Supporting Information (SI)

Measurement of the ligand field spectra of ferrous and ferric iron chlorides using 2p3d RIXS

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1. Sample Preparation of the iron chloride complexes

1.1. Fe(III)-O_h – $(CH_3NH_3)_3[Fe(III)Cl_6]$ * $(CH_3NH_3)Cl$:

Preparation:

$(CH_3NH_3)_3[Fe(III)Cl_6]$ * $(CH_3NH_3)Cl$ was prepared according to a published procedure.[1]

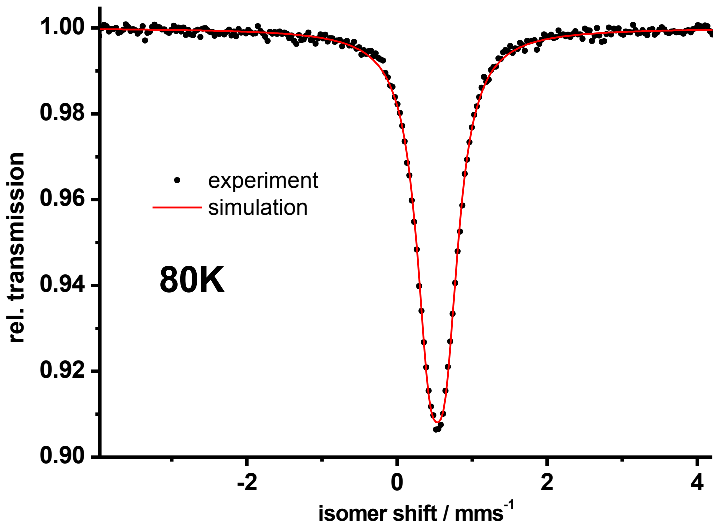

Figure S1: Mössbauer Spectrum (black dots) for Fe(III)-O_h@80K together with Simulation (red line): Isomer shift: 0.54 mms^{-1}, quadrupole splitting 0.22 mms^{-1}, line width 0.42 mms^{-1}

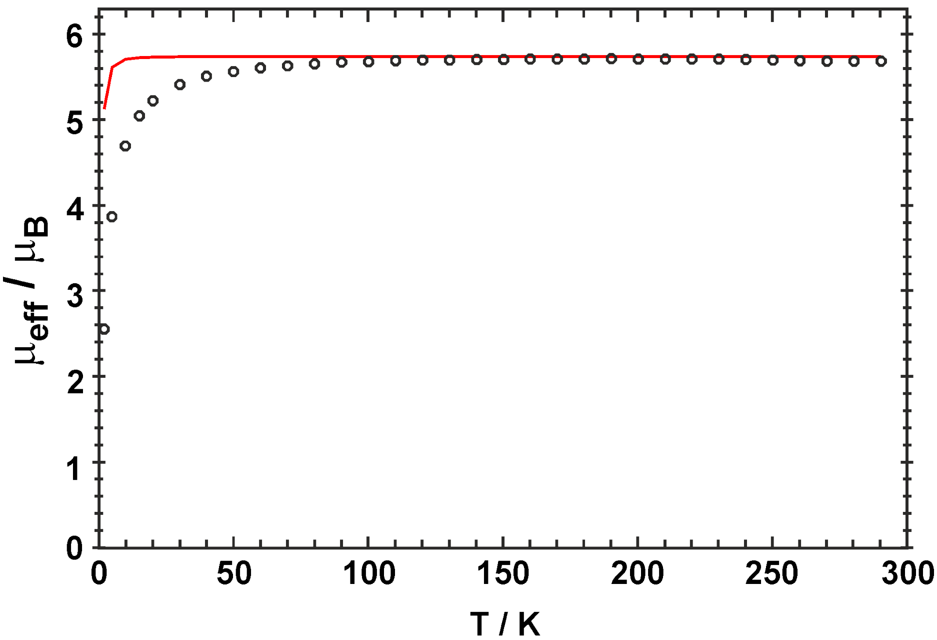

Figure S2: SQUID measurement (black dots) for Fe(III)-O_h together with simulation (red line). 5.8 BM is in accord with the calculated magnetic moment of 5.93 BM.

1.2. Fe(II)-O_h – poly-$(CH_3NH_3)_2[Fe(II)Cl_4]$: $[Fe(II)Cl_6]$ 2D-polymer

Preparation:
3.3 g (26 mmol) of $FeCl_2$ were dissolved in 80 ml conc. HCL (38%) under a nitrogen atmosphere. To the clear solution, 1.6 g (24 mmol) of methylammoniumchloride was added. The solution was heated and nitrogen was passed over the boiling solution until its volume was reduced to the point where crystals started to precipitate. Gray greenish crystals suitable for x-ray crystallography formed upon slow cooling to room temperature.

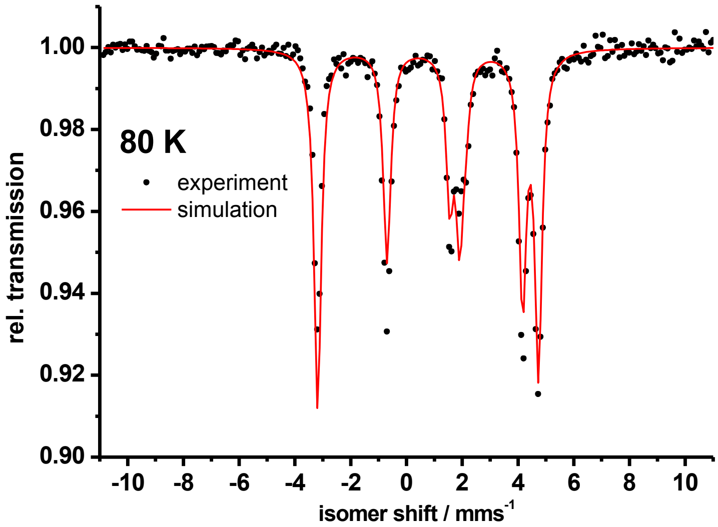

Figure S3: Mössbauer spectrum (black dots) for Fe(II)-O_h@80K together with simulation (red line). Isomer shift: 1.25 mms^{-1}, quadrupole splitting 2.53 mms^{-1}, line width 0.31 mms^{-1}.

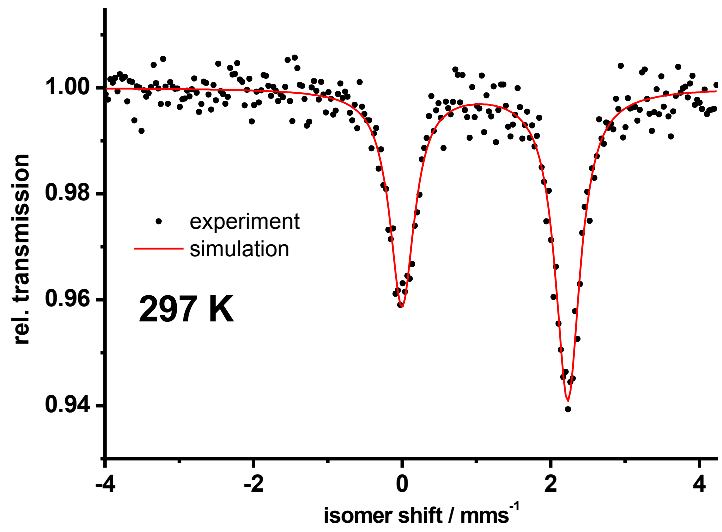

Figure S4: Mössbauer spectrum (black dots) for Fe(II)-O_h@293K together with simulation (red line). Isomer shift: 1.11 mms^{-1}, quadrupole splitting 2.23 mms^{-1}, line width 0.40 mms^{-1}

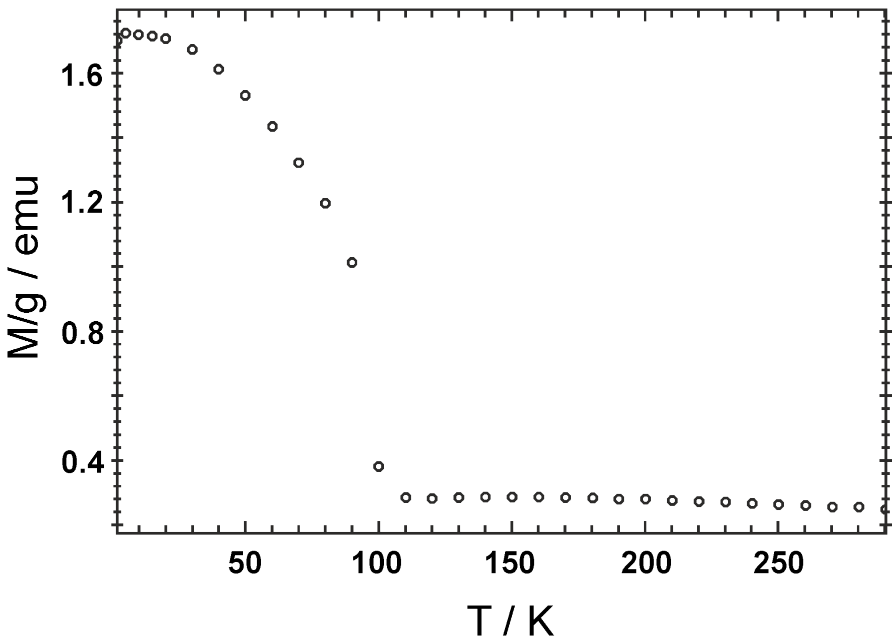

Figure S5: Magnetic susceptibility measurement (black cycles) for Fe(II)-O_h: Magnetic phase transition @100K in accord with literature.[2]

1.3. Fe(III)-T_d – $(NEt_4)[Fe(III)Cl_4]$:

Preparation:
Commercial Product – Sigma Aldrich

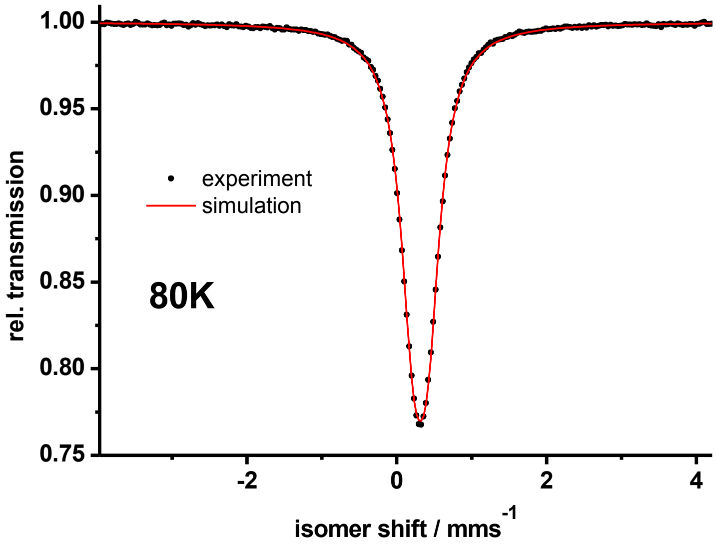

Figure S5: Mössbauer spectrum (black dots) for Fe(III)-T_d@80K together with simulation (red line). Isomer shift: 0.31 mms^{-1}, quadrupole splitting 0.19 mms^{-1}, line width 0.42 mms^{-1}

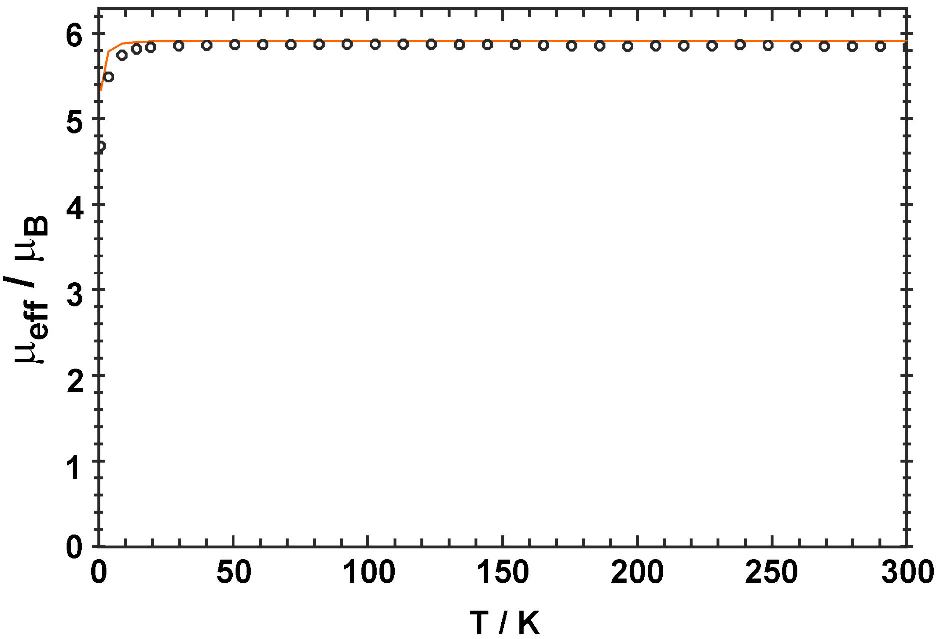

Figure S6: SQUID measurement (black dots) for Fe(III)-T_d together with simulation (red line)**:** 5.8 BM) is in accord with the calculated magnetic moment of 5.93 BM.

1.4. Fe(II)-T_d – $(NEt_4)_2[Fe(II)Cl_4]$:

Preparation:
The compound was prepared according to a published procedure.[3]

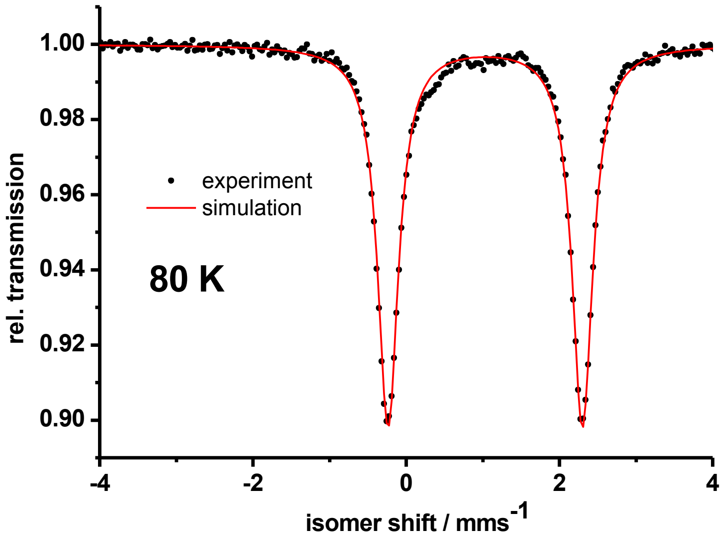

Figure S7: Mössbauer Spectrum (black dots) for Fe(II)-T_d@80K together with Simulation (red line). Isomer shift: 1.03 mms^{-1}, quadrupole splitting2.54 mms^{-1}, line width 0.33 mms^{-1}

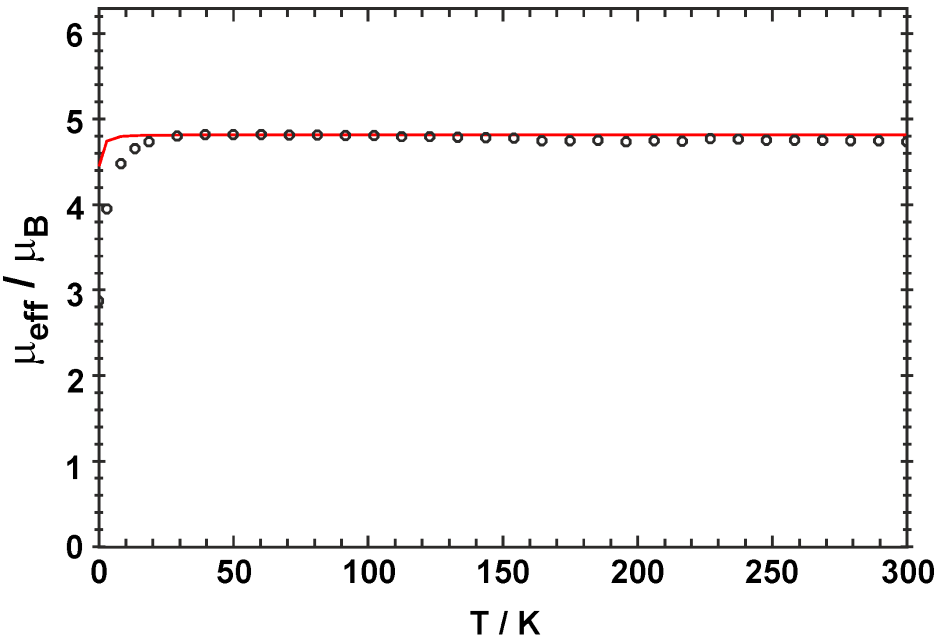

Figure S8: SQUID measurement (black dots) for Fe(II)-T_d together with simulation (red line)**:** 4.8 BM is in accord with the calculated magnetic moment of 4.9 BM.

2. Fit-Results for the Iron-Chloride series

Table S1: Fit-Results for $FeCl_6$ $-d^5$

Fe(III)-O_h					
Type	Position (eV)	FWHM (eV)	Position (cm^{-1})	FWHM (cm^{-1})	Amplitude
Gauss	0	0.30	0	2417	0.97
Gauss	1.13	0.33	9088	2637	0.34
Gauss	1.56	0.49	12598	3983	0.28
Gauss	2.37	0.50	19093	4071	0.31
Gauss	3.00	0.43	24236	3492	0.31
Gauss	3.36	0.33	27074	2686	0.12
Gauss	3.68	0.33	29668	2686	0.12
Gauss	4.09	0.67	32977	5372	0.28

Table S2: Fit-Results for $FeCl_6$ $-d^6$

Fe(II)-O_h					
Type	Position (eV)	FWHM (eV)	Position (cm^{-1})	FWHM (cm^{-1})	Amplitude
Gauss	0	0.35	0	2845	1.00
Gauss	0.51	0.33	4117	2682	0.45
Gauss	0.88	0.41	7137	3292	0.32
Gauss	1.51	0.41	12165	3269	0.19
Gauss	2.02	0.42	16329	3396	0.23
Gauss	2.39	0.26	19283	2107	0.18
Gauss	2.56	0.20	20627	1581	0.17
Gauss	2.87	0.43	23186	3485	0.27
Gauss	3.43	0.51	27686	4111	0.23
Gauss	3.85	0.76	31055	6132	0.19

Table S3: Fit-Results for $FeCl_4$ $-d^5$

Fe(III)-T_d					
Type	Location (eV)	FWHM (eV)	Location (cm)	FWHM (cm)	Amplitude
Gauss	0	0.28	0	2258	0.97
Gauss	1.67	0.3	13469	2420	0.25
Gauss	1.9	0.27	15325	2178	0.31
Gauss	2.32	0.37	18712	2984	0.44
Gauss	2.78	0.33	22422	2662	0.27
Gauss	3.26	0.51	26294	4113	0.13

Gauss	3.69	0.58	29762	4678	0.12
Gauss	4.37	0.6	35246	4839	0.19

Table S4: Fit-Results for $FeCl_4$ –d^6

Fe(II)-T_d					
Type	Location (eV)	FWHM (eV)	Location (cm)	FWHM (cm)	Amplitude
Gauss	0	0.22	0	1774	0.66
Gauss	0.32	0.48	2581	3871	1.31
Gauss	2	0.4	16131	3226	0.06
Gauss	2.35	0.4	18954	3226	0.14
Gauss	2.6	0.2	20970	1613	0.04
Gauss	2.8	0.4	22584	3226	0.14
Gauss	3.09	0.4	24923	3226	0.12
Gauss	3.46	0.6	27907	4839	0.06

Table S5: Term energies and the associated expectation value of S^2. The values are determined by averaging the energies and expectation values for each microstate that contributes to the term. Deviations from the ideal values of $\langle S^2 \rangle$ arise from spin-orbit coupling.

Fe(III)-Td			**Fe(III)-Oh**			**Fe(II)-Td**			**Fe(II)-Oh**		
Transition	Energy (eV)	$\langle S^2 \rangle$	Transition	Energy (eV)	$\langle S^2 \rangle$	Transition	Energy (eV)	$\langle S^2 \rangle$	Transition	Energy (eV)	$\langle S^2 \rangle$
$^6\Gamma$	0.00	8.73	$^6\Gamma$	0.00	8.72	$^5\Gamma$	0.00	5.99	$^5\Gamma$	0.00	5.99
$^4\Gamma$	1.66	3.73	$^2\Gamma$	1.13	1.82	$^5\Gamma$	0.34	5.99	$^5\Gamma$	0.05	5.99
$^4\Gamma$	1.91	3.73	$^4\Gamma$	1.25	3.28	$^3\Gamma$	1.77	2.00	$^5\Gamma$	0.54	5.99
$^4\Gamma$	2.13	3.73	$^4\Gamma$	1.63	3.72	$^3\Gamma$	1.94	1.99	$^5\Gamma$	0.91	5.99
$^2\Gamma$	2.27	0.86	$^2\Gamma$	2.31	2.00	$^3\Gamma$	2.04	1.99	$^3\Gamma$	1.52	2.00
			$^4\Gamma$	2.38	3.59	$^3\Gamma$	2.10	1.99	$^3\Gamma$	1.82	1.96
						$^3\Gamma$	2.23	1.99	$^3\Gamma$	1.85	1.99
									$^3\Gamma$	2.00	1.96
									$^1\Gamma$	2.10	0.40

References:

(1) James, B. D.; Bakalova, M.; Liesegang, J.; Reiff, W. M.; Hockless, D. C. R.; Skelton, B. W.; White, A. H., The hexachloroferrate(III) anion stabilized in hydrogen bonded packing arrangements. A comparison of the X-ray crystal structures and low temperature magnetism of tetrakis (methylammonium) hexachloroferrate (III) chloride (I) and tetrakis (hexamethylenediammonium) hexachloroferrate (III) tetrachloroferrate (III) tetrachloride (II), *Inorg. Chim. Acta.* **1996**, *247*, 169.

(2) Han, J.; Nishihara, S.; Inoue, K.; Kurmoo, M., On the Nature of the Structural and Magnetic Phase Transitions in the Layered Perovskite-Like $(CH_3NH_3)_2[Fe^{II}Cl_4]$. *Inorg. Chem.* **2014**, *53*, 2068.

(3) Styczeń, E.; Pattek-Janczyk, A.; Gazda, M.; Jóźwiak, W. K.; Wyrzykowski, D.; Thermal analysis of bis(tetraethylammonium) tetrachloroferrate(II). Warnke, Z. *Thermochim. Acta* **2008**, *480*, 30.