	1.06802900	0.93494900
N	-2.43460300	0.27815100	-1.41444900
N	-2.42067300	-1.33885300	0.43868300
N	1.30720000	-0.24774100	1.61967000
N	1.35437100	1.51500300	-0.57662500
N	1.32053100	-1.26509600	-1.01498900
C	-2.86268600	1.31164200	-0.45725100
H	-3.96189400	1.33510300	-0.47238700
H	-2.45765700	2.27705700	-0.77900400
C	-2.84766300	-1.05591800	-0.93468300
H	-3.94626100	-1.08653900	-0.95825100
H	-2.42844000	-1.81584200	-1.60248300
C	-2.86637300	-0.28575700	1.35463400
H	-2.46177000	-0.48511700	2.35253000
H	-3.96542000	-0.29956800	1.37442500
C	1.88351900	1.11200600	1.81188400
H	1.07491200	1.74349300	2.20568000
H	2.69509700	1.08823200	2.55942500
C	2.39440100	1.66275700	0.49439700
H	3.30906200	1.14572300	0.18086900
H	2.65736100	2.72395300	0.61165700
C	1.92174500	0.99185500	-1.85071200
H	1.11856900	1.04997500	-2.59847000
H	2.75576300	1.62880700	-2.19167700
C	2.38492400	-0.44238600	-1.67907000
H	3.30339300	-0.49280100	-1.08252900
H	2.62729000	-0.87177800	-2.66186100
C	1.86521500	-2.11360400	0.08062700
H	1.04441500	-2.76647800	0.40807900
H	2.68432500	-2.75146100	-0.29371400
C	2.34975400	-1.25430100	1.23365400
H	3.27620000	-0.72794200	0.97332900
H	2.58548700	-1.89367100	2.09680600
C	0.62613300	-0.67670800	2.86002800
H	-0.18058200	0.02797600	3.09345300
H	0.20070700	-1.67572700	2.71231900
H	1.34547200	-0.70228900	3.69559600
C	0.69425100	2.81778000	-0.82271200
H	-0.11472700	2.68248500	-1.54980900
H	0.27744900	3.19618200	0.11777100
H	1.42729100	3.54117300	-1.21688100
C	0.64772100	-2.12020900	-2.01668300
H	-0.17622200	-2.65963200	-1.53563000
H	0.24781900	-1.49085200	-2.82026200
H	1.36555600	-2.84336900	-2.43851900

DFT-D3 UBP86/ jorgeTZP, solvent methanol, SMD model		
Total electronic energy=	-2179.168139	E_0
Sum of electronic and zero-point Energies=	-2178.755149	$E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2178.734438	$E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2178.733494	$E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2178.794265	$E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.412990	
<Sx>= 0.0000 <Sy>= 0.0000 <Sz>= 0.5000 <S**2>= 1.6268 S= 0.8700		

Table S32. Selected structural parameters of **cation 5.1**.

Mn-O bond distances in **cation 5.1**, Å
1.84, 1.84, 1.88
Mn-N bond distances in **cation 5.1**, Å
2.12, 2.15, 2.15
Mulliken atom spin density
Mn: 1.06





Cation 5.2

Charge 1; multiplicity 4

Mn	-0.07387000	-0.00377300	0.00627800
O	-1.06897300	1.19996600	1.03665100
O	-1.05007000	0.30893500	-1.55641200
O	-1.07885000	-1.49795000	0.50964600
N	-2.46420000	1.08121900	0.91894300
N	-2.44739600	0.28552200	-1.41012400
N	-2.47309200	-1.33490800	0.44324600
N	1.33263200	-0.26109200	1.62740600
N	1.35478700	1.51523800	-0.57391700
N	1.34992200	-1.28029500	-1.01547600
C	-2.87823700	1.33327800	-0.47073000
H	-3.97667800	1.36606600	-0.49001700
H	-2.46073500	2.29260400	-0.79504000
C	-2.88532100	-1.03765100	-0.93811700
H	-3.98388100	-1.05455500	-0.96773500
H	-2.47215100	-1.80411200	-1.60275600
C	-2.90051900	-0.25682700	1.34960400
H	-2.49755100	-0.45529200	2.34874700
H	-3.99946300	-0.25667100	1.37098000
C	1.88863600	1.10660700	1.81521400
H	1.07063500	1.72631100	2.20868300
H	2.70087600	1.09620400	2.56236600
C	2.39209000	1.66702600	0.49721900
H	3.31254800	1.16084100	0.18222000
H	2.64570700	2.72986700	0.62116400
C	1.91739200	0.99048900	-1.84777600
H	1.10784600	1.03740700	-2.58983900
H	2.74267100	1.63257500	-2.20079900
C	2.39826500	-0.43986400	-1.67967300
H	3.32042300	-0.48030800	-1.08800200
H	2.64166400	-0.86251400	-2.66520000
C	1.89998000	-2.12122800	0.08248700
H	1.08320400	-2.77851900	0.41299500
H	2.72188200	-2.75695900	-0.28927100
C	2.38172900	-1.25710000	1.23437400
H	3.30179000	-0.72219700	0.96932800
H	2.62796000	-1.89522100	2.09554000
C	0.65262500	-0.70011700	2.86479600
H	-0.16438600	-0.00636400	3.09622000
H	0.24100800	-1.70514100	2.71595100
H	1.36925000	-0.71702100	3.70293700
C	0.68406000	2.81017400	-0.81899500
H	-0.12925100	2.66656000	-1.54011500
H	0.26867200	3.18788400	0.12258500
H	1.40765100	3.53965300	-1.21984400
C	0.67674300	-2.13619200	-2.01587200
H	-0.14025600	-2.68505600	-1.53246100
H	0.26553900	-1.50624000	-2.81341700
H	1.39695700	-2.85171000	-2.44655700

DFT-D3 UBP86/ jorgeTZP, solvent methanol, SMD model	
Total electronic energy=	-2179.197530 E_0
Sum of electronic and zero-point Energies=	-2178.784414 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2178.763722 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2178.762777 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2178.824291 $E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.413271

Table S33. Selected structural parameters of **cation 5.2**.

Mn-O bond distances in **cation 5.2**, Å
1.87, 1.87, 1.87
Mn-N bond distances in **cation 5.2**, Å
2.16, 2.17, 2.16
Mulliken atom spin density
Mn: 3.08

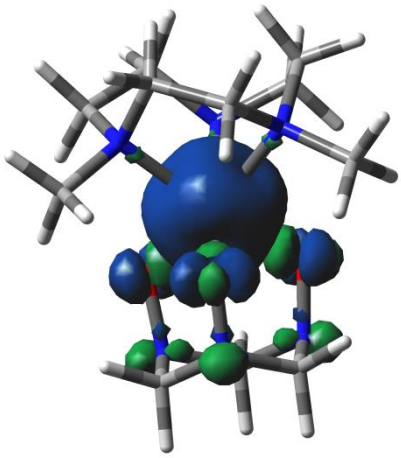


Figure S32. Spin density of **cation 5.2**.

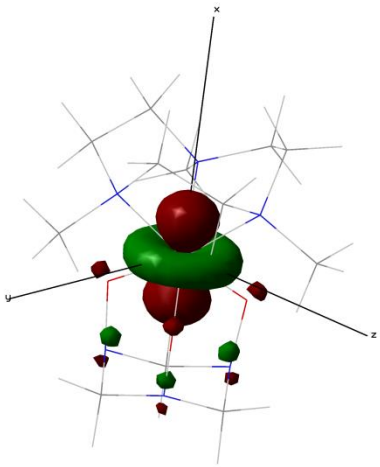


Figure S33. SOMO 94 of **cation 5.2** with strong dz^2 Mn AO contribution.

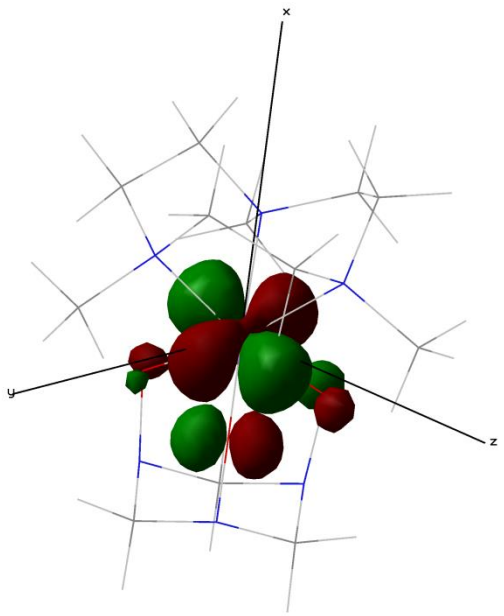


Figure S34. SOMO 95 of **cation 5.2** with strong dx^2-y^2 Mn AO contribution.

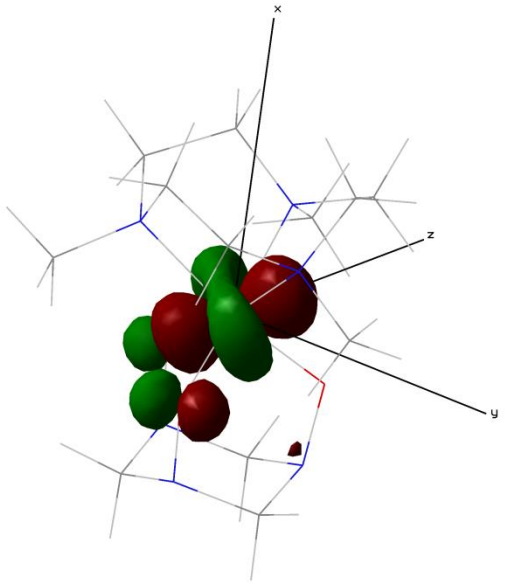
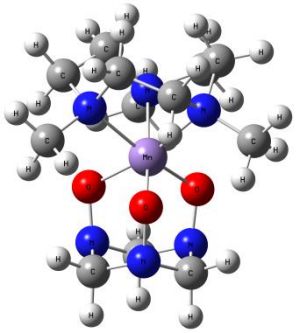
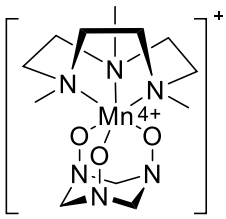


Figure S35. SOMO 96 of **cation 5.2** with strong dxy Mn AO contribution.





Cation 5.1*

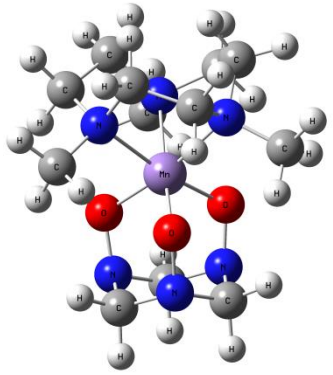
Charge 1; multiplicity 2

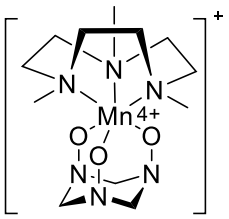
Mn	-0.04788500	0.06938500	-0.02561800
O	-1.00118100	1.14255300	1.02937300
O	-0.98765900	0.30792700	-1.51848600
O	-0.99451400	-1.46147200	0.48636200
N	-2.38189700	1.03636600	0.93290300
N	-2.37109600	0.26827200	-1.39297800
N	-2.37003700	-1.32454700	0.42805400
N	1.27649100	-0.25203500	1.59060800
N	1.32748700	1.51510600	-0.57876100
N	1.28647400	-1.24770100	-0.98863800
C	-2.78796300	1.29032900	-0.44164200
H	-3.87878000	1.31677700	-0.45506200
H	-2.38104500	2.24943400	-0.75611600
C	-2.79978600	-1.05211700	-0.92726200
H	-3.89003800	-1.06219400	-0.95009800
H	-2.39609700	-1.81071900	-1.59411600
C	-2.81640600	-0.30001500	1.34644900
H	-2.42439100	-0.50995700	2.33928200
H	-3.90683800	-0.29529300	1.35551400
C	1.84546300	1.09989100	1.79066700
H	1.04277500	1.73174100	2.17615300
H	2.64546200	1.06600800	2.53782000
C	2.36187700	1.65152900	0.48096100
H	3.26913200	1.13815700	0.16790300
H	2.62476000	2.70426700	0.59969500
C	1.88695300	0.98705400	-1.84192100
H	1.09003900	1.03195100	-2.58714100
H	2.71444100	1.61851500	-2.18155700
C	2.34851300	-0.44054900	-1.65020300
H	3.25846500	-0.48301800	-1.05493000
H	2.59239300	-0.88208900	-2.61830500
C	1.83676100	-2.10245400	0.08423900
H	1.02740500	-2.75301500	0.42010700
H	2.64608400	-2.72729600	-0.30725100
C	2.32288600	-1.24115600	1.22692300
H	3.24092100	-0.71676000	0.96619900
H	2.55669700	-1.86452900	2.09203700
C	0.60586000	-0.68153900	2.82647100
H	-0.22152700	-0.00960500	3.04817300
H	0.22637900	-1.69398200	2.70088000
H	1.32175700	-0.66380700	3.65423900
C	0.68846500	2.81864000	-0.82260500
H	-0.13450700	2.69587400	-1.52519800
H	0.30736200	3.21454300	0.11792400
H	1.42288600	3.51559700	-1.23735100
C	0.62689400	-2.09810200	-1.99199900
H	-0.20852600	-2.62209100	-1.53248900
H	0.26356200	-1.47859100	-2.81074400
H	1.34580300	-2.82573200	-2.38103000

DFT-D3 ROMN15/ Def2TZVP, solvent methanol, SMD model		
Total electronic energy=	-2177.775766	E_0
Sum of electronic and zero-point Energies=	-2177.346197	$E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2177.326574	$E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2177.325630	$E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2177.384334	$E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.429569	

Table S34. Selected structural parameters of **cation 5.1**.*

Mn-O bond distances in **cation 5.1***, Å
1.78, 1.87, 1.87
Mn-N bond distances in **cation 5.1***, Å
2.07, 2.11, 2.11
Mulliken atom spin density
Mn: 0.88





Cation 5.2*

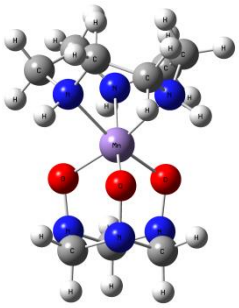
Charge 1; multiplicity 4

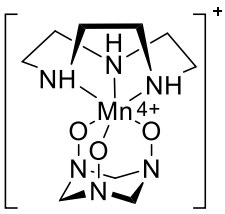
Mn	-0.05692900	-0.00088700	0.00366900
O	-1.02798800	1.16952500	1.00750700
O	-1.01040700	0.29087800	-1.52101800
O	-1.03201100	-1.45536600	0.50474200
N	-2.41079400	1.06463100	0.90346200
N	-2.39449300	0.27164800	-1.39079700
N	-2.41448800	-1.31833700	0.44306000
N	1.30695600	-0.25474200	1.60067800
N	1.33240300	1.49344900	-0.56471000
N	1.32061300	-1.25599800	-0.99999700
C	-2.82398900	1.31417300	-0.46984500
H	-3.91412800	1.34359700	-0.48827700
H	-2.41226500	2.26758300	-0.79562500
C	-2.82833900	-1.03684100	-0.92423300
H	-3.91858900	-1.05384300	-0.94959100
H	-2.42048000	-1.80066000	-1.58374300
C	-2.84530400	-0.25484500	1.33864300
H	-2.45022400	-0.44869000	2.33425000
H	-3.93591600	-0.25569100	1.35418900
C	1.86247100	1.10062000	1.80100700
H	1.05176100	1.72441500	2.18335500
H	2.66214000	1.07540800	2.54802000
C	2.37137800	1.65019400	0.48683800
H	3.28272300	1.14328100	0.17492300
H	2.62350700	2.70632600	0.59725300
C	1.88799600	0.98490800	-1.83651100
H	1.08226900	1.02187500	-2.57284400
H	2.70117200	1.63191000	-2.18038300
C	2.37126700	-0.43797400	-1.66186600
H	3.28563300	-0.47626500	-1.07300900
H	2.61080100	-0.86982200	-2.63511600
C	1.86536600	-2.10461200	0.08152900
H	1.05247800	-2.75131400	0.41891500
H	2.67320500	-2.73559000	-0.30214700
C	2.35357900	-1.24193400	1.22465800
H	3.26869900	-0.71432600	0.96123700
H	2.59187900	-1.86757500	2.08666600
C	0.63081200	-0.69672300	2.83078700
H	-0.20875800	-0.03742500	3.04498200
H	0.26849400	-1.71492000	2.69928300
H	1.34013500	-0.66915400	3.66330900
C	0.66947700	2.78623100	-0.79834000
H	-0.16729100	2.64975700	-1.48152300
H	0.30468500	3.18279600	0.14784500
H	1.38724100	3.48849600	-1.23263500
C	0.65253100	-2.10266000	-2.00137700
H	-0.18820500	-2.61896700	-1.54105700
H	0.29336300	-1.48089200	-2.81985400
H	1.36583500	-2.83610200	-2.38887800

DFT-D3 ROMN15/ Def2TZVP, solvent methanol, SMD model		
Total electronic energy=	-2177.820887	E_0
Sum of electronic and zero-point Energies=	-2177.390620	$E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2177.371234	$E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2177.370290	$E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2177.428966	$E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.430267	

Table S35. Selected structural parameters of **cation 5.2***.

Mn-O bond distances in **cation 5.2***, Å
1.82, 1.82, 1.82
Mn-N bond distances in **cation 5.2***, Å
2.12, 2.12, 2.12
Mulliken atom spin density
Mn: 2.69





Cation 4

Charge 1; multiplicity 4

Mn	-0.06387500	-0.00201700	0.00217800
O	-1.03891500	1.22670800	1.01883400
O	-1.02575000	0.28757800	-1.57270200
O	-1.04639100	-1.49930700	0.53363800
N	-2.43816000	1.09862200	0.90226500
N	-2.42680200	0.26127400	-1.41695400
N	-2.44464500	-1.33075300	0.46743800
N	1.33837300	-0.24816600	1.57129900
N	1.36162200	1.46580800	-0.55920500
N	1.35770200	-1.23430600	-0.97871400
C	-2.85239900	1.32412300	-0.49224900
H	-3.95095200	1.35926400	-0.51005000
H	-2.43382000	2.27721900	-0.83414000
C	-2.85612000	-1.05570400	-0.91859500
H	-3.95470600	-1.07895900	-0.94867800
H	-2.43932300	-1.83176200	-1.57016500
C	-2.86525800	-0.23471700	1.35629300
H	-2.45381900	-0.41470800	2.35575600
H	-3.96408100	-0.23747500	1.38743900
C	1.89489600	1.10446200	1.82688800
H	1.07936200	1.70686700	2.24961700
H	2.71691000	1.07040800	2.56006900
C	2.37777900	1.70114300	0.51010200
H	3.32167600	1.23546400	0.19711800
H	2.56717000	2.77713100	0.62615000
C	1.91985600	1.00680900	-1.85572500
H	1.10928300	1.08015900	-2.59348600
H	2.75050800	1.65037900	-2.18782200
C	2.38716400	-0.43643900	-1.71083900
H	3.32713500	-0.48425100	-1.14561700
H	2.57765800	-0.87660300	-2.69923500
C	1.89755000	-2.13408200	0.07158500
H	1.07815400	-2.80418300	0.36520900
H	2.72774000	-2.74920500	-0.31150300
C	2.35786200	-1.29495800	1.25821700
H	3.30909900	-0.79480100	1.03353100
H	2.52582300	-1.93581800	2.13454100
H	0.81630200	-1.78908600	-1.64892300
H	0.78569000	-0.54129800	2.38275900
H	0.81997800	2.32208900	-0.71151500

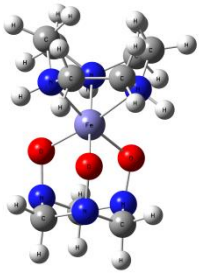
DFT-D3 UBP86/ jorgeTZP, solvent methanol, SMD model	
Total electronic energy=	-2061.22994938 E_0
Sum of electronic and zero-point Energies=	-2060.896742 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2060.880183 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2060.879239 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2060.933435 $E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.333207
Mulliken atom spin density Mn: 3.03	

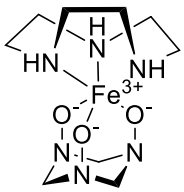
12.3. Procedure for DFT calculation of Mössbauer parameters

Geometry of reduced complex **2** (structures **2.4** – **2.6**) and **FeTMCO**$^{2+}$ cation was optimized by the method used for cations **2**, **3-5** (see section 12.2 of SI). Acetonitrile was used for **FeTMCO**$^{2+}$ as a solvent, SMD model.

Keywords:

 # opt freq UBP86/Gen scrf=(smd,solvent=Acetonitrile) EmpiricalDispersion=GD3BJ pressure=469 test



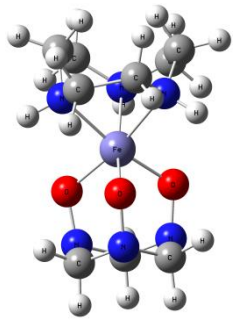


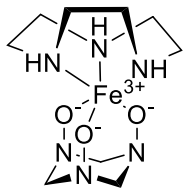
Reduced complex 2.4

Charge 0; multiplicity 2

Fe	0.07679300	-0.08422800	-0.02322100
O	-0.96371400	-0.74054000	-1.43329700
O	-0.94774300	1.57303500	0.10906200
N	-2.38214100	-0.63458200	-1.28892100
N	-2.35857900	1.41930200	0.10829000
N	1.36190000	-1.65018200	-0.12686400
H	0.80781100	-2.50704100	-0.22173400
N	1.41653500	0.66507100	1.36392800
H	0.88351200	0.80486600	2.22664200
C	-2.80388700	-1.38289700	-0.09530000
H	-2.41528600	-2.40704900	-0.17174100
H	-3.90636000	-1.40366000	-0.09331800
C	-2.78207600	0.77559000	-1.14126200
H	-2.36415300	1.34514900	-1.98183400
H	-3.88385400	0.80632600	-1.18291300
C	2.08176900	-1.71762200	1.16897300
H	1.37140300	-2.14796900	1.88952200
H	2.96064200	-2.38391100	1.11475800
C	2.50637100	-0.32582700	1.62300500
H	3.40512600	-0.00069700	1.08446300
C	1.91002600	1.98950200	0.88884600
H	1.30333300	2.76713000	1.36858200
H	2.95045400	2.13481500	1.21628300
O	-0.95393700	-0.94070500	1.30099300
N	-2.37163200	-0.81599300	1.19006200
C	-2.77081700	0.60018000	1.25496900
H	-2.34248800	1.04003300	2.16530500
H	-3.87203500	0.62658900	1.31227900
N	1.41508500	0.84414100	-1.28402300
H	0.92185900	1.03817500	-2.16093100
C	2.18199100	-1.50118500	-1.35553300
H	1.54745900	-1.83603900	-2.18926100
H	3.07896000	-2.14420300	-1.32893800
C	2.57970800	-0.04479300	-1.56381500
H	3.39977400	0.23811100	-0.89226800
C	1.78252300	2.13387100	-0.65222000
H	0.97361300	2.83677800	-0.88337400
H	2.71458200	2.53120900	-1.08620000
H	2.76526200	-0.34305800	2.69274400
H	2.94511300	0.10484900	-2.59167400

DFT-D3 UBP86/ jorgeTZP, solvent methanol, SMD model	
Total electronic energy=	-2174.12308754 E_0
Sum of electronic and zero-point Energies=	-2173.791924 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2173.774930 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2173.773985 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2173.828904 $E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.331164
Mulliken atom spin density Fe: 1.00	



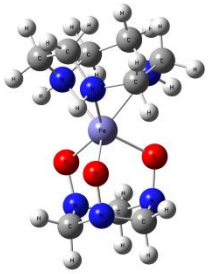


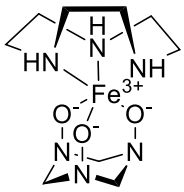
Reduced complex 2.5

Charge 0; multiplicity 4

Fe	0.02905500	-0.07680200	-0.05813800
O	-1.03675900	-0.53220900	-1.55403100
O	-1.11816000	1.64374200	0.32464400
N	-2.44072400	-0.54898700	-1.34736200
N	-2.51806200	1.33564700	0.29675900
N	1.62312800	-1.71805800	-0.21898000
H	1.17204600	-2.61880400	-0.38593600
N	1.44833500	0.62351600	1.39813100
H	0.91663800	0.73436700	2.26436100
C	-2.79039300	-1.47030200	-0.25737300
H	-2.33244300	-2.44633800	-0.46308200
H	-3.88755000	-1.56585400	-0.24392400
C	-2.91004500	0.81274800	-1.01762000
H	-2.53945200	1.49771400	-1.79052800
H	-4.01198700	0.78131600	-1.04591300
C	2.26250000	-1.74353900	1.10419500
H	1.55688900	-2.25355600	1.77703700
H	3.20557000	-2.32364400	1.10508900
C	2.56262500	-0.34031400	1.63767300
H	3.46839100	0.05588800	1.16158700
C	1.90360600	1.97144500	0.94482400
H	1.35039800	2.73238900	1.51021800
H	2.96928300	2.09497400	1.18881900
O	-0.95829900	-1.07163900	1.19025100
N	-2.37011400	-1.02868000	1.08059200
C	-2.84873000	0.34534400	1.32806000
H	-2.43370500	0.68549400	2.28519800
H	-3.94772000	0.28956100	1.39757700
N	1.42314000	0.92392600	-1.27714900
H	0.98065200	1.12638600	-2.17886700
C	2.44171000	-1.36377100	-1.38976200
H	1.88885000	-1.71694500	-2.27332400
H	3.42500600	-1.87185600	-1.38487000
C	2.67174800	0.14435900	-1.50735000
H	3.41977400	0.47771000	-0.77781800
C	1.65412900	2.20462800	-0.56665600
H	0.74420400	2.80216500	-0.70184000
H	2.49934800	2.75774100	-1.01097100
H	2.77951400	-0.40853200	2.71497100
H	3.08379700	0.37239300	-2.50297200

DFT-D3 UBP86/ jorgeTZP, solvent methanol, SMD model	
Total electronic energy=	-2174.10418604 E_0
Sum of electronic and zero-point Energies=	-2173.774527 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2173.756714 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2173.755770 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2173.814078 $E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.329659
Mulliken atom spin density Fe: 2.70	



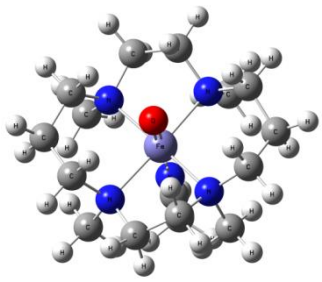


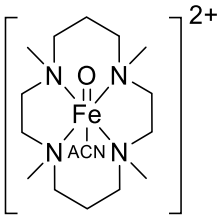
Reduced complex 2.6

Charge 0; multiplicity 6

Fe	-0.04115400	-0.08142600	-0.04803500
O	-1.22794200	0.62866300	-1.47692700
O	-0.95791300	0.95636800	1.38172500
N	-2.61900500	0.63510800	-1.14876200
N	-2.38577600	0.91078100	1.32331700
N	1.46025500	-1.72394700	0.06722400
H	0.86909100	-2.55807400	0.09843200
N	1.75681800	0.86397000	1.12140500
H	1.25227100	1.24898800	1.92116700
C	-3.09128700	-0.73670600	-0.90374000
H	-2.78979000	-1.36381200	-1.75211700
H	-4.19119100	-0.69392900	-0.84615500
C	-2.86156100	1.46105800	0.04436500
H	-2.38862300	2.43918200	-0.10861300
H	-3.95310600	1.58629100	0.13290600
C	2.14608600	-1.58639100	1.36323200
H	1.38757600	-1.79919600	2.13201600
H	2.96219000	-2.32398000	1.48007000
C	2.70799000	-0.17803600	1.56874900
H	3.64484500	-0.06242600	1.00736200
C	2.33813100	1.95643300	0.31009500
H	2.08990900	2.92928300	0.75763700
H	3.43552600	1.87249900	0.32091800
O	-1.22532600	-1.67610300	0.23418300
N	-2.61793100	-1.37209700	0.33567900
C	-2.86156700	-0.47357200	1.47482700
H	-2.38797400	-0.90637000	2.36495200
H	-3.95297700	-0.42525000	1.62137600
N	1.50857500	0.55857400	-1.56296500
H	1.00172900	0.57793500	-2.45148100
C	2.27913100	-1.76000300	-1.15882600
H	1.66091600	-2.24807100	-1.92717700
H	3.19268000	-2.36817900	-1.02605500
C	2.66437000	-0.35713900	-1.64216800
H	3.47855300	0.05007600	-1.03027100
C	1.81488200	1.93552000	-1.14087500
H	0.87091700	2.49602300	-1.20995300
H	2.55031500	2.42940400	-1.80263100
H	2.96291400	-0.05055900	2.63326300
H	3.05214000	-0.42373600	-2.67170500

DFT-D3 UBP86/ jorgeTZP, solvent methanol, SMD model	
Total electronic energy=	-2174.10079023 E_0
Sum of electronic and zero-point Energies=	-2173.772196 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2173.754297 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2173.753353 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2173.811190 $E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.328594
Mulliken atom spin density on Fe: 3.91; on O atoms: 0.21 on each atom	





FeTMCO^{2+}

Charge +2; multiplicity 3

Fe	-0.03793000	0.00249200	-0.22467100
O	-0.06563700	0.01762000	-1.87166200
N	-1.40431100	1.58461100	-0.28283000
N	1.42924800	1.55152300	-0.19853000
N	1.40552000	-1.56251500	-0.22292600
N	-1.42335800	-1.56164300	-0.31248200
C	-0.65232100	2.63115600	-1.04302200
H	-1.22947300	3.57082700	-1.04330300
H	-0.55893100	2.27300300	-2.07453900
C	0.69784300	2.85131000	-0.41861000
H	0.59109500	3.33883500	0.55726700
H	1.31217500	3.51226600	-1.04841900
C	2.34764100	1.29955200	-1.35733000
H	3.06195900	2.14026900	-1.38936200
H	1.73246800	1.33083900	-2.26470100
C	3.12797100	-0.00879400	-1.29263100
H	3.79635100	-0.00730300	-2.16850400
H	3.79858800	-0.02031900	-0.42045600
C	2.33022700	-1.30517100	-1.37574800
H	1.71639900	-1.31650600	-2.28450200
H	3.03380600	-2.15435300	-1.41782500
C	0.66296500	-2.85195200	-0.46608900
H	1.27108400	-3.50713400	-1.10764700
H	0.55047300	-3.35632400	0.50043100
C	-0.68379200	-2.60543500	-1.08838100
H	-1.27305200	-3.53739400	-1.10416600
H	-0.58465300	-2.23223500	-2.11406100
C	-2.65730300	-1.23221000	-1.08756600
H	-3.32425300	-2.10811700	-1.01889600
H	-2.35440200	-1.11572600	-2.13667000
C	-3.37550900	0.02554000	-0.63539300
H	-3.59032100	0.01508400	0.44340900
H	-4.35582400	0.03611200	-1.13630800
C	-2.64374100	1.28449400	-1.06156500
H	-2.34426900	1.18636300	-2.11351400
H	-3.30085300	2.16607200	-0.97349200
C	-1.79823000	2.10747400	1.05213700
H	-2.43379600	2.99657800	0.91292400
H	-0.91549700	2.38263600	1.63583400
H	-2.35760200	1.34257000	1.59954200
C	2.23804400	1.75314900	1.03424300
H	2.92682600	2.59793500	0.87115300
H	2.82803200	0.86888800	1.28155300
H	1.57471600	1.98827700	1.87182800
C	2.20380100	-1.78231800	1.01327400
H	2.91496900	-2.60537400	0.83625200

H	1.53496300	-2.05711600	1.83422900
H	2.76384500	-0.88959100	1.29647700
C	-1.82646000	-2.10056900	1.01345000
H	-2.47522200	-2.97760200	0.85915400
H	-2.37490500	-1.33601100	1.57240200
H	-0.94858300	-2.39860500	1.59314900
N	-0.02486500	-0.01363000	1.77124200
C	0.01761900	-0.03064900	2.92868300
C	0.07467100	-0.05695900	4.36531700
H	0.98780500	-0.58000500	4.68654700
H	-0.80631100	-0.58498000	4.75957300
H	0.08747000	0.97225000	4.75342700

DFT-D3 UBP86/ jorge-tzp, solvent CH_3CN, SMD model		
Total electronic energy=	-2243.939298	E_0
Sum of electronic and zero-point Energies=	-2243.427644	$E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2243.402860	$E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2243.401915	$E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2243.472881	$E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.511654	

Calculation of Mössbauer isomer shift

Calculations were performed with the ORCA 4.2.1[16] quantum chemistry program. For calculation of Mössbauer isomer shift calibration line is needed.[54] When the line is obtained then substitution of calculated contact electron density RHO (taken directly from ORCA output) as x gives a calculated isomer shift as y. Calibration set was taken from Romelt et al.[55] Procedure for geometry optimization and calculation of contact electron density on Fe nucleus was taken from Bjornsson et al.[56]

Optimized geometries for calibration test set were calculated using TPSSh DFT functional with D3BJ empirical dispersion correction and ZORA-def2-TZVP SARC/J basis set. Relativistic effects were taken into account by requesting a ZORA relativistic calculation. Calculations were performed in water (CPCMC model).

Also %scf Stabperform true end keyword was used to check wavefunction stability (one center approximation, no solvent)

Sample input file for geometry optimization and frequencies for calibration test set:

```
! UKS TPSSh CPCMC(water) OPT NumFreq ZORA RIJCOSX D3BJ ZORA-def2-TZVP SARC/J TightSCF Grid5 FinalGrid6 SlowConv
%method
IntaccX 4.01,4.01,4.34 # Changing the 3 radial grids
GridX 1,1,2 # Changing the 3 angular grids
end
*xyz -2 5
Fe -0.005543 -0.010542 0.000078
…
Cl -0.709344 -1.000639 2.005220
*
```

RHO was calculated with B3LYP DFT functional using CP(PPP) basis set on Fe and def2-TZVP basis set on other atoms. Relativistic effects were taken into account by requesting a Douglas-Kroll-Hess 2nd order scalar relativistic calculation.

Keywords:

```
! SP UKS B3LYP NORI DKH2 DKH-def2-TZVP TightSCF Grid5 FinalGrid6 SlowConv CPCMC(water)
%basis
newgto Fe "CP(PPP)" end
end
```

```
%method SpecialGridAtoms 26
SpecialGridIntAcc 7
end
%scf MaxIter 2000 end
*xyz 0 2
Fe      0.076793000     -0.084228000     -0.023221000
…
O       -0.947743000      1.573035000      0.109062000
*
%eprnmr nuclei = all 26 {rho, fgrad}
End
```

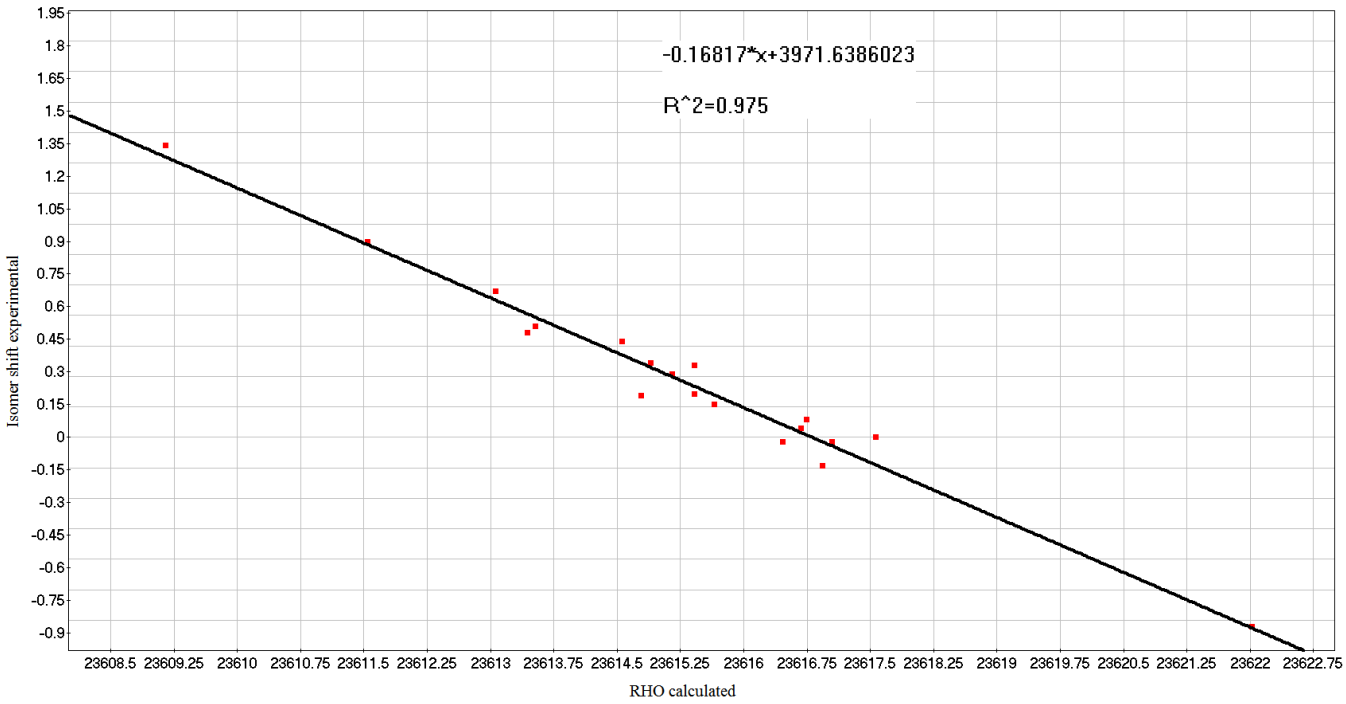
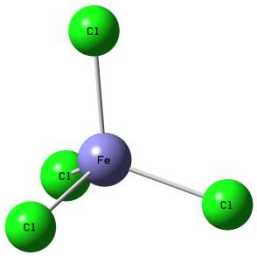


Figure S36. Calibration line for ^{57}Fe Mössbauer isomer shift

Table S36. List of complexes used for calibration of Mössbauer isomer shift DFT calculation.

#	Compound	Exp. isomer shift δ, (mm/s)	Contact electron density on Fe nucleus (RHO) calculated a.u.$^{-3}$
1	$[FeCl_4]^{2-}$	0.9	23611.543
2	$[Fe(CN_6)]^{4-}$	-0.02	23616.463
3	$[FeF_6]^{4-}$	1.34	23609.151
4	$[FeAz]^{+}$	0.29	23615.154
5	$[FeCl_4]^{-}$	0.19	23614.784
6	$[Fe(CN_6)]^{3-}$	-0.13	23616.936
7	$[FeF_6]^{3-}$	0.48	23613.435
8	$[Fe(H_2O_6)]^{3+}$	0.51	23613.535
9	$[Fe(MAC)]^{2-}$	0.15	23615.655
10	$[Fe(OEPPY)]^{+}$	0.2	23615.417
11	$[Fe(Por(O_2))]^{-}$	0.67	23613.064
12	$[Fe(MAC)]^{-}$	-0.02	23617.045
13	$[Fe(Por(O))]^{+}$	0.08	23616.745
14	$[FeO_4]^{2-}$	-0.87	23622.017
15	$Fe(CO)_5$	0	23617.562
16	$[\{FeNO\}^{6}]^{+}$	0.04	23616.677
17	$[\{FeNO\}^{7}]$	0.33	23615.418
18	$[Fe(PH_3)]$	0.34	23614.893
19	[Fe(SMe)]	0.44	23614.562

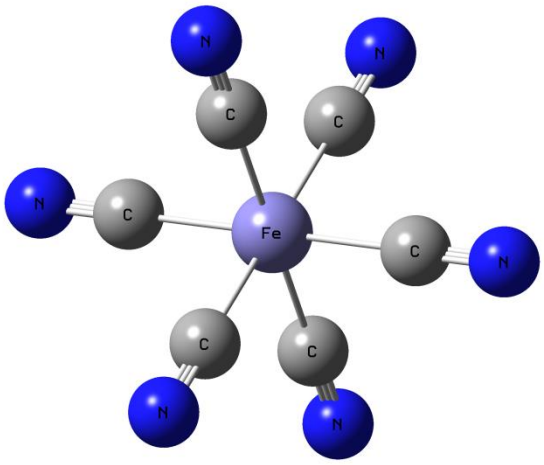


$[FeCl_4]^{2-}$

Charge -2; multiplicity 5

Fe	0.00109800	-0.00216400	-0.00135700
Cl	2.32226400	0.00714000	-0.08091500
Cl	-0.77115400	2.18480400	0.08015100
Cl	-0.71008100	-1.14055800	-1.89204400
Cl	-0.84212700	-1.04922300	1.89416500

Final single point energy -3128.337351894359

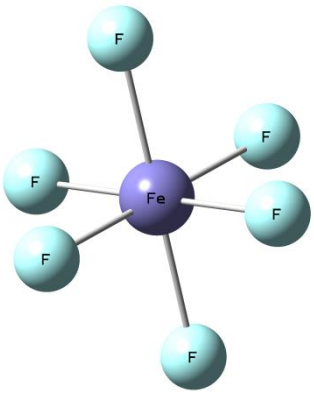


$[Fe(CN_6)]^{4-}$

Charge -4; multiplicity 1

Fe	-0.00007100	0.00000700	0.00000200
C	1.90904500	0.00001800	-0.00067000
C	-1.90915800	0.00000900	0.00067400
C	0.00000300	1.91028800	0.00000000
C	0.00001800	-1.91028100	-0.00000300
C	-0.00148200	-0.00001900	1.90988500
C	0.00146000	-0.00001800	-1.90988200
N	3.08407600	0.00003400	-0.00265600
N	-3.08418900	0.00004600	0.00266700
N	0.00011200	3.08535000	-0.00000700
N	0.00010900	-3.08534200	-0.00001300
N	-0.00212800	-0.00004200	3.08490400
N	0.00220300	-0.00005100	-3.08490000

Final single point energy -1836.282447877332

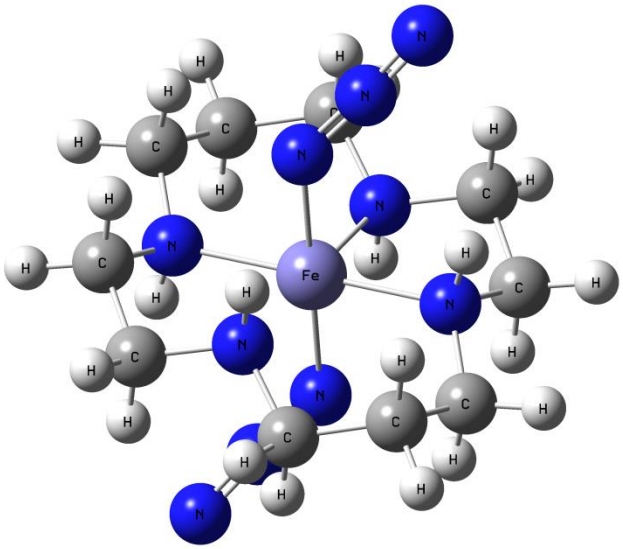


$[FeF_6]^{4-}$

Charge -4; multiplicity 5

Fe	0.00009500	0.00013100	0.00001200
F	2.17238400	-0.00071300	0.00568700
F	-2.17251500	0.00045300	-0.00629700
F	-0.00059200	2.16524800	0.00033500
F	0.00062200	-2.16522100	0.00015300
F	0.00121100	0.00009600	2.02438900
F	-0.00120300	0.00000400	-2.02427900

Final single point energy -1878.668729434674



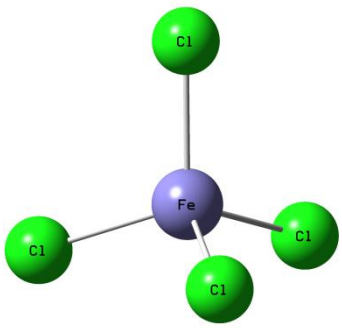
[FeAz]$^{+}$

Charge 1; multiplicity 2

Fe	0.00486800	-0.00896500	-0.00160400
N	1.97741200	-0.14732900	-0.37195200
H	2.45396200	0.33802400	0.38811600
N	-0.04186000	-1.52413200	1.31975400
H	0.30557500	-1.06890700	2.16495200
N	0.28673100	1.15099000	1.52660600
N	1.12560000	1.99017600	1.71109900
N	1.89693500	2.80912400	1.95853500
C	2.25825100	0.59945800	-1.62487400
H	1.92326500	-0.02741000	-2.45204300
H	3.32832400	0.78918900	-1.73014300
C	2.54083800	-1.52069500	-0.42141800
H	3.61711600	-1.44383700	-0.59971100
H	2.08239600	-2.02182400	-1.27405300
C	2.27522300	-2.29308200	0.86143600
H	2.62543500	-1.72049700	1.72754400
H	2.87393000	-3.20585600	0.83130500
C	0.82251400	-2.69766900	1.05689700
H	0.44137100	-3.20044700	0.16699800
H	0.73551700	-3.38721800	1.90115300
C	-1.45425100	-1.90018900	1.57384800
H	-1.54188300	-2.46124400	2.50647000
H	-1.78692700	-2.54126200	0.75626800
C	1.46317900	1.88169600	-1.57693100
N	0.05066900	1.50618600	-1.32283300
N	-1.96821400	0.12862600	0.36689500
H	-2.44332200	-0.35540000	-0.39498500
C	-2.25148300	-0.61907100	1.61869400
H	-1.92206100	0.00885700	2.44716000
H	-3.32147300	-0.81168200	1.72003600
N	-0.27630000	-1.16955800	-1.52934700
N	-1.11335900	-2.01162200	-1.70958900
N	-1.88598400	-2.82983200	-1.95582600
C	-2.53257200	1.50168900	0.41685900
H	-3.60899000	1.42362200	0.59386500

H	-2.07555400	2.00271800	1.27035300
C	-2.26628600	2.27577100	-0.86481300
H	-2.61656800	1.70489700	-1.73197400
H	-2.86429800	3.18895500	-0.83257600
C	-0.81324300	2.67996400	-1.05868700
H	-0.29687300	1.05257100	-2.16882600
H	-0.43252400	3.18114700	-0.16770500
H	1.55089200	2.44446200	-2.50852600
H	1.79697000	2.52075500	-0.75824400
H	-0.72517200	3.37044300	-1.90207800

Final single point energy -2222.002758619165

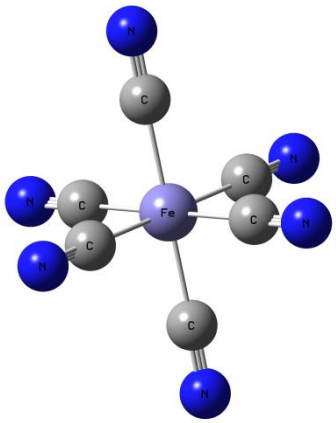


$[FeCl_4]^-$

Charge -1; multiplicity 6

Fe	0.00193200	-0.00097900	0.00004200
Cl	2.20864400	0.00593100	0.00015300
Cl	-0.73148400	2.07971900	-0.00022500
Cl	-0.73968000	-1.04219700	-1.79805900
Cl	-0.73941200	-1.04247400	1.79808900

Final single point energy -3128.182295571258

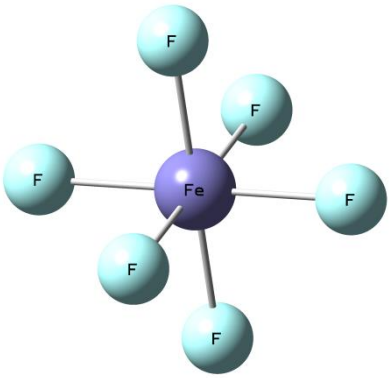


$[Fe(CN_6)]^{3-}$

Charge -3; multiplicity 2

Fe	-0.00007200	0.00002300	-0.00002600
C	1.93404100	-0.03137200	0.03242200
C	-1.93416200	0.03138200	-0.03248900
C	-0.03150700	1.93432200	0.03106100
C	0.03153200	-1.93426800	-0.03104000
C	0.02981900	0.03097300	1.93421000
C	-0.02983600	-0.03093800	-1.93426800
N	3.10033400	-0.04260200	0.03878900
N	-3.10045500	0.04260200	-0.03874000
N	-0.04224600	3.10064600	0.03683400
N	0.04241700	-3.10059200	-0.03669200
N	0.04090100	0.03725900	3.10050500
N	-0.04076500	-0.03743800	-3.10056300

Final single point energy -1836.142488940173

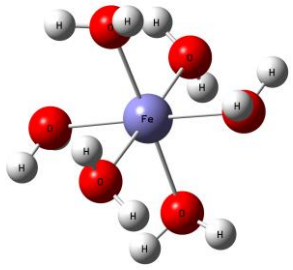


$[FeF_6]^{3-}$

Charge -3; multiplicity 6

Fe	0.00038500	0.00004900	0.00025200
F	1.95844900	-0.00008300	0.00004500
F	-1.95825900	0.00002000	0.00033700
F	0.00008600	1.95268800	-0.00021900
F	0.00019000	-1.95269700	-0.00015400
F	-0.00057300	-0.00002200	1.95641600
F	-0.00027700	0.00004400	-1.95667800

Final single point energy -1878.635276903576



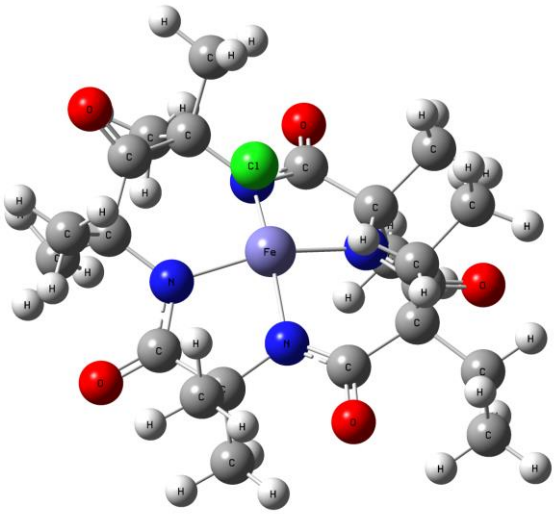
$[Fe(H_2O)_6]^{3+}$

Geometry of **$[Fe(H_2O)_6]^{3+}$** cation was optimized by the method used for cations **2**, **3-5** (see section 12.2 of SI).

Charge 3; multiplicity 6

Fe	-0.07893200	-0.08114900	0.02145400
O	-0.43583000	1.12297300	1.73053300
H	0.35940400	1.60974800	2.02689300
O	-1.22930600	1.24572500	-1.14235700
H	-1.28627000	2.13918300	-0.74765600
O	-1.79276500	-1.26048800	0.42890700
H	-2.56107000	-0.72217900	0.70749900
O	0.35528800	-1.22963300	-1.71392600
H	0.67758700	-0.70167300	-2.47123500
O	1.14280200	-1.35192100	1.19027600
H	1.70184000	-0.85207400	1.81946500
O	1.63821700	1.16113800	-0.29420900
H	2.41128900	0.64722800	-0.60289400
H	-0.91164200	1.36336500	-2.05970200
H	1.44511500	1.80745900	-1.00361600
H	-0.75225400	0.61211900	2.50221500
H	1.76029500	-1.85653800	0.62238200
H	-0.43329100	-1.71435500	-2.03150100
H	-1.61750700	-1.88719800	1.16036700

E_0(UB-P86) = -1722.41499003



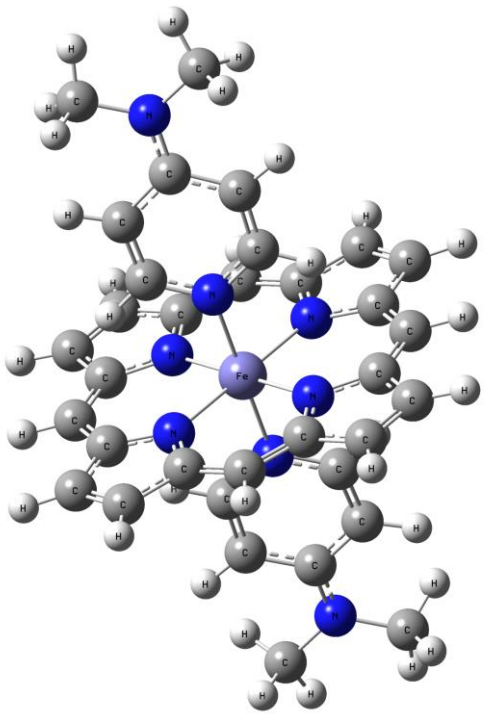
[Fe(MAC)]$^{2-}$

Charge -2; multiplicity 4

Fe	-0.13426600	-0.02321600	0.07602900
Cl	-0.67996000	-0.08496500	2.44508100
N	1.09155700	-1.45704400	-0.26254100
N	-1.45704700	-1.33870800	-0.38567600
N	-1.33925900	1.43309800	-0.27906900
N	1.21085300	1.28931800	-0.28741400
O	-1.69260900	-3.38845900	-1.43105100
O	-4.22860000	0.09296700	1.32319100
O	-1.41404200	3.61492200	-1.03785500
O	3.37008000	1.97599500	-0.58894700
O	3.11153200	-2.49909800	-0.02086100
C	0.49263400	-2.71969800	-0.72422800
C	-1.00306200	-2.48882100	-0.90997800
C	-2.89266400	-1.25243200	-0.08939600
C	-3.29051300	0.09386700	0.54187100
C	-2.76534600	1.45885400	0.07007400
C	-0.79603800	2.57626600	-0.72498800
C	0.72647700	2.57403700	-0.81950600
C	2.54266900	1.11717000	-0.22025900
C	3.08459800	-0.15847000	0.44123100
C	2.40697300	-1.46805300	0.00999100
C	1.09333400	-3.18179000	-2.05624500
C	0.56554900	-3.82541000	0.35087000
C	-3.79087900	-1.39449200	-1.34552800
C	-3.24450700	-2.35235800	0.92668900
C	-2.98341700	2.46282700	1.21460000
C	-3.67650200	1.83435600	-1.12857200
C	1.20143400	3.77248000	0.02042200
C	1.09667100	2.74911800	-2.30177000
C	2.85319800	-0.04656700	1.97997300
C	3.21748400	1.30303000	2.59215600
C	4.59722800	-0.27196600	0.17005400
C	4.98972100	-0.47782300	-1.29307100
H	0.51965000	-4.03150400	-2.43028200
H	2.13513800	-3.46871000	-1.92800500
H	1.03392400	-2.37296400	-2.78969700
H	1.59893900	-4.11468900	0.52446000
H	-0.01323700	-4.68924100	0.01831200
H	0.13520200	-3.45150800	1.28352700

H	-4.80739600	-1.06505400	-1.11828300
H	-3.80552400	-2.43855200	-1.64791900
H	-3.40127200	-0.80100700	-2.17225100
H	-2.97148000	-3.31839600	0.50609900
H	-4.31100500	-2.34539000	1.14950800
H	-2.68480300	-2.17970400	1.84703400
H	-4.04102700	2.53093200	1.46813700
H	-2.62457700	3.43865900	0.89407300
H	-2.42465000	2.13213400	2.09106700
H	-3.57615300	2.89875900	-1.32423100
H	-4.71626600	1.60084800	-0.88896600
H	-3.38656500	1.28821800	-2.02584300
H	2.27874500	3.89001900	-0.06185800
H	0.93646600	3.61626100	1.06958600
H	0.69723000	4.67249300	-0.33437200
H	2.17594500	2.83453400	-2.41272600
H	0.61357600	3.64759500	-2.69163300
H	0.74569300	1.88695000	-2.87574200
H	1.80028400	-0.24577800	2.18562500
H	3.43819800	-0.84522100	2.44816700
H	3.03569700	1.28281100	3.67051400
H	2.60095700	2.09695700	2.16556000
H	4.26629100	1.56392300	2.42998500
H	4.96622900	-1.11101200	0.76326100
H	5.07306100	0.63463200	0.54657800
H	6.07386700	-0.59653800	-1.38597300
H	4.68937300	0.37851000	-1.89811500
H	4.51906200	-1.37613700	-1.69661700

Final single point energy -3196.691328796657



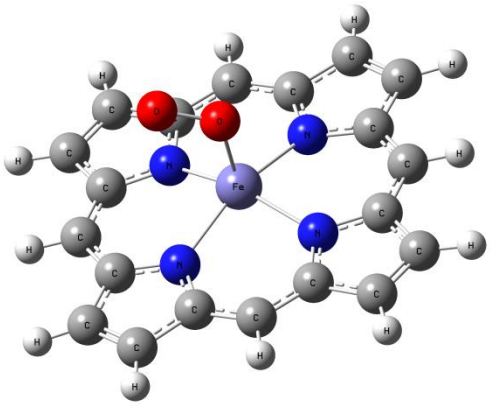
[Fe(OEPPY)]$^{+}$

Charge 1; multiplicity 2

Fe	0.11592100	-0.00179500	0.00029600
N	1.50428900	1.43474700	0.00073700
N	-1.29129700	1.42172900	-0.00011300
N	0.09975200	-0.00190300	-1.98167500
N	-0.24423600	-0.00508500	-6.14774900
C	2.86320200	1.24044000	0.00059500
C	1.32245200	2.79920600	0.00150600
C	-1.12387600	2.78750000	-0.00057900
C	-2.64790700	1.21291300	-0.00071300
C	3.54795100	2.50581700	0.00149900
C	2.59193100	3.47254500	0.00219300
C	-2.40008800	3.44779600	-0.00163900
C	-3.34601500	2.47112600	-0.00160600
C	3.50525000	0.01520500	-0.00097000
C	0.09618500	3.44137700	0.00062200
C	0.06126900	1.14688700	-2.68984800
C	-0.03097800	1.19686500	-4.05777300
C	-0.10369500	-0.00351400	-4.80792500
C	-0.02150400	-1.20270100	-4.05708500
C	0.07016900	-1.15128400	-2.68925500
C	-0.23939300	-1.26030100	-6.89051500
C	-0.25435100	1.24889900	-6.89253800
H	0.10813600	2.06188100	-2.12044600
H	-0.05086700	2.16425000	-4.53729000
H	-0.03382200	-2.17041600	-4.53611500
H	0.12361500	-2.06561100	-2.11942400
H	-0.51604700	-1.04966400	-7.92032700
H	-0.96717400	-1.95586900	-6.46886200
H	0.74914200	-1.73014300	-6.87596600
H	-0.54032900	1.03504500	-7.91919000
H	0.73123500	1.72519700	-6.88884700
H	-0.98221600	1.94003700	-6.46424600
H	4.58803600	0.02059300	-0.00214700
H	0.09122200	4.52367100	0.00071400
N	-1.27709300	-1.43948500	0.00022900

N	1.51847600	-1.42426000	-0.00013600
N	0.09836600	-0.00205600	1.98234600
C	-3.27736500	-0.01883800	0.00017800
C	2.87541000	-1.21631200	-0.00175900
C	-2.63570500	-1.24432400	0.00105200
C	-1.09593600	-2.80350500	0.00094200
C	1.35039000	-2.79050100	-0.00106800
C	0.07002200	-1.15141400	2.69001000
C	0.05691800	1.14665400	2.69038600
H	-4.36015900	-0.02412900	0.00057400
C	3.57279100	-2.47481800	-0.00409100
C	-3.32117400	-2.50941900	0.00234900
C	-2.36551400	-3.47658000	0.00228600
C	0.13060900	-3.44504300	0.00000400
C	2.62649300	-3.45105200	-0.00357400
C	-0.02400200	-1.20285200	4.05773300
H	0.12690000	-2.06566100	2.12034400
C	-0.03777400	1.19651000	4.05812400
H	0.10319500	2.06168900	2.12103300
H	0.13658900	-4.52733300	-0.00023000
C	-0.11047700	-0.00375600	4.80830100
H	-0.03388900	-2.17052800	4.53685700
H	-0.05925500	2.16382800	4.53755200
N	-0.25465300	-0.00448200	6.14794900
C	-0.25989600	1.24995600	6.89198500
C	-0.24555400	-1.25827300	6.89299000
H	-0.54378100	1.03735400	7.91945500
H	0.72687500	1.72384500	6.88566300
H	-0.98710000	1.94286000	6.46533700
H	-0.53958900	-1.04929000	7.91839400
H	-0.95943700	-1.96236500	6.46234300
H	0.74828700	-1.71726100	6.89348500
H	4.62201800	2.61901100	0.00118100
H	2.71506800	4.54539100	0.00265900
H	-2.53432900	4.51931100	-0.00191200
H	-4.42119600	2.57309500	-0.00174700
H	4.64793900	-2.57729700	-0.00628100
H	-4.39528500	-2.62215700	0.00347200
H	-2.48903400	-4.54938500	0.00319000
H	2.76035300	-4.52261200	-0.00504400

Final single point energy -3032.907373520165

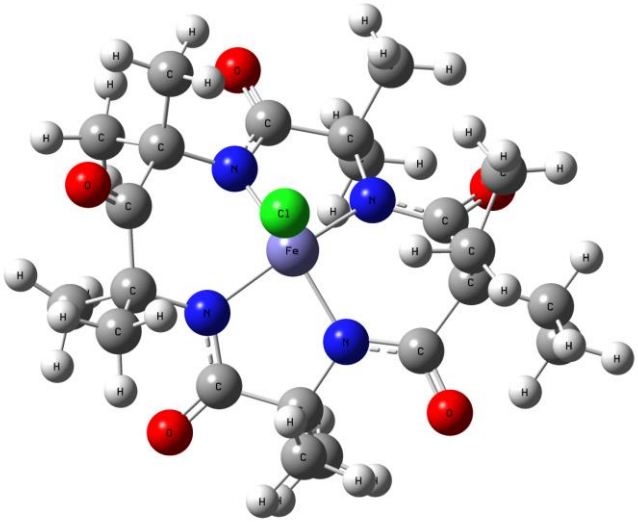


[Fe(Por(O_2))]$^-$

Charge -1; multiplicity 6

Fe	0.01727300	-0.01695000	-0.13159400
N	-2.02032000	-0.18836600	0.24488900
C	-2.92442100	0.84045000	0.24743600
C	-4.26528400	0.30710700	0.28148900
C	-4.15240100	-1.05098200	0.30027900
C	-2.74038000	-1.35348000	0.27983300
C	-2.19128100	-2.63384900	0.30640200
C	-0.83560300	-2.95852900	0.31900500
C	-0.30565700	-4.29883300	0.38662100
C	1.05298300	-4.18713800	0.39892600
C	1.36005200	-2.77887000	0.33823900
N	0.19656100	-2.05526900	0.28655500
C	2.64300400	-2.23391600	0.34354300
C	2.96941100	-0.87935600	0.32292900
C	4.30781000	-0.34232800	0.37491400
C	4.19224100	1.01528500	0.35109600
C	2.78098100	1.31493500	0.28714500
N	2.06249200	0.14665500	0.26390300
C	2.23383100	2.59610400	0.27312200
C	0.87851300	2.92374900	0.25884800
C	0.34745800	4.26547800	0.27103000
C	-1.01128700	4.15249400	0.26149000
C	-1.31592300	2.74218400	0.24183800
N	-0.15161500	2.02065200	0.24192900
C	-2.59753700	2.19496900	0.23559600
O	0.07850300	-0.08976800	-2.03766800
H	-1.74708400	4.94406300	0.26956300
H	0.94347700	5.16653500	0.29134700
H	-5.16714900	0.90241400	0.29313300
H	-4.94246500	-1.78746600	0.33391700
H	-0.90305500	-5.19816900	0.42966600
H	1.78769100	-4.97804800	0.45088100
H	4.98001200	1.75416700	0.38575700
H	5.20972200	-0.93515200	0.42961700
H	-2.88927400	-3.46277700	0.33506600
H	-3.42531800	2.89512600	0.23873500
H	3.46925200	-2.93433100	0.38814400
H	2.93391000	3.42358100	0.29081000
O	-0.75647400	0.68910600	-2.78197900

Final single point energy -2418.223359721235



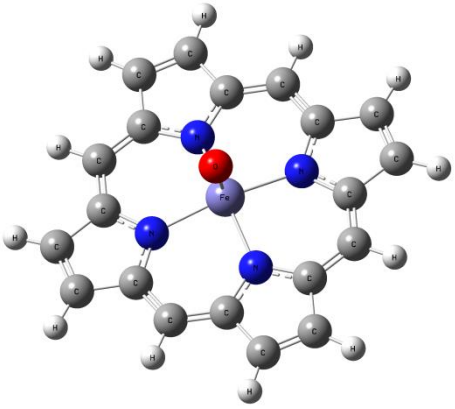
[Fe(MAC)]$^-$

Charge -1; multiplicity 5

Fe	-0.15337300	-0.01307700	0.07586100
Cl	-0.65949200	0.01500300	2.39208700
N	1.06966900	-1.44982200	-0.19078800
N	-1.47094100	-1.31986300	-0.34637100
N	-1.35022600	1.40720400	-0.34898500
N	1.19584800	1.27022600	-0.33626100
O	-1.71068100	-3.33976400	-1.42391800
O	-4.14379800	0.15464600	1.46868200
O	-1.43536200	3.48640900	-1.32916300
O	3.34659900	1.95652100	-0.60621000
O	3.07773300	-2.48532000	0.07032800
C	0.48425400	-2.70759500	-0.70399600
C	-1.00788000	-2.47439700	-0.89998200
C	-2.89452200	-1.24190400	0.01736500
C	-3.26381300	0.12482200	0.63143500
C	-2.76352400	1.46577800	0.05832900
C	-0.80029800	2.51068400	-0.92297000
C	0.72218300	2.51178000	-0.98844200
C	2.54375200	1.10162800	-0.22059300
C	3.07789700	-0.13941000	0.49519800
C	2.40342900	-1.45067500	0.09185600
C	1.10863600	-3.12316100	-2.03894500
C	0.54443400	-3.83614300	0.34856200
C	-3.84403100	-1.42187500	-1.19421800
C	-3.17788300	-2.32343500	1.07006000
C	-2.91794100	2.53810000	1.14644400
C	-3.71817800	1.77461200	-1.12477900
C	1.16345100	3.77251100	-0.22231800
C	1.13655000	2.57606100	-2.46639200
C	2.83283300	0.02374600	2.03099800
C	3.13152200	1.41397100	2.58379100
C	4.59341200	-0.25996900	0.24087700
C	5.00607800	-0.49532200	-1.21181200
H	0.53395200	-3.95554900	-2.44762200
H	2.14289600	-3.43035200	-1.90063400
H	1.06970800	-2.29103400	-2.74559400
H	1.57339300	-4.13854100	0.51937000
H	-0.03704600	-4.68386000	-0.01705900
H	0.10893300	-3.48797600	1.28797300

H	-4.84185300	-1.06554100	-0.93166400
H	-3.89402100	-2.47752900	-1.44728600
H	-3.48419000	-0.87311300	-2.06297200
H	-2.93721200	-3.29848000	0.64960400
H	-4.23033500	-2.30539200	1.34993900
H	-2.56898200	-2.14264900	1.95627900
H	-3.96329500	2.61933700	1.44177100
H	-2.58254300	3.49429400	0.74933400
H	-2.31983900	2.26840200	2.01700100
H	-3.67057700	2.83652200	-1.34940300
H	-4.73901100	1.50936900	-0.84402800
H	-3.43496800	1.21750200	-2.01631600
H	2.23697700	3.91235100	-0.30570500
H	0.88886100	3.68772900	0.83175900
H	0.64168500	4.62895700	-0.65061900
H	2.21415000	2.69780700	-2.55102600
H	0.63604600	3.42529800	-2.93454000
H	0.83439600	1.66204200	-2.98302800
H	1.79417500	-0.22348000	2.25252400
H	3.45722100	-0.72670900	2.52382200
H	2.97232500	1.41972600	3.66505600
H	2.46286300	2.15890300	2.14704200
H	4.16039000	1.72428400	2.38885400
H	4.95254300	-1.08522000	0.85826600
H	5.06189600	0.65358600	0.60938200
H	6.09338600	-0.58876100	-1.28272500
H	4.69743900	0.33514400	-1.84752700
H	4.56601100	-1.41572400	-1.59968200

Final single point energy -3196.523105742589

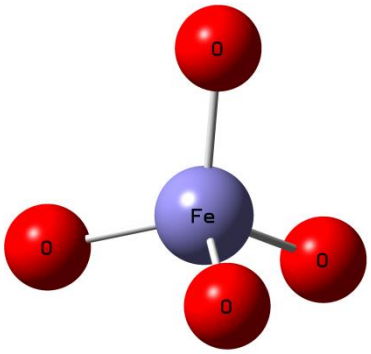


[Fe(Por(O))]$^{+}$

Charge 1; multiplicity 4

Fe	0.00008000	0.00006600	-0.16375100
N	-1.37970800	1.40263900	0.10633000
C	-1.19150500	2.76488800	0.10723800
C	-2.46196600	3.46317000	0.12801200
C	-3.42259600	2.51844100	0.12903300
C	-2.74568300	1.23639300	0.10841300
C	-3.40799600	0.02818000	0.10487700
C	-2.76441900	-1.19102000	0.11547900
C	-3.46257000	-2.46138200	0.14302800
C	-2.51788500	-3.42206400	0.14209000
C	-1.23593200	-2.74533000	0.11449100
N	-1.40204900	-1.37922400	0.11128200
C	-0.02800400	-3.40804200	0.10359800
C	1.19145600	-2.76492000	0.10824900
C	2.46192200	-3.46321800	0.12884400
C	3.42257500	-2.51850100	0.12952300
C	2.74563500	-1.23643500	0.10981400
N	1.37966700	-1.40266000	0.10766500
C	3.40789300	-0.02819300	0.10671000
C	2.76431000	1.19101300	0.11702700
C	3.46248200	2.46138500	0.14395800
C	2.51779500	3.42207200	0.14274700
C	1.23585100	2.74534600	0.11490000
N	1.40195500	1.37924100	0.11223300
C	0.02793100	3.40805300	0.10320000
O	0.00102900	-0.00024600	-1.77830800
H	2.63470500	4.49467600	0.16434100
H	4.53684600	2.56036000	0.16656200
H	-2.56101600	4.53760400	0.14642500
H	-4.49519900	2.63535300	0.14895600
H	-4.53692200	-2.56034100	0.16648500
H	-2.63482200	-4.49464600	0.16450200
H	4.49519500	-2.63546300	0.14824200
H	2.56100700	-4.53768000	0.14687000
H	-4.48931700	0.03656400	0.10768400
H	0.03665800	4.48934000	0.10484800
H	-0.03691900	-4.48933300	0.10495800
H	4.48922200	-0.03657700	0.10882000

Final single point energy -2342.633952094590

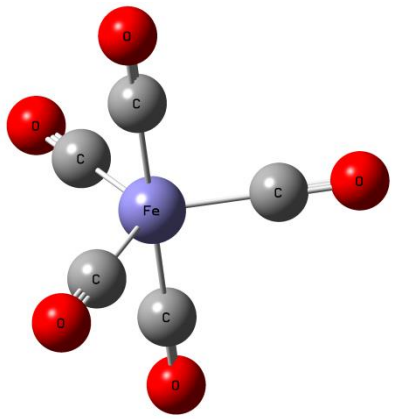


$[FeO_4]^{2-}$

Charge -2; multiplicity 3

Fe	-0.00162400	-0.00143700	-0.00004500
O	1.64093200	-0.00070500	-0.00033500
O	-0.54742400	1.54765700	0.00040800
O	-0.54566200	-0.77300100	-1.34489400
O	-0.54622200	-0.77251400	1.34486700

Final single point energy -1579.469785572756

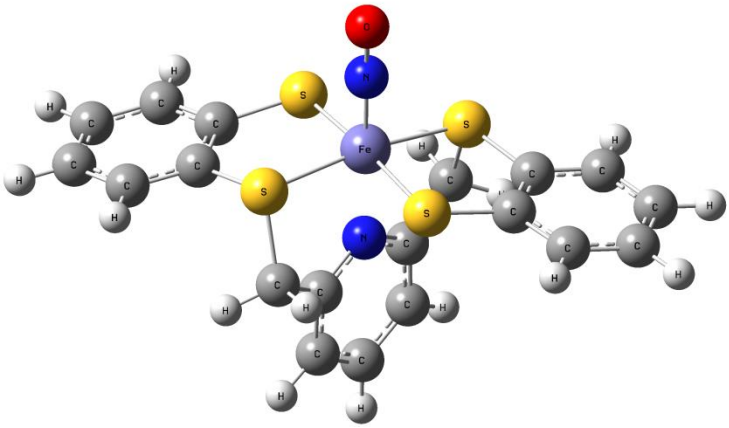


$Fe(CO)_5$

Charge 0; multiplicity 1

Fe	0.00169900	0.00009600	-0.00006100
C	1.79627200	0.00000400	0.00012700
C	-0.90237300	1.54981500	-0.00010500
C	-0.90238100	-1.54959800	0.00006800
C	0.00506400	0.00000500	-1.80377000
C	0.00513100	0.00000100	1.80355400
O	2.94334100	-0.00014800	0.00032300
O	-1.48418600	2.53829700	-0.00012700
O	-1.48418500	-2.53808600	0.00020100
O	0.01062900	-0.00001200	-2.94540100
O	0.01098900	-0.00037500	2.94519100

Final single point energy -1845.428357514791

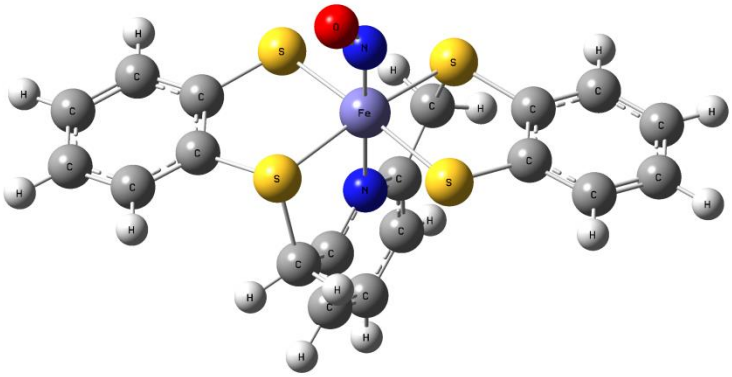


[{FeNO}^{6}]$^{+}$

Charge 1; multiplicity 1

Fe	0.00793800	-0.79220100	-0.00547500
N	0.00200600	-2.41517600	-0.00518200
O	-0.00233900	-3.54574000	-0.00265900
S	-1.61317800	-0.58408800	-1.53716900
S	-1.52686800	-0.67726600	1.69564700
S	1.53859800	-0.67742800	-1.70931700
S	1.63602100	-0.59922700	1.52344300
C	-5.40585800	0.01098100	0.87914300
C	-5.45554000	0.04452100	-0.51669600
C	-4.28794000	-0.12952100	-1.24421700
C	-3.08088000	-0.31980100	-0.56948800
C	-3.01316000	-0.36980400	0.82653100
C	-4.20738500	-0.19364600	1.54501100
C	3.02822200	-0.37578400	-0.84407400
C	3.10040500	-0.33237700	0.55200000
C	4.22044700	-0.19881200	-1.56563300
C	5.42135600	0.00118500	-0.90275400
C	5.47542800	0.02898200	0.49304200
C	4.30991500	-0.14653600	1.22355400
C	-1.21338400	1.10397200	-2.08860800
C	1.23911900	1.08488000	2.08735500
C	0.63688100	1.89032900	0.98766900
C	-0.61083600	1.89950800	-0.98165100
N	0.01250100	1.21551200	0.00012800
C	-0.64244100	3.28577700	-0.99024900
C	0.66950600	3.27648700	1.00867800
C	0.01351500	3.98554400	0.01260900
H	-6.31441000	0.14161600	1.45514200
H	-6.39557100	0.19874100	-1.03088300
H	-4.30489100	-0.11665500	-2.32782400
H	-4.18255200	-0.22378300	2.62779400
H	4.19202600	-0.22447300	-2.64845000
H	6.32827000	0.13269200	-1.48112100
H	6.41724300	0.17966800	1.00499100
H	4.33045500	-0.13831800	2.30713000
H	-2.12200400	1.55649100	-2.48267900
H	-0.49888000	0.97631900	-2.90490200
H	2.14793600	1.53382600	2.48505100
H	0.52463100	0.95035200	2.90274500
H	-1.16534300	3.79899800	-1.78585400
H	1.19319800	3.78242700	1.80844900
H	0.01331000	5.06806100	0.01797200

Final single point energy -3796.574895725928

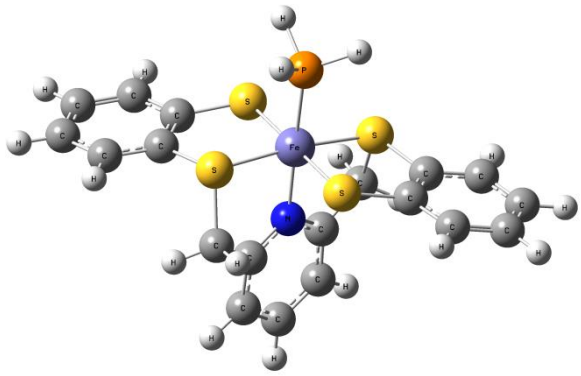


[{FeNO}^{7}]

Charge 0; multiplicity 2

Fe	0.01237100	-0.09289300	-0.75402900
S	1.65383700	-1.60017700	-0.32784300
S	1.57872300	1.59223800	-0.80614500
S	-1.53145200	-1.76236900	-0.47572100
S	-1.61284800	1.42859500	-0.73555800
C	5.45906300	0.86516500	0.01339600
C	5.50603700	-0.51668600	0.21948000
C	4.33573200	-1.25497700	0.11983300
C	3.12865100	-0.61496500	-0.16728700
C	3.06319700	0.76863700	-0.38954800
C	4.26288400	1.49784300	-0.28539600
C	-3.02337800	-0.88340700	-0.24904300
C	-3.09190300	0.51307300	-0.34829700
C	-4.22070300	-1.57425200	0.01575400
C	-5.41663300	-0.89082400	0.16756200
C	-5.46559500	0.50218700	0.05745200
C	-4.29758500	1.20206900	-0.20965700
C	1.23951900	-1.93105200	1.41659700
C	-1.23048500	2.19325700	0.87616300
C	-0.63416800	1.20268900	1.82620100
C	0.61982200	-0.74011400	2.07997300
N	-0.00349000	0.14583000	1.28425300
C	0.64641300	-0.58265700	3.45955500
C	-0.67660500	1.39679300	3.20019100
C	-0.01818600	0.49648800	4.02761900
H	6.36708300	1.45344800	0.08263000
H	6.44290300	-1.00970200	0.44726600
H	4.34899300	-2.32913000	0.26760900
H	4.24088600	2.56912700	-0.45018600
H	-4.19601700	-2.65462000	0.10217400
H	-6.32369800	-1.44867000	0.37124700
H	-6.40305200	1.03176900	0.17267400
H	-4.31393000	2.28141500	-0.31198600
H	2.13399000	-2.27103800	1.93613400
H	0.52179000	-2.75420400	1.37925900
H	-2.13266600	2.65751800	1.27139400
H	-0.50350700	2.97578500	0.64548500
H	1.17153000	-1.30441900	4.07156200
H	-1.20411200	2.25004000	3.60586100
H	-0.02137200	0.63689400	5.10142700
N	0.02659700	-0.28854100	-2.46855200
O	-0.48626600	0.00476800	-3.48861900

Final single point energy -3796.728137896860

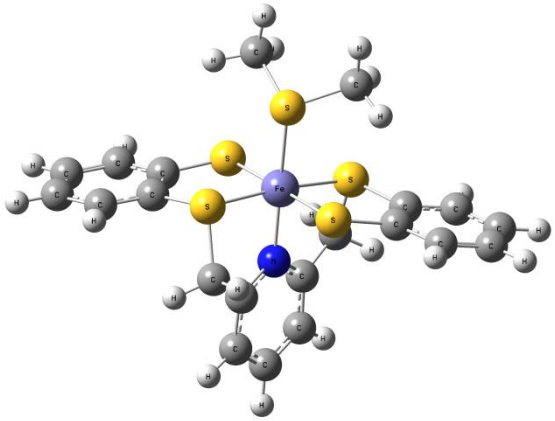


[Fe(PH$_3$)]

Charge 0; multiplicity 1

Fe	-0.00506800	-0.64748900	0.03239000
P	0.05935700	-2.84106700	0.01156700
H	1.29475200	-3.47650400	0.24856600
S	-1.60317100	-0.54619000	-1.48175300
S	-1.56362100	-0.60226200	1.70871100
S	1.55171900	-0.69971700	-1.65363400
S	1.60235500	-0.46097100	1.53088200
C	-5.48260500	-0.12728800	0.85255900
C	-5.51195700	-0.09570900	-0.54606600
C	-4.32100200	-0.21138600	-1.24896000
C	-3.11397700	-0.34112500	-0.55994700
C	-3.06303800	-0.38414200	0.84302800
C	-4.28533500	-0.26948800	1.53517900
C	3.04981300	-0.39003700	-0.80999400
C	3.10479700	-0.27092100	0.58780300
C	4.26145000	-0.26680000	-1.51771900
C	5.45722700	-0.04531600	-0.85295500
C	5.49285100	0.05744600	0.54150900
C	4.31111700	-0.06481700	1.25923300
C	-1.27557600	1.15233800	-2.07748000
C	1.26101000	1.26074100	2.04409000
C	0.63322600	2.03832600	0.93276400
C	-0.65149400	1.98700400	-1.00674300
N	-0.00774000	1.32898100	-0.01991700
C	-0.68998200	3.37444400	-1.05524300
C	0.66653800	3.42640200	0.91241500
C	-0.01274700	4.10693900	-0.08948500
H	-6.40679100	-0.04529000	1.41383200
H	-6.45045600	0.00933200	-1.07631600
H	-4.31876100	-0.20125900	-2.33351000
H	-4.27716700	-0.29762600	2.61914000
H	4.24793200	-0.34874000	-2.59884800
H	6.37398600	0.04513000	-1.42504300
H	6.42983800	0.22498300	1.05836000
H	4.31610200	0.00382200	2.34163800
H	-2.19268800	1.59051700	-2.46877400
H	-0.57157200	1.01553900	-2.90210300
H	2.17467700	1.72408400	2.41397200
H	0.55715500	1.15943700	2.87386500
H	-1.23078900	3.86517700	-1.85402500
H	1.20589500	3.95809400	1.68559000
H	-0.01421000	5.18946000	-0.11767300
H	-0.26436000	-3.50031100	-1.19069500
H	-0.73392200	-3.60945100	0.88865700

Final single point energy -4011.125891854638



[Fe(SMe)]

Charge 0; multiplicity 1

Fe	0.01132900	-0.43436400	-0.06503000
S	0.13710700	-2.67703300	-0.48394800
C	1.78511800	-3.29540100	-0.06136800
S	-1.62000300	-0.25322900	-1.54505400
S	-1.52178400	-0.58511800	1.62067100
S	1.57075300	-0.23936600	-1.73716100
S	1.61051800	-0.35658700	1.45336300
C	-5.45929000	-0.05321600	0.88882000
C	-5.51682400	0.08707300	-0.50214500
C	-4.33939200	0.03292600	-1.23531100
C	-3.11823200	-0.14392200	-0.58342800
C	-3.03931900	-0.30076200	0.81032800
C	-4.24785600	-0.24522200	1.53352800
C	3.06171300	-0.00008900	-0.85681400
C	3.11122500	-0.03358400	0.54617700
C	4.27657800	0.20334000	-1.54031600
C	5.46788300	0.35802600	-0.84933200
C	5.49650400	0.31639100	0.54869800
C	4.31208700	0.11212300	1.24262100
C	-1.32705800	1.49509100	-1.99047400
C	1.21650800	1.29642000	2.12654600
C	0.55957400	2.15334400	1.09316100
C	-0.72694800	2.24380300	-0.84434500
N	-0.05976600	1.51455700	0.07657000
C	-0.81242400	3.62700000	-0.76027900
C	0.54674800	3.53723400	1.20287100
C	-0.15886800	4.28766000	0.27161300
H	-6.37194600	-0.01759100	1.47350000
H	-6.46609700	0.22953900	-1.00377600
H	-4.35919700	0.13046100	-2.31540800
H	-4.21762000	-0.35951400	2.61157000
H	4.26878200	0.23476100	-2.62412400
H	6.38743400	0.50941100	-1.40378300
H	6.43004000	0.43403500	1.08525100
H	4.31036100	0.06392800	2.32615200
H	-2.24949400	1.95000200	-2.34855500
H	-0.61453500	1.44432700	-2.81751200
H	2.11600200	1.75348700	2.53682100
H	0.51919800	1.09551600	2.94337600
H	-1.37315000	4.17143100	-1.50910400
H	1.07075400	4.01077600	2.02302700

H	-0.19943400	5.36693900	0.34975400
H	1.97075600	-3.18012500	1.00675000
C	-0.83672500	-3.71091900	0.64044600
H	2.49533200	-2.70363500	-0.63585600
H	1.85210400	-4.34455500	-0.34868800
H	-0.55643300	-3.51819700	1.67496200
H	-0.66787000	-4.75519000	0.37638100
H	-1.88229700	-3.44868200	0.49046500

Final single point energy -4146.512104945432

Calculation of electric field gradient

Electric field gradient was calculated[57] for all discussed structures (see section 11 of SI) as a single point job. Calculations were performed with the ORCA 4.2.1[16] quantum chemistry program. TPSS DFT functional with DKH-def2-QZVPP basis set on Fe and def2-TZVP basis set on other atoms was used. Relativistic effects were taken into account by requesting a Douglas-Kroll-Hess 2nd order scalar relativistic calculation with inclusion of picture change effects.

Sample input file:

```
! SP UKS TPSS NORI DKH2 DKH-def2-TZVP Decontract VERYTIGHTSCF Grid5
FinalGrid6 SlowConv

%basis

newgto Fe "DKH-def2-QZVPP" end

end

%method SpecialGridAtoms 26

SpecialGridIntAcc 7

end

%scf MaxIter 2000 end

*xyz 0 2

Fe      0.076793000     -0.084228000     -0.023221000

…

H       2.945113000      0.104849000     -2.591674000

*

%eprnmr nuclei = all 26 {fgrad}

end

%rel PictureChange true

end
```

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