Supporting Information

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Syntheses

L_{ox}

L_{ox} was produced as described in: (*i*) R. A. Gossage in *Experiments in Green and Sustainable Chemistry* (Eds.: H. W. Roesky, D. K. Kennepohl), Wiley-VCH, Weinheim, **2009**, pp. 19–24; (*ii*) Button, K. M.; Gossage, R. A. *J. Heterocyclic Chem.*, **2003**, *40*, 513.

Compound **1**

Complex **1** was synthesized as described in: Handley, D. A.; Hitchcock, P. B.; Leigh, G. J. *Inorg. Chim. Acta* **2001**, *314*, 1; IR and X-ray diffraction (A. J. Lough, R. A. Gossage, *unpublished results*) confirmed the identity of **1**.

Synthesis and characterization of **2** and **3**.

Identical methods were used in the synthesis of these two materials and hence **2** will be given as representative.

A sample of 4,4-dimethyl-2-(2'-anilinyl)-2-oxazoline (0.76 g: 4.0 mmol) was dissolved in $CHCl_3$ (40 mL) in a 100 mL round-bottomed flask equipped with a reflux condenser. Solid $NiCl_2$•$6H_2O$ (0.31 g: 1.3 mmol) was then added. The mixture was then heated to reflux temperature for a period of 22 h. The resulting light green opaque mixture was then treated with 7 mL of 95% EtOH and heating continued (18 h) as the mixture dissolved and turned deep green in colour. The resulting solution was filtered and volatile components of the mixture were removed (*vacuo*). The resulting green oil was treated with Et_2O (75 mL) and the green solid precipitate collected and washed with further Et_2O (50 mL) and hexanes (20 mL), yielding a green solid (0.30 g: 73%).

Complex **2** (M_w: 941.1): Anal. Calcd. for $C_{23}H_{73}N_6O_4Ni_3Cl_5$: C 42.12; H 4.61; N 8.93. Found: C 41.88; H 4.88, N 9.09. Crystals, suitable for X-ray diffraction, were grown *via* the slow evaporation of

an CH_3CN solution of the complex at ambient temperature and pressure. IR (KBr: cm^{-1}): 3292m, 3217m, 3117m, 2968m, 1703m, 1627s,1583m, 1501m, 1450m, 1394w, 1374m, 1327m, 1296w, 1239w, 1071m, 1043w, 961w, 746m, 696m. μ_B (RT) = 5.43 B.M.; λ_{max} (RT, CH_2Cl_2, [**2**] = 9.99×10^{-5} M) = 289 ($\varepsilon = 4.9 \times 10^3$), 325 ($\varepsilon = 4.9 \times 10^3$), 410 (sh).

Complex **3** (M_w: 1228.0): Yield: 70%. Anal. Calcd. for $C_{23}H_{73}N_6O_4Ni_3Br_5 \bullet (C_6H_{14})_{0.75}$: C 36.68; H 4.39; N 6.84. Found: C 36.85, 36.79; H 4.67, 4.57; N 7.31, 7.24. Crystals (X-ray) were obtained from the slow evaporation and cooling of an initially boiling 95% aq. EtOH solution of **3**. IR (KBr: cm^{-1}): 3288s, 3188s, 3111m, 2969m, 1625s,1574m, 1501m, 1451m, 1393w, 1373s, 1329m, 1297w, 1219w, 1195w, 1072m, 1036w, 966w, 906w, 893w, 834w, 776w, 744m, 695m, 617w, 464m. μ_B (RT) = 4.55 B.M.; λ_{max} (RT, CH_2Cl_2, [**3**] = 1.01×10^{-4} M) = 293 ($\varepsilon = 1.1 \times 10^4$), 518 nm ($\varepsilon = 115$); 669 nm ($\varepsilon = 5$).

X-ray data for complex **2**.

General:

Data was collected at -100°C on a Nonius Kappa CCD diffractometer, using the COLLECT program (Nonius, 1998). Cell refinement and data reductions used the programs DENZO and SCALEPACK (Otwinowski & Minor, 1997). SIR97 (Altomare et al., 1999) was used to solve the structure and SHELXL97 (Sheldrick, 1997) was used to refine the structure. ORTEP-3 for Windows (Farrugia , 1997) was used for molecular graphics and PLATON (Spek, 2001) was used to prepare material for publication. H atoms were placed in calculated positions with U_{iso} constrained to be 1.5 times U_{eq} of the carrier atom for all methyl hydrogen atoms and 1.2 times U_{eq} of the carrier atom for all other H atoms.

The H on O4 could not be found in F maps. It was placed by geometry. The R dropped from 0.0513 to 0.0510 with the addition of H4a. There is an approximate C3 axis through Cl4 to O4 and H4a. The free chloride ion is disordered and was modeled by two different sites 0.826(17)Å apart. The only checkCIF ALERTs were at the C level. There was a void of 53 $Å^3$. The only molecule which could fit into this void is a water molecule, but no significant)F peak could be attributed to a molecule in this site.

Altomare, A., Burla, M.C., Camalli, M., Cascarano, G, Giacovazzo, C., Guagliardi, A., Moliterni, A.G.G., Polidori, G. & Spagna, R. (1999). J. Appl. Cryst. 32, 115-119.

Bruker-AXS (2000). SHELXTL 6.10. Bruker-AXS, Madison, USA

Farrugia, L.J. (1997). J. Appl. Cryst. 30, 565. (one page only)

Nonius (1998). COLLECT. Nonius BV, Delft, The Netherlands

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C.W. Carter & R.M. Sweet, pp. 307-326. London: Academic Press.

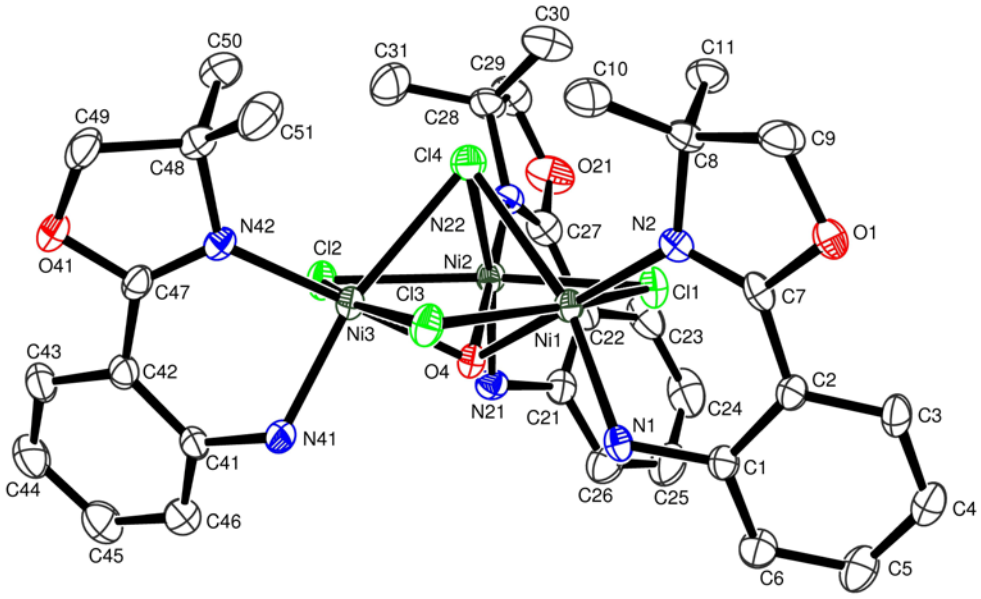
Sheldrick, G.M. (1997). SHELXL-97. University of Göttingen. Germany.

Spek, A.L. (2001). PLATON. University of Utrecht, The Netherlands.

Caption for ORTEP.

A general ORTEP (Farrugia, 1997) view of the title compound with non-hydrogen displacement ellipsoids draw at the 50% probability level.

ORTEP of cationic component of **2**.



Core of **2**.

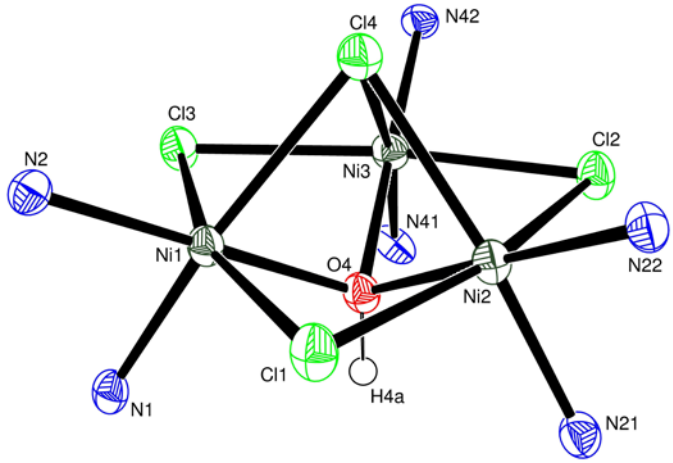


Table 1. Crystal data and structure refinement for complex 2.

Identification code	1070	
Empirical formula	C33 H43 Cl5 N6 Ni3 O4	
Formula weight	941.05	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.4038(4) Å	α= 93.865(2)°.
	b = 11.9005(4) Å	β= 104.381(2)°.
	c = 17.2457(6) Å	γ = 116.686(2)°.
Volume	1981.83(13) $Å^3$	
Z	2	
Density (calculated)	1.577 Mg/m^3	
Absorption coefficient	1.792 mm^{-1}	
F(000)	968	
Crystal size	0.07 x 0.05 x 0.05 mm^3	
Theta range for data collection	2.53 to 27.52°.	
Index ranges	-14<=h<=14, -15<=k<=15, -21<=l<=22	
Reflections collected	28922	
Independent reflections	9086 [R(int) = 0.0934]	
Completeness to theta = 27.52°	99.5 %	

Absorption correction	Psi-scan
Max. and min. transmission	0.914 and 0.861
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9086 / 0 / 478
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.0953
R indices (all data)	R1 = 0.0885, wR2 = 0.1108
Extinction coefficient	0.0036(4)
Largest diff. peak and hole	0.830 and -0.603 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex 2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	303(1)	3921(1)	2987(1)	26(1)
Cl(2)	4550(1)	8001(1)	3622(1)	25(1)
Cl(3)	1375(1)	6415(1)	867(1)	24(1)
Cl(4)	1143(1)	6976(1)	2759(1)	25(1)
Cl(5)	6207(2)	5788(2)	8239(5)	46(1)
Cl(6)	6279(6)	5695(7)	8717(14)	35(4)
O(4)	2475(3)	5650(2)	2357(2)	19(1)
Ni(1)	476(1)	4906(1)	1786(1)	19(1)
O(1)	-3718(3)	2596(3)	458(2)	28(1)
N(1)	423(3)	3518(3)	969(2)	20(1)
N(2)	-1584(3)	4138(3)	1202(2)	20(1)
C(1)	-620(4)	2215(4)	853(2)	20(1)
C(2)	-1986(4)	1949(4)	727(2)	21(1)
C(3)	-3011(4)	659(4)	568(2)	26(1)
C(4)	-2680(5)	-323(4)	552(3)	29(1)
C(5)	-1320(5)	-46(4)	709(3)	33(1)
C(6)	-297(5)	1224(4)	851(3)	27(1)
C(7)	-2360(4)	2971(4)	809(2)	22(1)
C(8)	-2484(4)	4733(4)	1235(2)	22(1)
C(9)	-3863(5)	3745(4)	592(3)	32(1)
C(10)	-1936(5)	6042(4)	1004(3)	33(1)
C(11)	-2611(5)	4803(4)	2096(3)	29(1)

Ni(2)	2478(1)	5946(1)	3508(1)	20(1)
O(21)	2738(4)	5859(3)	5966(2)	41(1)
N(21)	3761(4)	5158(3)	3893(2)	23(1)
N(22)	2506(3)	6251(3)	4695(2)	21(1)
C(21)	3364(4)	4220(4)	4384(3)	24(1)
C(22)	2904(4)	4439(4)	5032(3)	28(1)
C(23)	2553(5)	3506(5)	5516(3)	38(1)
C(24)	2629(5)	2390(5)	5346(3)	45(1)
C(25)	3042(5)	2179(5)	4695(3)	44(1)
C(26)	3415(5)	3084(4)	4219(3)	36(1)
C(27)	2724(5)	5566(4)	5193(2)	29(1)
C(28)	2221(5)	7192(4)	5128(3)	30(1)
C(29)	2513(5)	6960(5)	6006(3)	40(1)
C(30)	710(5)	6848(5)	4763(3)	44(1)
C(31)	3180(6)	8563(5)	5088(3)	49(2)
Ni(3)	3175(1)	7447(1)	2206(1)	19(1)
O(41)	5599(3)	11250(3)	2056(2)	28(1)
N(41)	4626(3)	7393(3)	1697(2)	24(1)
N(42)	3936(3)	9297(3)	2065(2)	20(1)
C(41)	6029(4)	8378(4)	2107(2)	23(1)
C(42)	6306(4)	9660(4)	2264(2)	23(1)
C(43)	7687(5)	10618(4)	2623(3)	31(1)
C(44)	8734(5)	10319(5)	2840(3)	41(1)
C(45)	8431(5)	9031(5)	2704(3)	41(1)
C(46)	7083(5)	8071(4)	2337(3)	34(1)
C(47)	5202(4)	10012(4)	2110(2)	22(1)
C(48)	3280(4)	10134(4)	2046(3)	25(1)

C(49)	4331(5)	11330(4)	1824(3)	32(1)
C(50)	3179(5)	10430(4)	2894(3)	35(1)
C(51)	1862(5)	9505(4)	1408(3)	40(1)

Table 3. Bond lengths [Å] and angles [°] for complex **2**.

Cl(1)-Ni(2)	2.4493(11)	C(2)-C(3)	1.404(5)	N(21)-H(21A)	0.9200
Cl(1)-Ni(1)	2.4550(11)	C(2)-C(7)	1.468(6)	N(21)-H(21B)	0.9200
Cl(2)-Ni(3)	2.4094(11)	C(3)-C(4)	1.381(6)	N(22)-C(27)	1.280(5)
Cl(2)-Ni(2)	2.4739(11)	C(3)-H(3)	0.9500	N(22)-C(28)	1.501(5)
Cl(3)-Ni(3)	2.4612(11)	C(4)-C(5)	1.380(6)	C(21)-C(26)	1.392(6)
Cl(3)-Ni(1)	2.5153(11)	C(4)-H(4)	0.9500	C(21)-C(22)	1.402(6)
Cl(4)-Ni(2)	2.5302(12)	C(5)-C(6)	1.389(6)	C(22)-C(23)	1.407(6)
Cl(4)-Ni(1)	2.5666(11)	C(5)-H(5)	0.9500	C(22)-C(27)	1.464(6)
Cl(4)-Ni(3)	2.5676(11)	C(6)-H(6)	0.9500	C(23)-C(24)	1.385(7)
Cl(5)-Cl(6)	0.826(17)	C(8)-C(10)	1.520(6)	C(23)-H(23)	0.9500
O(4)-Ni(1)	1.976(3)	C(8)-C(11)	1.527(5)	C(24)-C(25)	1.371(8)
O(4)-Ni(3)	1.980(3)	C(8)-C(9)	1.543(6)	C(24)-H(24)	0.9500
O(4)-Ni(2)	1.991(3)	C(9)-H(9A)	0.9900	C(25)-C(26)	1.377(7)
O(4)-H(4A)	1.0000	C(9)-H(9B)	0.9900	C(25)-H(25)	0.9500
Ni(1)-N(2)	2.035(3)	C(10)-H(10A)	0.9800	C(26)-H(26)	0.9500
Ni(1)-N(1)	2.067(3)	C(10)-H(10B)	0.9800	C(28)-C(31)	1.520(6)
O(1)-C(7)	1.357(5)	C(10)-H(10C)	0.9800	C(28)-C(30)	1.526(7)
O(1)-C(9)	1.459(5)	C(11)-H(11A)	0.9800	C(28)-C(29)	1.539(6)
N(1)-C(1)	1.429(5)	C(11)-H(11B)	0.9800	C(29)-H(29A)	0.9900
N(1)-H(1A)	0.9200	C(11)-H(11C)	0.9800	C(29)-H(29B)	0.9900
N(1)-H(1B)	0.9200	Ni(2)-N(22)	2.044(3)	C(30)-H(30A)	0.9800
N(2)-C(7)	1.282(5)	Ni(2)-N(21)	2.072(3)	C(30)-H(30B)	0.9800
N(2)-C(8)	1.494(5)	O(21)-C(27)	1.349(5)	C(30)-H(30C)	0.9800
C(1)-C(6)	1.385(6)	O(21)-C(29)	1.445(6)	C(31)-H(31A)	0.9800
C(1)-C(2)	1.398(6)	N(21)-C(21)	1.426(5)	C(31)-H(31B)	0.9800

C(31)-H(31C)	0.9800	C(41)-C(42)	1.403(5)	C(48)-C(50)	1.525(6)
Ni(3)-N(42)	2.030(3)	C(42)-C(43)	1.404(6)	C(48)-C(49)	1.543(6)
Ni(3)-N(41)	2.079(3)	C(42)-C(47)	1.467(6)	C(49)-H(49A)	0.9900
O(41)-C(47)	1.351(5)	C(43)-C(44)	1.368(7)	C(49)-H(49B)	0.9900
O(41)-C(49)	1.449(5)	C(43)-H(43)	0.9500	C(50)-H(50A)	0.9800
N(41)-C(41)	1.441(5)	C(44)-C(45)	1.400(7)	C(50)-H(50B)	0.9800
N(41)-H(41A)	0.9200	C(44)-H(44)	0.9500	C(50)-H(50C)	0.9800
N(41)-H(41B)	0.9200	C(45)-C(46)	1.383(7)	C(51)-H(51A)	0.9800
N(42)-C(47)	1.284(5)	C(45)-H(45)	0.9500	C(51)-H(51B)	0.9800
N(42)-C(48)	1.489(5)	C(46)-H(46)	0.9500	C(51)-H(51C)	0.9800
C(41)-C(46)	1.383(6)	C(48)-C(51)	1.518(6)		

Ni(2)-Cl(1)-Ni(1)	76.22(3)	N(2)-Ni(1)-Cl(1)	97.60(9)	Ni(1)-N(1)-H(1B)	107.7
Ni(3)-Cl(2)-Ni(2)	75.85(3)	N(1)-Ni(1)-Cl(1)	102.09(9)	H(1A)-N(1)-H(1B)	107.1
Ni(3)-Cl(3)-Ni(1)	75.94(3)	O(4)-Ni(1)-Cl(3)	81.41(8)	C(7)-N(2)-C(8)	108.1(3)
Ni(2)-Cl(4)-Ni(1)	72.86(3)	N(2)-Ni(1)-Cl(3)	98.80(9)	C(7)-N(2)-Ni(1)	123.7(3)
Ni(2)-Cl(4)-Ni(3)	72.15(3)	N(1)-Ni(1)-Cl(3)	86.24(9)	C(8)-N(2)-Ni(1)	127.7(2)
Ni(1)-Cl(4)-Ni(3)	73.23(3)	Cl(1)-Ni(1)-Cl(3)	162.03(4)	C(6)-C(1)-C(2)	120.1(4)
Ni(1)-O(4)-Ni(3)	101.46(12)	O(4)-Ni(1)-Cl(4)	74.63(8)	C(6)-C(1)-N(1)	121.0(4)
Ni(1)-O(4)-Ni(2)	99.46(12)	N(2)-Ni(1)-Cl(4)	105.28(10)	C(2)-C(1)-N(1)	118.9(4)
Ni(3)-O(4)-Ni(2)	98.22(11)	N(1)-Ni(1)-Cl(4)	165.50(9)	C(1)-C(2)-C(3)	118.3(4)
Ni(1)-O(4)-H(4A)	118.0	Cl(1)-Ni(1)-Cl(4)	85.14(4)	C(1)-C(2)-C(7)	122.1(4)
Ni(3)-O(4)-H(4A)	118.0	Cl(3)-Ni(1)-Cl(4)	83.51(3)	C(3)-C(2)-C(7)	119.5(4)
Ni(2)-O(4)-H(4A)	118.0	C(7)-O(1)-C(9)	106.1(3)	C(4)-C(3)-C(2)	121.0(4)
O(4)-Ni(1)-N(2)	179.76(12)	C(1)-N(1)-Ni(1)	118.4(2)	C(4)-C(3)-H(3)	119.5
O(4)-Ni(1)-N(1)	93.74(12)	C(1)-N(1)-H(1A)	107.7	C(2)-C(3)-H(3)	119.5
N(2)-Ni(1)-N(1)	86.39(13)	Ni(1)-N(1)-H(1A)	107.7	C(5)-C(4)-C(3)	120.2(4)
O(4)-Ni(1)-Cl(1)	82.17(8)	C(1)-N(1)-H(1B)	107.7	C(5)-C(4)-H(4)	119.9

C(3)-C(4)-H(4)	119.9	H(10B)-C(10)-H(10C)	109.5	Ni(2)-N(21)-H(21B)	107.9
C(4)-C(5)-C(6)	119.5(4)	C(8)-C(11)-H(11A)	109.5	H(21A)-N(21)-H(21B)	107.2
C(4)-C(5)-H(5)	120.2	C(8)-C(11)-H(11B)	109.5	C(27)-N(22)-C(28)	108.1(3)
C(6)-C(5)-H(5)	120.2	H(11A)-C(11)-H(11B)	109.5	C(27)-N(22)-Ni(2)	122.4(3)
C(1)-C(6)-C(5)	120.8(4)	C(8)-C(11)-H(11C)	109.5	C(28)-N(22)-Ni(2)	129.4(3)
C(1)-C(6)-H(6)	119.6	H(11A)-C(11)-H(11C)	109.5	C(26)-C(21)-C(22)	119.9(4)
C(5)-C(6)-H(6)	119.6	H(11B)-C(11)-H(11C)	109.5	C(26)-C(21)-N(21)	120.5(4)
N(2)-C(7)-O(1)	116.9(4)	O(4)-Ni(2)-N(22)	179.23(13)	C(22)-C(21)-N(21)	119.6(4)
N(2)-C(7)-C(2)	128.2(4)	O(4)-Ni(2)-N(21)	92.09(12)	C(21)-C(22)-C(23)	118.0(4)
O(1)-C(7)-C(2)	114.8(3)	N(22)-Ni(2)-N(21)	87.23(13)	C(21)-C(22)-C(27)	122.3(4)
N(2)-C(8)-C(10)	112.2(3)	O(4)-Ni(2)-Cl(1)	82.01(8)	C(23)-C(22)-C(27)	119.6(4)
N(2)-C(8)-C(11)	107.5(3)	N(22)-Ni(2)-Cl(1)	98.43(10)	C(24)-C(23)-C(22)	121.1(5)
C(10)-C(8)-C(11)	112.1(4)	N(21)-Ni(2)-Cl(1)	97.24(10)	C(24)-C(23)-H(23)	119.5
N(2)-C(8)-C(9)	101.8(3)	O(4)-Ni(2)-Cl(2)	82.81(8)	C(22)-C(23)-H(23)	119.5
C(10)-C(8)-C(9)	111.0(4)	N(22)-Ni(2)-Cl(2)	96.80(10)	C(25)-C(24)-C(23)	119.9(5)
C(11)-C(8)-C(9)	111.7(3)	N(21)-Ni(2)-Cl(2)	88.58(10)	C(25)-C(24)-H(24)	120.1
O(1)-C(9)-C(8)	104.4(3)	Cl(1)-Ni(2)-Cl(2)	163.92(4)	C(23)-C(24)-H(24)	120.1
O(1)-C(9)-H(9A)	110.9	O(4)-Ni(2)-Cl(4)	75.25(8)	C(24)-C(25)-C(26)	120.4(5)
C(8)-C(9)-H(9A)	110.9	N(22)-Ni(2)-Cl(4)	105.39(10)	C(24)-C(25)-H(25)	119.8
O(1)-C(9)-H(9B)	110.9	N(21)-Ni(2)-Cl(4)	166.41(9)	C(26)-C(25)-H(25)	119.8
C(8)-C(9)-H(9B)	110.9	Cl(1)-Ni(2)-Cl(4)	86.05(4)	C(25)-C(26)-C(21)	120.7(5)
H(9A)-C(9)-H(9B)	108.9	Cl(2)-Ni(2)-Cl(4)	84.98(4)	C(25)-C(26)-H(26)	119.6
C(8)-C(10)-H(10A)	109.5	C(27)-O(21)-C(29)	106.2(4)	C(21)-C(26)-H(26)	119.6
C(8)-C(10)-H(10B)	109.5	C(21)-N(21)-Ni(2)	117.4(3)	N(22)-C(27)-O(21)	117.6(4)
H(10A)-C(10)-H(10B)	109.5	C(21)-N(21)-H(21A)	107.9	N(22)-C(27)-C(22)	128.5(4)
C(8)-C(10)-H(10C)	109.5	Ni(2)-N(21)-H(21A)	107.9	O(21)-C(27)-C(22)	113.9(4)
H(10A)-C(10)-H(10C)	109.5	C(21)-N(21)-H(21B)	107.9	N(22)-C(28)-C(31)	111.1(4)

N(22)-C(28)-C(30)	109.8(4)	N(42)-Ni(3)-Cl(2)	94.34(10)	C(44)-C(43)-C(42)	121.5(4)
C(31)-C(28)-C(30)	111.2(4)	N(41)-Ni(3)-Cl(2)	97.44(10)	C(44)-C(43)-H(43)	119.2
N(22)-C(28)-C(29)	101.7(4)	O(4)-Ni(3)-Cl(3)	82.75(8)	C(42)-C(43)-H(43)	119.2
C(31)-C(28)-C(29)	111.9(4)	N(42)-Ni(3)-Cl(3)	98.24(10)	C(43)-C(44)-C(45)	119.6(4)
C(30)-C(28)-C(29)	110.8(4)	N(41)-Ni(3)-Cl(3)	90.17(10)	C(43)-C(44)-H(44)	120.2
O(21)-C(29)-C(28)	105.9(3)	Cl(2)-Ni(3)-Cl(3)	165.75(4)	C(45)-C(44)-H(44)	120.2
O(21)-C(29)-H(29A)	110.6	O(4)-Ni(3)-Cl(4)	74.55(8)	C(46)-C(45)-C(44)	120.0(5)
C(28)-C(29)-H(29A)	110.6	N(42)-Ni(3)-Cl(4)	106.28(10)	C(46)-C(45)-H(45)	120.0
O(21)-C(29)-H(29B)	110.6	N(41)-Ni(3)-Cl(4)	167.47(9)	C(44)-C(45)-H(45)	120.0
C(28)-C(29)-H(29B)	110.6	Cl(2)-Ni(3)-Cl(4)	85.50(4)	C(45)-C(46)-C(41)	120.2(4)
H(29A)-C(29)-H(29B)	108.7	Cl(3)-Ni(3)-Cl(4)	84.57(4)	C(45)-C(46)-H(46)	119.9
C(28)-C(30)-H(30A)	109.5	C(47)-O(41)-C(49)	105.2(3)	C(41)-C(46)-H(46)	119.9
C(28)-C(30)-H(30B)	109.5	C(41)-N(41)-Ni(3)	114.8(2)	N(42)-C(47)-O(41)	117.2(4)
H(30A)-C(30)-H(30B)	109.5	C(41)-N(41)-H(41A)	108.6	N(42)-C(47)-C(42)	127.2(4)
C(28)-C(30)-H(30C)	109.5	Ni(3)-N(41)-H(41A)	108.6	O(41)-C(47)-C(42)	115.4(3)
H(30A)-C(30)-H(30C)	109.5	C(41)-N(41)-H(41B)	108.6	N(42)-C(48)-C(51)	111.4(3)
H(30B)-C(30)-H(30C)	109.5	Ni(3)-N(41)-H(41B)	108.6	N(42)-C(48)-C(50)	108.8(3)
C(28)-C(31)-H(31A)	109.5	H(41A)-N(41)-H(41B)	107.6	C(51)-C(48)-C(50)	110.6(4)
C(28)-C(31)-H(31B)	109.5	C(47)-N(42)-C(48)	107.4(3)	N(42)-C(48)-C(49)	101.1(3)
H(31A)-C(31)-H(31B)	109.5	C(47)-N(42)-Ni(3)	123.1(3)	C(51)-C(48)-C(49)	112.2(4)
C(28)-C(31)-H(31C)	109.5	C(48)-N(42)-Ni(3)	128.7(3)	C(50)-C(48)-C(49)	112.3(4)
H(31A)-C(31)-H(31C)	109.5	C(46)-C(41)-C(42)	120.6(4)	O(41)-C(49)-C(48)	104.2(3)
H(31B)-C(31)-H(31C)	109.5	C(46)-C(41)-N(41)	120.9(4)	O(41)-C(49)-H(49A)	110.9
O(4)-Ni(3)-N(42)	178.74(13)	C(42)-C(41)-N(41)	118.5(4)	C(48)-C(49)-H(49A)	110.9
O(4)-Ni(3)-N(41)	93.53(12)	C(41)-C(42)-C(43)	118.0(4)	O(41)-C(49)-H(49B)	110.9
N(42)-Ni(3)-N(41)	85.71(13)	C(41)-C(42)-C(47)	122.2(4)	C(48)-C(49)-H(49B)	110.9
O(4)-Ni(3)-Cl(2)	84.76(8)	C(43)-C(42)-C(47)	119.7(4)	H(49A)-C(49)-H(49B)	108.9

C(48)-C(50)-H(50A)	109.5	H(50A)-C(50)-H(50C)	109.5	H(51A)-C(51)-H(51B)	109.5
C(48)-C(50)-H(50B)	109.5	H(50B)-C(50)-H(50C)	109.5	C(48)-C(51)-H(51C)	109.5
H(50A)-C(50)-H(50B)	109.5	C(48)-C(51)-H(51A)	109.5	H(51A)-C(51)-H(51C)	109.5
C(48)-C(50)-H(50C)	109.5	C(48)-C(51)-H(51B)	109.5	H(51B)-C(51)-H(51C)	109.5

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for complex 2. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	22(1)	23(1)	24(1)	7(1)	7(1)	4(1)
Cl(2)	21(1)	22(1)	22(1)	3(1)	3(1)	5(1)
Cl(3)	25(1)	20(1)	20(1)	4(1)	4(1)	7(1)
Cl(4)	23(1)	24(1)	25(1)	3(1)	6(1)	11(1)
Cl(5)	29(1)	34(1)	76(4)	-2(1)	15(1)	20(1)
Cl(6)	18(3)	29(3)	53(9)	-8(4)	4(3)	12(2)
O(4)	20(1)	15(1)	18(1)	4(1)	5(1)	5(1)
Ni(1)	16(1)	17(1)	19(1)	2(1)	4(1)	6(1)
O(1)	13(1)	28(2)	35(2)	0(1)	2(1)	7(1)
N(1)	13(2)	20(2)	22(2)	3(1)	4(1)	5(1)
N(2)	19(2)	23(2)	20(2)	5(1)	7(1)	10(1)
C(1)	17(2)	20(2)	20(2)	2(2)	4(2)	7(2)
C(2)	19(2)	19(2)	21(2)	-1(2)	4(2)	6(2)
C(3)	20(2)	21(2)	24(2)	0(2)	4(2)	2(2)
C(4)	32(3)	19(2)	27(2)	1(2)	6(2)	7(2)
C(5)	37(3)	22(2)	36(3)	10(2)	6(2)	14(2)
C(6)	24(2)	26(2)	32(2)	7(2)	4(2)	14(2)
C(7)	12(2)	27(2)	21(2)	5(2)	4(2)	6(2)
C(8)	17(2)	28(2)	25(2)	5(2)	7(2)	14(2)
C(9)	25(2)	38(3)	36(3)	2(2)	6(2)	21(2)
C(10)	31(3)	36(3)	40(3)	10(2)	11(2)	23(2)
C(11)	31(2)	32(2)	26(2)	1(2)	13(2)	16(2)

Ni(2)	19(1)	19(1)	18(1)	3(1)	5(1)	7(1)
O(21)	51(2)	62(2)	20(2)	11(2)	16(2)	34(2)
N(21)	24(2)	24(2)	19(2)	1(1)	6(1)	11(2)
N(22)	18(2)	23(2)	19(2)	0(1)	5(1)	9(1)
C(21)	19(2)	24(2)	28(2)	8(2)	2(2)	10(2)
C(22)	22(2)	34(2)	27(2)	13(2)	7(2)	14(2)
C(23)	30(3)	51(3)	42(3)	28(2)	16(2)	22(2)
C(24)	36(3)	47(3)	59(3)	36(3)	13(3)	22(2)
C(25)	37(3)	30(3)	62(4)	12(2)	6(3)	19(2)
C(26)	36(3)	31(2)	37(3)	6(2)	5(2)	16(2)
C(27)	26(2)	37(2)	18(2)	3(2)	6(2)	12(2)
C(28)	29(2)	32(2)	27(2)	-4(2)	12(2)	13(2)
C(29)	36(3)	49(3)	25(2)	-7(2)	11(2)	14(2)
C(30)	43(3)	59(3)	40(3)	5(3)	17(2)	33(3)
C(31)	59(4)	31(3)	51(3)	-5(2)	27(3)	12(3)
Ni(3)	19(1)	16(1)	21(1)	4(1)	6(1)	6(1)
O(41)	31(2)	16(1)	38(2)	7(1)	12(1)	10(1)
N(41)	26(2)	17(2)	26(2)	1(1)	12(2)	7(2)
N(42)	24(2)	17(2)	20(2)	5(1)	6(1)	10(1)
C(41)	21(2)	20(2)	26(2)	4(2)	13(2)	6(2)
C(42)	26(2)	20(2)	22(2)	5(2)	12(2)	8(2)
C(43)	26(2)	25(2)	36(3)	4(2)	16(2)	5(2)
C(44)	23(3)	37(3)	52(3)	3(2)	14(2)	6(2)
C(45)	27(3)	43(3)	53(3)	11(2)	15(2)	16(2)
C(46)	35(3)	29(2)	44(3)	11(2)	20(2)	17(2)
C(47)	29(2)	15(2)	19(2)	2(2)	9(2)	7(2)
C(48)	28(2)	21(2)	28(2)	6(2)	9(2)	14(2)

C(49)	36(3)	18(2)	44(3)	12(2)	12(2)	14(2)
C(50)	36(3)	27(2)	39(3)	-1(2)	12(2)	16(2)
C(51)	34(3)	26(2)	52(3)	5(2)	-1(2)	16(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for complex 2.

	x	y	z	U(eq)
H(4A)	2955	5174	2221	23
H(1A)	331	3749	468	24
H(1B)	1268	3543	1136	24
H(3)	-3948	458	470	31
H(4)	-3389	-1191	433	35
H(5)	-1087	-718	720	39
H(6)	637	1414	948	32
H(9A)	-4650	3567	800	38
H(9B)	-4007	4061	79	38
H(10A)	-1041	6640	1407	50
H(10B)	-2590	6367	996	50
H(10C)	-1824	5962	461	50
H(11A)	-2926	3949	2230	43
H(11B)	-3278	5099	2120	43
H(11C)	-1708	5406	2491	43
H(21A)	3840	4790	3436	27
H(21B)	4625	5819	4183	27
H(23)	2259	3644	5965	45
H(24)	2394	1772	5681	54
H(25)	3072	1404	4571	52
H(26)	3710	2931	3772	43

H(29A)	3342	7722	6381	47
H(29B)	1717	6785	6205	47
H(30A)	534	6955	4195	65
H(30B)	507	7414	5081	65
H(30C)	116	5952	4780	65
H(31A)	4142	8743	5297	74
H(31B)	3040	9163	5423	74
H(31C)	2978	8668	4520	74
H(41A)	4585	6603	1699	29
H(41B)	4388	7466	1160	29
H(43)	7898	11494	2716	37
H(44)	9662	10982	3081	49
H(45)	9152	8817	2865	49
H(46)	6880	7198	2242	41
H(49A)	4027	11309	1230	39
H(49B)	4455	12129	2131	39
H(50A)	2677	9623	3063	52
H(50B)	2685	10926	2878	52
H(50C)	4110	10930	3286	52
H(51A)	1924	9200	885	60
H(51B)	1529	10132	1340	60
H(51C)	1219	8776	1585	60

Table 6. Torsion angles [°] for complex 2.

Ni(3)-O(4)-Ni(1)-N(1)	121.02(13)
Ni(2)-O(4)-Ni(1)-N(1)	-138.52(12)
Ni(3)-O(4)-Ni(1)-Cl(1)	-137.27(10)
Ni(2)-O(4)-Ni(1)-Cl(1)	-36.81(8)
Ni(3)-O(4)-Ni(1)-Cl(3)	35.39(9)
Ni(2)-O(4)-Ni(1)-Cl(3)	135.85(10)
Ni(3)-O(4)-Ni(1)-Cl(4)	-50.19(8)
Ni(2)-O(4)-Ni(1)-Cl(4)	50.27(8)
Ni(2)-Cl(1)-Ni(1)-O(4)	29.65(8)
Ni(2)-Cl(1)-Ni(1)-N(2)	-150.26(10)
Ni(2)-Cl(1)-Ni(1)-N(1)	121.82(9)
Ni(2)-Cl(1)-Ni(1)-Cl(3)	5.49(14)
Ni(2)-Cl(1)-Ni(1)-Cl(4)	-45.46(3)
Ni(3)-Cl(3)-Ni(1)-O(4)	-28.07(8)
Ni(3)-Cl(3)-Ni(1)-N(2)	151.81(10)
Ni(3)-Cl(3)-Ni(1)-N(1)	-122.43(9)
Ni(3)-Cl(3)-Ni(1)-Cl(1)	-3.87(14)
Ni(3)-Cl(3)-Ni(1)-Cl(4)	47.29(3)
Ni(2)-Cl(4)-Ni(1)-O(4)	-38.67(8)
Ni(3)-Cl(4)-Ni(1)-O(4)	37.32(8)
Ni(2)-Cl(4)-Ni(1)-N(2)	141.10(10)
Ni(3)-Cl(4)-Ni(1)-N(2)	-142.92(10)
Ni(2)-Cl(4)-Ni(1)-N(1)	-76.2(4)
Ni(3)-Cl(4)-Ni(1)-N(1)	-0.2(4)
Ni(2)-Cl(4)-Ni(1)-Cl(1)	44.53(3)
Ni(3)-Cl(4)-Ni(1)-Cl(1)	120.52(4)
Ni(2)-Cl(4)-Ni(1)-Cl(3)	-121.51(4)
Ni(3)-Cl(4)-Ni(1)-Cl(3)	-45.53(3)

O(4)-Ni(1)-N(1)-C(1)	130.7(3)
N(2)-Ni(1)-N(1)-C(1)	-49.1(3)
Cl(1)-Ni(1)-N(1)-C(1)	47.9(3)
Cl(3)-Ni(1)-N(1)-C(1)	-148.2(3)
Cl(4)-Ni(1)-N(1)-C(1)	166.7(3)
N(1)-Ni(1)-N(2)-C(7)	25.2(3)
Cl(1)-Ni(1)-N(2)-C(7)	-76.5(3)
Cl(3)-Ni(1)-N(2)-C(7)	110.9(3)
Cl(4)-Ni(1)-N(2)-C(7)	-163.5(3)
N(1)-Ni(1)-N(2)-C(8)	-163.2(3)
Cl(1)-Ni(1)-N(2)-C(8)	95.0(3)
Cl(3)-Ni(1)-N(2)-C(8)	-77.6(3)
Cl(4)-Ni(1)-N(2)-C(8)	8.0(3)
Ni(1)-N(1)-C(1)-C(6)	-133.6(3)
Ni(1)-N(1)-C(1)-C(2)	47.3(5)
C(6)-C(1)-C(2)-C(3)	-2.5(6)
N(1)-C(1)-C(2)-C(3)	176.5(3)
C(6)-C(1)-C(2)-C(7)	173.4(4)
N(1)-C(1)-C(2)-C(7)	-7.5(6)
C(1)-C(2)-C(3)-C(4)	1.3(6)
C(7)-C(2)-C(3)-C(4)	-174.7(4)
C(2)-C(3)-C(4)-C(5)	1.2(6)
C(3)-C(4)-C(5)-C(6)	-2.5(7)
C(2)-C(1)-C(6)-C(5)	1.3(6)
N(1)-C(1)-C(6)-C(5)	-177.8(4)
C(4)-C(5)-C(6)-C(1)	1.3(7)
C(8)-N(2)-C(7)-O(1)	6.5(5)
Ni(1)-N(2)-C(7)-O(1)	179.4(2)

C(8)-N(2)-C(7)-C(2)	-169.6(4)
Ni(1)-N(2)-C(7)-C(2)	3.3(6)
C(9)-O(1)-C(7)-N(2)	4.6(5)
C(9)-O(1)-C(7)-C(2)	-178.8(3)
C(1)-C(2)-C(7)-N(2)	-21.2(7)
C(3)-C(2)-C(7)-N(2)	154.7(4)
C(1)-C(2)-C(7)-O(1)	162.7(4)
C(3)-C(2)-C(7)-O(1)	-21.5(5)
C(7)-N(2)-C(8)-C(10)	-132.5(4)
Ni(1)-N(2)-C(8)-C(10)	54.9(4)
C(7)-N(2)-C(8)-C(11)	103.8(4)
Ni(1)-N(2)-C(8)-C(11)	-68.8(4)
C(7)-N(2)-C(8)-C(9)	-13.7(4)
Ni(1)-N(2)-C(8)-C(9)	173.6(3)
C(7)-O(1)-C(9)-C(8)	-12.9(4)
N(2)-C(8)-C(9)-O(1)	15.8(4)
C(10)-C(8)-C(9)-O(1)	135.4(4)
C(11)-C(8)-C(9)-O(1)	-98.7(4)
Ni(1)-O(4)-Ni(2)-N(21)	133.95(13)
Ni(3)-O(4)-Ni(2)-N(21)	-122.90(13)
Ni(1)-O(4)-Ni(2)-Cl(1)	36.93(8)
Ni(3)-O(4)-Ni(2)-Cl(1)	140.08(10)
Ni(1)-O(4)-Ni(2)-Cl(2)	-137.74(10)
Ni(3)-O(4)-Ni(2)-Cl(2)	-34.59(9)
Ni(1)-O(4)-Ni(2)-Cl(4)	-51.07(8)
Ni(3)-O(4)-Ni(2)-Cl(4)	52.09(9)
Ni(1)-Cl(1)-Ni(2)-O(4)	-29.41(8)
Ni(1)-Cl(1)-Ni(2)-N(22)	151.23(10)

Ni(1)-Cl(1)-Ni(2)-N(21)	-120.52(9)
Ni(1)-Cl(1)-Ni(2)-Cl(2)	-9.97(16)
Ni(1)-Cl(1)-Ni(2)-Cl(4)	46.23(3)
Ni(3)-Cl(2)-Ni(2)-O(4)	28.43(8)
Ni(3)-Cl(2)-Ni(2)-N(22)	-152.25(10)
Ni(3)-Cl(2)-Ni(2)-N(21)	120.72(9)
Ni(3)-Cl(2)-Ni(2)-Cl(1)	9.03(16)
Ni(3)-Cl(2)-Ni(2)-Cl(4)	-47.30(3)
Ni(1)-Cl(4)-Ni(2)-O(4)	38.18(8)
Ni(3)-Cl(4)-Ni(2)-O(4)	-39.24(8)
Ni(1)-Cl(4)-Ni(2)-N(22)	-142.26(10)
Ni(3)-Cl(4)-Ni(2)-N(22)	140.33(10)
Ni(1)-Cl(4)-Ni(2)-N(21)	60.0(4)
Ni(3)-Cl(4)-Ni(2)-N(21)	-17.4(4)
Ni(1)-Cl(4)-Ni(2)-Cl(1)	-44.59(3)
Ni(3)-Cl(4)-Ni(2)-Cl(1)	-122.01(3)
Ni(1)-Cl(4)-Ni(2)-Cl(2)	122.05(3)
Ni(3)-Cl(4)-Ni(2)-Cl(2)	44.64(3)
O(4)-Ni(2)-N(21)-C(21)	-131.3(3)
N(22)-Ni(2)-N(21)-C(21)	49.0(3)
Cl(1)-Ni(2)-N(21)-C(21)	-49.1(3)
Cl(2)-Ni(2)-N(21)-C(21)	145.9(3)
Cl(4)-Ni(2)-N(21)-C(21)	-152.4(3)
N(21)-Ni(2)-N(22)-C(27)	-26.1(3)
Cl(1)-Ni(2)-N(22)-C(27)	70.8(3)
Cl(2)-Ni(2)-N(22)-C(27)	-114.3(3)
Cl(4)-Ni(2)-N(22)-C(27)	159.0(3)
N(21)-Ni(2)-N(22)-C(28)	157.6(3)

Cl(1)-Ni(2)-N(22)-C(28)	-105.5(3)
Cl(2)-Ni(2)-N(22)-C(28)	69.4(3)
Cl(4)-Ni(2)-N(22)-C(28)	-17.3(3)
Ni(2)-N(21)-C(21)-C(26)	134.2(4)
Ni(2)-N(21)-C(21)-C(22)	-45.1(5)
C(26)-C(21)-C(22)-C(23)	2.2(6)
N(21)-C(21)-C(22)-C(23)	-178.5(4)
C(26)-C(21)-C(22)-C(27)	-175.0(4)
N(21)-C(21)-C(22)-C(27)	4.3(6)
C(21)-C(22)-C(23)-C(24)	-1.4(7)
C(27)-C(22)-C(23)-C(24)	175.9(5)
C(22)-C(23)-C(24)-C(25)	-0.5(8)
C(23)-C(24)-C(25)-C(26)	1.5(8)
C(24)-C(25)-C(26)-C(21)	-0.7(8)
C(22)-C(21)-C(26)-C(25)	-1.2(7)
N(21)-C(21)-C(26)-C(25)	179.5(4)
C(28)-N(22)-C(27)-O(21)	-3.8(5)
Ni(2)-N(22)-C(27)-O(21)	179.2(3)
C(28)-N(22)-C(27)-C(22)	173.1(4)
Ni(2)-N(22)-C(27)-C(22)	-3.9(6)
C(29)-O(21)-C(27)-N(22)	-1.2(5)
C(29)-O(21)-C(27)-C(22)	-178.6(4)
C(21)-C(22)-C(27)-N(22)	24.3(7)
C(23)-C(22)-C(27)-N(22)	-152.9(5)
C(21)-C(22)-C(27)-O(21)	-158.8(4)
C(23)-C(22)-C(27)-O(21)	24.1(6)
C(27)-N(22)-C(28)-C(31)	125.8(4)
Ni(2)-N(22)-C(28)-C(31)	-57.4(5)

C(27)-N(22)-C(28)-C(30)	-110.8(4)
Ni(2)-N(22)-C(28)-C(30)	66.0(5)
C(27)-N(22)-C(28)-C(29)	6.6(4)
Ni(2)-N(22)-C(28)-C(29)	-176.6(3)
C(27)-O(21)-C(29)-C(28)	5.5(5)
N(22)-C(28)-C(29)-O(21)	-7.2(4)
C(31)-C(28)-C(29)-O(21)	-125.8(4)
C(30)-C(28)-C(29)-O(21)	109.5(4)
Ni(1)-O(4)-Ni(3)-N(41)	-125.88(13)
Ni(2)-O(4)-Ni(3)-N(41)	132.66(13)
Ni(1)-O(4)-Ni(3)-Cl(2)	136.96(10)
Ni(2)-O(4)-Ni(3)-Cl(2)	35.50(9)
Ni(1)-O(4)-Ni(3)-Cl(3)	-36.15(9)
Ni(2)-O(4)-Ni(3)-Cl(3)	-137.62(10)
Ni(1)-O(4)-Ni(3)-Cl(4)	50.19(8)
Ni(2)-O(4)-Ni(3)-Cl(4)	-51.27(8)
Ni(2)-Cl(2)-Ni(3)-O(4)	-28.50(8)
Ni(2)-Cl(2)-Ni(3)-N(42)	152.38(10)
Ni(2)-Cl(2)-Ni(3)-N(41)	-121.39(9)
Ni(2)-Cl(2)-Ni(3)-Cl(3)	0.39(18)
Ni(2)-Cl(2)-Ni(3)-Cl(4)	46.36(3)
Ni(1)-Cl(3)-Ni(3)-O(4)	27.92(8)
Ni(1)-Cl(3)-Ni(3)-N(42)	-152.85(10)
Ni(1)-Cl(3)-Ni(3)-N(41)	121.46(10)
Ni(1)-Cl(3)-Ni(3)-Cl(2)	-1.09(18)
Ni(1)-Cl(3)-Ni(3)-Cl(4)	-47.15(3)
Ni(2)-Cl(4)-Ni(3)-O(4)	39.67(8)
Ni(1)-Cl(4)-Ni(3)-O(4)	-37.25(8)

Ni(2)-Cl(4)-Ni(3)-N(42)	-139.34(10)
Ni(1)-Cl(4)-Ni(3)-N(42)	143.74(10)
Ni(2)-Cl(4)-Ni(3)-N(41)	58.0(5)
Ni(1)-Cl(4)-Ni(3)-N(41)	-18.9(5)
Ni(2)-Cl(4)-Ni(3)-Cl(2)	-46.12(3)
Ni(1)-Cl(4)-Ni(3)-Cl(2)	-123.05(3)
Ni(2)-Cl(4)-Ni(3)-Cl(3)	123.63(3)
Ni(1)-Cl(4)-Ni(3)-Cl(3)	46.71(3)
O(4)-Ni(3)-N(41)-C(41)	-124.2(3)
N(42)-Ni(3)-N(41)-C(41)	54.8(3)
Cl(2)-Ni(3)-N(41)-C(41)	-39.0(3)
Cl(3)-Ni(3)-N(41)-C(41)	153.1(3)
Cl(4)-Ni(3)-N(41)-C(41)	-141.9(4)
N(41)-Ni(3)-N(42)-C(47)	-31.5(3)
Cl(2)-Ni(3)-N(42)-C(47)	65.6(3)
Cl(3)-Ni(3)-N(42)-C(47)	-121.1(3)
Cl(4)-Ni(3)-N(42)-C(47)	152.2(3)
N(41)-Ni(3)-N(42)-C(48)	160.4(3)
Cl(2)-Ni(3)-N(42)-C(48)	-102.5(3)
Cl(3)-Ni(3)-N(42)-C(48)	70.8(3)
Cl(4)-Ni(3)-N(42)-C(48)	-15.9(3)
Ni(3)-N(41)-C(41)-C(46)	129.7(4)
Ni(3)-N(41)-C(41)-C(42)	-50.8(4)
C(46)-C(41)-C(42)-C(43)	3.1(6)
N(41)-C(41)-C(42)-C(43)	-176.4(3)
C(46)-C(41)-C(42)-C(47)	-173.4(4)
N(41)-C(41)-C(42)-C(47)	7.1(6)
C(41)-C(42)-C(43)-C(44)	-2.2(6)

C(47)-C(42)-C(43)-C(44)	174.4(4)
C(42)-C(43)-C(44)-C(45)	0.0(7)
C(43)-C(44)-C(45)-C(46)	1.4(8)
C(44)-C(45)-C(46)-C(41)	-0.5(7)
C(42)-C(41)-C(46)-C(45)	-1.8(7)
N(41)-C(41)-C(46)-C(45)	177.7(4)
C(48)-N(42)-C(47)-O(41)	-5.7(5)
Ni(3)-N(42)-C(47)-O(41)	-176.0(2)
C(48)-N(42)-C(47)-C(42)	170.3(4)
Ni(3)-N(42)-C(47)-C(42)	0.0(6)
C(49)-O(41)-C(47)-N(42)	-9.1(5)
C(49)-O(41)-C(47)-C(42)	174.4(3)
C(41)-C(42)-C(47)-N(42)	22.6(6)
C(43)-C(42)-C(47)-N(42)	-153.8(4)
C(41)-C(42)-C(47)-O(41)	-161.3(4)
C(43)-C(42)-C(47)-O(41)	22.3(5)
C(47)-N(42)-C(48)-C(51)	136.1(4)
Ni(3)-N(42)-C(48)-C(51)	-54.3(5)
C(47)-N(42)-C(48)-C(50)	-101.6(4)
Ni(3)-N(42)-C(48)-C(50)	67.9(4)
C(47)-N(42)-C(48)-C(49)	16.7(4)
Ni(3)-N(42)-C(48)-C(49)	-173.7(3)
C(47)-O(41)-C(49)-C(48)	18.9(4)
N(42)-C(48)-C(49)-O(41)	-21.3(4)
C(51)-C(48)-C(49)-O(41)	-140.1(4)
C(50)-C(48)-C(49)-O(41)	94.5(4)

Table 7. Hydrogen bonds for complex 2 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4A)...Cl(5)#1	1.00	2.02	3.015(4)	170.9
O(4)-H(4A)...Cl(6)#1	1.00	2.40	3.311(13)	151.9
N(1)-H(1A)...Cl(3)#2	0.92	2.55	3.345(3)	145.2
N(1)-H(1B)...Cl(6)#1	0.92	2.46	3.327(7)	157.2
N(1)-H(1B)...Cl(5)#1	0.92	2.52	3.421(4)	165.0
N(21)-H(21A)...Cl(5)#1	0.92	2.91	3.786(8)	160.8
N(41)-H(41A)...Cl(6)#1	0.92	2.43	3.309(8)	158.7
N(41)-H(41A)...Cl(5)#1	0.92	2.59	3.482(4)	163.6

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x,-y+1,-z

X-ray data for complex **3**.

General:

Data was collected at -100°C on a Nonius Kappa CCD diffractometer, using the COLLECT program (Nonius, 1998). Cell refinement and data reductions used the programs DENZO and SCALEPACK (Otwinowski & Minor, 1997). SIR97 (Altomare et al., 1999) was used to solve the structure and SHELXL97 (Sheldrick, 1997) was used to refine the structure. ORTEP-3 for Windows (Farrugia , 1997) was used for molecular graphics and PLATON (Spek, 2001) was used to prepare material for publication. H atoms were placed in calculated positions with U_{iso} constrained to be 1.5 times U_{eq} for methyl hydrogen atoms and 1.2 times U_{eq} of the carrier atom for all other hydrogen atoms.

The A ALERT and one of the B ALERTs are due to the low diffracting power of the crystal. The large H Ueq(max)/Ueq(min) of 4.14 results because the U's of the H atoms are determined by the U of the attached atom (see previous paragraph). O4 is held very rigidly, whereas the terminal methyl groups are in flexible positions and have much high Ueq. Bond precision is low because the diffraction is dominated by the very electron rich Br and Ni atoms. The Hirshfeld Test Diff ALERTs are commonly found for heavy halogen atoms on metals.

The large number of Least-Squares Restraints were necessary to keep one N and five C atoms from going NPD or to extreme prolate or oblate ellipsoids.

References:

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Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C.W. Carter & R.M. Sweet, pp. 307-326. London: Academic Press.

Sheldrick, G.M. (1997). SHELXL-97. University of Göttingen. Germany.

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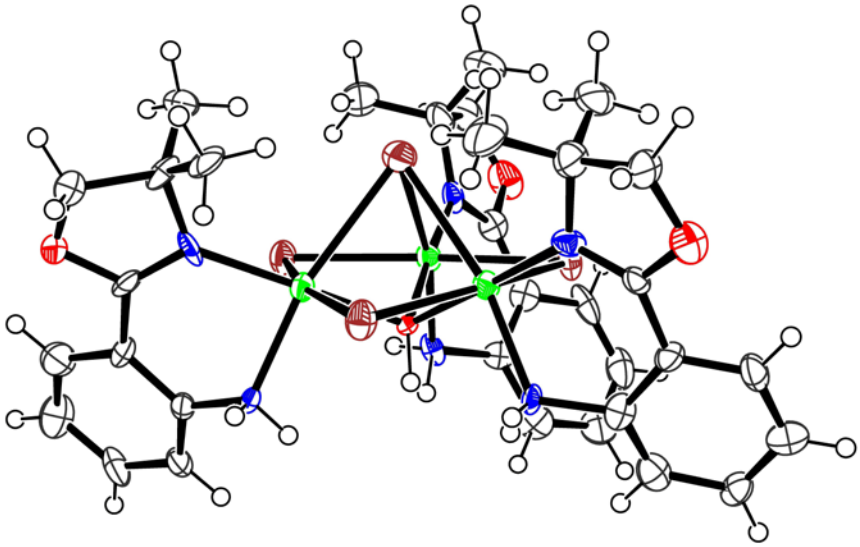
Caption for ORTEP.

A general ORTEP (Farrugia, 1997) view of the title compound with non-hydrogen displacement ellipsoids draw at the 50% probability level.

ORTEP of **3**.



Core of **3**.

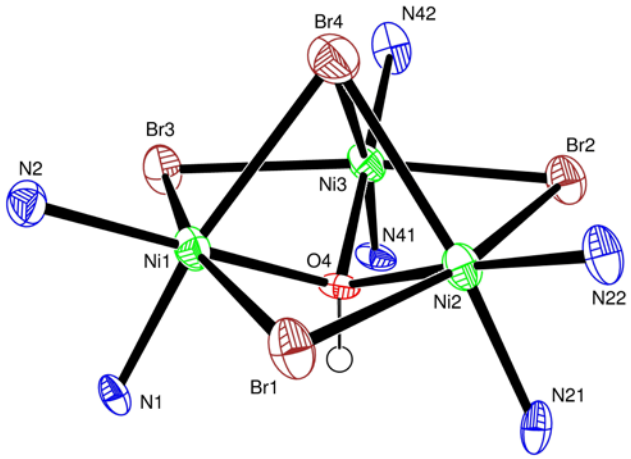


Table 1. Crystal data and structure refinement for complex 3.

Identification code	1092	
Empirical formula	C33 H43 Br5 N6 Ni3 O4	
Formula weight	1163.41	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.648(2) Å	α= 73.57(3)°.
	b = 11.780(2) Å	β= 71.43(3)°.
	c = 17.747(4) Å	γ = 64.57(3)°.
Volume	2054.1(9) $Å^3$	
Z	2	
Density (calculated)	1.881 Mg/m^3	
Absorption coefficient	6.267 mm^{-1}	
F(000)	1148	
Crystal size	0.05 x 0.02 x 0.02 mm^3	
Theta range for data collection	3.26 to 23.26°.	
Index ranges	-12<=h<=12, -13<=k<=11, -19<=l<=18	
Reflections collected	12086	
Independent reflections	5713 [R(int) = 0.1145]	
Completeness to theta = 23.26°	97.0 %	
Absorption correction	Psi-scan	

Max. and min. transmission	0.882 and 0.759
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5713 / 36 / 467
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0718, wR2 = 0.1283
R indices (all data)	R1 = 0.1311, wR2 = 0.1503
Extinction coefficient	0.0019(3)
Largest diff. peak and hole	0.718 and -0.844 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex 3. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	2873(1)	4032(1)	1951(1)	30(1)
Br(2)	-820(1)	8256(1)	1267(1)	30(1)
Br(3)	-471(1)	6541(1)	4193(1)	32(1)
Br(4)	1718(1)	7291(2)	2307(1)	36(1)
Br(5)	8211(1)	4312(2)	2962(1)	38(1)
Ni(1)	1450(2)	5093(2)	3190(1)	23(1)
Ni(2)	1110(2)	6110(2)	1425(1)	24(1)
Ni(3)	-874(2)	7651(2)	2766(1)	23(1)
O(1)	4120(10)	2808(10)	4648(6)	43(3)
O(4)	77(8)	5880(8)	2556(5)	17(2)
O(21)	3223(10)	5576(11)	-924(6)	45(3)
O(41)	-3578(9)	11352(9)	2989(6)	30(2)
N(1)	832(10)	3619(9)	3815(6)	20(3)
N(2)	2806(10)	4326(11)	3880(6)	26(3)
N(21)	182(10)	5290(11)	1028(6)	22(3)
N(22)	2181(10)	6242(11)	268(6)	26(3)
N(41)	-2708(9)	7509(10)	3140(6)	22(3)
N(42)	-1872(10)	9476(11)	2991(6)	28(3)
C(1)	1795(14)	2322(14)	3899(7)	28(4)
C(2)	2910(13)	2115(13)	4140(8)	29(4)
C(3)	3768(13)	875(15)	4302(8)	34(4)
C(4)	3567(15)	-130(16)	4184(8)	35(4)
C(5)	2482(13)	85(14)	3905(8)	30(3)

C(6)	1632(14)	1342(15)	3752(8)	35(4)
C(7)	3217(12)	3162(13)	4216(7)	23(3)
C(8)	3597(15)	4928(15)	4001(9)	38(4)
C(9)	4258(16)	3937(16)	4679(11)	55(5)
C(10)	2763(18)	6226(16)	4281(11)	57(5)
C(11)	4600(15)	5031(17)	3208(10)	55(5)
C(21)	1031(13)	4223(14)	635(7)	24(3)
C(22)	2110(14)	4305(14)	19(8)	30(4)
C(23)	2895(13)	3248(17)	-365(9)	39(4)
C(24)	2643(16)	2153(17)	-135(10)	46(5)
C(25)	1637(16)	2042(17)	476(10)	46(5)
C(26)	788(15)	3103(15)	873(8)	39(4)
C(27)	2457(13)	5391(14)	-169(7)	27(4)
C(28)	2906(13)	7100(15)	-189(8)	36(4)
C(29)	3407(15)	6752(16)	-1018(9)	42(4)
C(30)	4014(14)	6831(17)	217(9)	46(5)
C(31)	2007(16)	8484(16)	-226(11)	58(5)
C(41)	-3679(12)	8450(13)	2700(8)	25(3)
C(42)	-3861(13)	9715(13)	2620(8)	26(3)
C(43)	-4829(14)	10647(16)	2230(9)	39(4)
C(44)	-5545(16)	10298(16)	1915(9)	44(5)
C(45)	-5323(13)	9024(16)	2007(9)	41(4)
C(46)	-4378(12)	8100(15)	2392(9)	32(4)
C(47)	-3045(13)	10124(13)	2870(8)	24(3)
C(48)	-1425(14)	10362(13)	3174(8)	30(4)
C(49)	-2714(14)	11479(15)	3371(10)	39(4)
C(50)	-496(13)	10716(15)	2405(8)	35(4)
C(51)	-775(14)	9743(14)	3875(8)	34(4)

Table 3. Bond lengths [Å] and angles [°] for complex 3.

Br(1)-Ni(1)	2.569(2)	N(2)-C(8)	1.47(2)	C(28)-C(30)	1.55(2)
Br(1)-Ni(2)	2.587(2)	N(21)-C(21)	1.426(17)	C(41)-C(46)	1.35(2)
Br(2)-Ni(3)	2.539(2)	N(22)-C(27)	1.309(19)	C(41)-C(42)	1.38(2)
Br(2)-Ni(2)	2.576(2)	N(22)-C(28)	1.492(19)	C(42)-C(43)	1.400(18)
Br(3)-Ni(3)	2.588(2)	N(41)-C(41)	1.454(15)	C(42)-C(47)	1.46(2)
Br(3)-Ni(1)	2.643(2)	N(42)-C(47)	1.301(16)	C(43)-C(44)	1.38(2)
Br(4)-Ni(1)	2.710(3)	N(42)-C(48)	1.494(19)	C(44)-C(45)	1.38(2)
Br(4)-Ni(3)	2.737(2)	C(1)-C(6)	1.35(2)	C(45)-C(46)	1.376(19)
Br(4)-Ni(2)	2.770(3)	C(1)-C(2)	1.40(2)	C(48)-C(51)	1.505(19)
Ni(1)-O(4)	1.991(8)	C(2)-C(3)	1.381(19)	C(48)-C(50)	1.527(19)
Ni(1)-N(2)	2.046(10)	C(2)-C(7)	1.47(2)	C(48)-C(49)	1.529(19)
Ni(1)-N(1)	2.059(11)	C(3)-C(4)	1.38(2)		
Ni(2)-O(4)	1.996(8)	C(4)-C(5)	1.40(2)		
Ni(2)-N(22)	2.037(11)	C(5)-C(6)	1.390(19)		
Ni(2)-N(21)	2.089(12)	C(8)-C(11)	1.53(2)		
Ni(3)-O(4)	1.978(8)	C(8)-C(10)	1.54(2)		
Ni(3)-N(42)	2.044(12)	C(8)-C(9)	1.559(19)		
Ni(3)-N(41)	2.091(11)	C(21)-C(26)	1.39(2)		
O(1)-C(7)	1.350(16)	C(21)-C(22)	1.398(19)		
O(1)-C(9)	1.42(2)	C(22)-C(23)	1.40(2)		
O(21)-C(27)	1.370(16)	C(22)-C(27)	1.42(2)		
O(21)-C(29)	1.45(2)	C(23)-C(24)	1.37(2)		
O(41)-C(47)	1.357(16)	C(24)-C(25)	1.34(2)		
O(41)-C(49)	1.454(18)	C(25)-C(26)	1.42(2)		
N(1)-C(1)	1.456(16)	C(28)-C(29)	1.50(2)		
N(2)-C(7)	1.273(17)	C(28)-C(31)	1.51(2)		

Ni(1)-Br(1)-Ni(2)	74.19(7)
Ni(3)-Br(2)-Ni(2)	74.74(7)
Ni(3)-Br(3)-Ni(1)	74.29(7)
Ni(1)-Br(4)-Ni(3)	70.89(7)
Ni(1)-Br(4)-Ni(2)	69.14(7)
Ni(3)-Br(4)-Ni(2)	68.64(7)
O(4)-Ni(1)-N(2)	177.6(4)
O(4)-Ni(1)-N(1)	93.7(4)
N(2)-Ni(1)-N(1)	86.1(4)
O(4)-Ni(1)-Br(1)	84.0(2)
N(2)-Ni(1)-Br(1)	98.4(3)
N(1)-Ni(1)-Br(1)	95.8(3)
O(4)-Ni(1)-Br(3)	80.0(2)
N(2)-Ni(1)-Br(3)	97.6(3)
N(1)-Ni(1)-Br(3)	87.6(3)
Br(1)-Ni(1)-Br(3)	163.87(8)
O(4)-Ni(1)-Br(4)	74.3(3)
N(2)-Ni(1)-Br(4)	105.7(3)
N(1)-Ni(1)-Br(4)	167.2(3)
Br(1)-Ni(1)-Br(4)	87.49(7)
Br(3)-Ni(1)-Br(4)	85.94(8)
O(4)-Ni(2)-N(22)	176.7(5)
O(4)-Ni(2)-N(21)	92.0(4)
N(22)-Ni(2)-N(21)	85.7(5)
O(4)-Ni(2)-Br(2)	84.0(2)

N(22)-Ni(2)-Br(2)	98.3(3)
N(21)-Ni(2)-Br(2)	88.8(3)
O(4)-Ni(2)-Br(1)	83.4(2)
N(22)-Ni(2)-Br(1)	94.6(3)
N(21)-Ni(2)-Br(1)	98.3(3)
Br(2)-Ni(2)-Br(1)	165.78(8)
O(4)-Ni(2)-Br(4)	72.8(3)
N(22)-Ni(2)-Br(4)	109.7(4)
N(21)-Ni(2)-Br(4)	163.7(3)
Br(2)-Ni(2)-Br(4)	84.07(7)
Br(1)-Ni(2)-Br(4)	85.89(7)
O(4)-Ni(3)-N(42)	179.5(4)
O(4)-Ni(3)-N(41)	94.4(4)
N(42)-Ni(3)-N(41)	85.1(4)
O(4)-Ni(3)-Br(2)	85.4(2)
N(42)-Ni(3)-Br(2)	94.9(3)
N(41)-Ni(3)-Br(2)	96.4(3)
O(4)-Ni(3)-Br(3)	81.7(2)
N(42)-Ni(3)-Br(3)	98.1(3)
N(41)-Ni(3)-Br(3)	89.3(3)
Br(2)-Ni(3)-Br(3)	166.22(8)
O(4)-Ni(3)-Br(4)	73.8(3)
N(42)-Ni(3)-Br(4)	106.7(3)
N(41)-Ni(3)-Br(4)	167.9(3)
Br(2)-Ni(3)-Br(4)	85.44(7)
Br(3)-Ni(3)-Br(4)	86.48(7)
C(7)-O(1)-C(9)	107.2(11)

Ni(3)-O(4)-Ni(1)	105.5(4)
Ni(3)-O(4)-Ni(2)	102.8(4)
Ni(1)-O(4)-Ni(2)	102.5(4)
C(27)-O(21)-C(29)	107.4(12)
C(47)-O(41)-C(49)	105.9(10)
C(1)-N(1)-Ni(1)	119.0(9)
C(7)-N(2)-C(8)	107.2(11)
C(7)-N(2)-Ni(1)	124.4(10)
C(8)-N(2)-Ni(1)	128.0(9)
C(21)-N(21)-Ni(2)	115.3(8)
C(27)-N(22)-C(28)	108.5(11)
C(27)-N(22)-Ni(2)	120.5(10)
C(28)-N(22)-Ni(2)	130.5(10)
C(41)-N(41)-Ni(3)	115.6(8)
C(47)-N(42)-C(48)	107.9(12)
C(47)-N(42)-Ni(3)	120.8(11)
C(48)-N(42)-Ni(3)	130.6(8)
C(6)-C(1)-C(2)	120.4(13)
C(6)-C(1)-N(1)	121.9(13)
C(2)-C(1)-N(1)	117.7(14)
C(3)-C(2)-C(1)	118.3(15)
C(3)-C(2)-C(7)	118.8(13)
C(1)-C(2)-C(7)	122.8(12)
C(2)-C(3)-C(4)	120.8(14)
C(3)-C(4)-C(5)	120.8(15)
C(6)-C(5)-C(4)	117.1(15)
C(1)-C(6)-C(5)	122.2(14)

N(2)-C(7)-O(1)	116.9(14)
N(2)-C(7)-C(2)	127.9(12)
O(1)-C(7)-C(2)	115.1(12)
N(2)-C(8)-C(11)	106.9(13)
N(2)-C(8)-C(10)	112.7(13)
C(11)-C(8)-C(10)	112.5(15)
N(2)-C(8)-C(9)	102.3(12)
C(11)-C(8)-C(9)	111.5(13)
C(10)-C(8)-C(9)	110.4(14)
O(1)-C(9)-C(8)	102.8(13)
C(26)-C(21)-C(22)	120.4(13)
C(26)-C(21)-N(21)	119.8(12)
C(22)-C(21)-N(21)	119.9(13)
C(23)-C(22)-C(21)	117.9(15)
C(23)-C(22)-C(27)	121.0(14)
C(21)-C(22)-C(27)	120.9(13)
C(24)-C(23)-C(22)	121.5(15)
C(25)-C(24)-C(23)	121.3(15)
C(24)-C(25)-C(26)	119.4(17)
C(21)-C(26)-C(25)	119.5(15)
N(22)-C(27)-O(21)	113.9(14)
N(22)-C(27)-C(22)	130.6(13)
O(21)-C(27)-C(22)	115.5(13)
N(22)-C(28)-C(29)	102.9(14)
N(22)-C(28)-C(31)	111.2(11)
C(29)-C(28)-C(31)	110.1(13)
N(22)-C(28)-C(30)	109.5(11)

C(29)-C(28)-C(30) 112.9(12)

C(31)-C(28)-C(30) 110.0(16)

O(21)-C(29)-C(28) 105.4(12)

C(46)-C(41)-C(42) 121.9(13)

C(46)-C(41)-N(41) 121.3(13)

C(42)-C(41)-N(41) 116.8(14)

C(41)-C(42)-C(43) 118.1(15)

C(41)-C(42)-C(47) 123.6(12)

C(43)-C(42)-C(47) 118.1(13)

C(44)-C(43)-C(42) 120.3(16)

C(43)-C(44)-C(45) 119.4(14)

C(46)-C(45)-C(44) 120.9(17)

C(41)-C(46)-C(45) 119.4(15)

N(42)-C(47)-O(41) 115.7(13)

N(42)-C(47)-C(42) 128.9(13)

O(41)-C(47)-C(42) 115.5(11)

N(42)-C(48)-C(51) 110.8(11)

N(42)-C(48)-C(50) 106.7(11)

C(51)-C(48)-C(50) 112.0(12)

N(42)-C(48)-C(49) 101.4(12)

C(51)-C(48)-C(49) 112.6(12)

C(50)-C(48)-C(49) 112.8(12)

O(41)-C(49)-C(48) 104.3(12)

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3)for complex 3. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	23(1)	26(1)	27(1)	-2(1)	-5(1)	2(1)
Br(2)	29(1)	24(1)	29(1)	0(1)	-9(1)	-4(1)
Br(3)	35(1)	28(1)	25(1)	-3(1)	-7(1)	-5(1)
Br(4)	31(1)	33(1)	43(1)	1(1)	-13(1)	-14(1)
Br(5)	30(1)	28(1)	59(1)	-5(1)	-14(1)	-13(1)
Ni(1)	20(1)	22(1)	23(1)	2(1)	-7(1)	-7(1)
Ni(2)	20(1)	23(1)	22(1)	0(1)	-5(1)	-5(1)
Ni(3)	21(1)	17(1)	26(1)	-1(1)	-6(1)	-4(1)
O(1)	43(6)	44(7)	48(6)	10(5)	-36(5)	-14(6)
O(4)	14(4)	11(5)	28(5)	-5(4)	-5(4)	-6(4)
O(21)	35(6)	57(8)	26(6)	-2(5)	3(5)	-12(6)
O(41)	22(5)	21(6)	43(6)	-9(4)	1(4)	-7(4)
N(1)	20(6)	12(6)	21(6)	2(5)	-8(5)	0(5)
N(2)	25(6)	31(7)	23(6)	4(5)	-9(5)	-16(6)
N(21)	16(6)	31(7)	9(5)	-5(5)	1(4)	-2(5)
N(22)	19(6)	24(7)	24(6)	4(5)	-8(5)	1(5)
N(41)	19(5)	10(5)	36(5)	-4(4)	-8(4)	-3(4)
N(42)	9(6)	32(7)	25(6)	-3(5)	2(5)	2(5)
C(1)	36(9)	27(9)	19(7)	-2(6)	-10(6)	-8(7)
C(2)	27(8)	18(8)	37(8)	-9(6)	-1(7)	-9(7)
C(3)	21(8)	35(10)	31(8)	6(7)	-7(6)	-3(7)
C(4)	45(10)	42(10)	23(8)	-4(7)	-5(7)	-24(8)

C(5)	36(5)	23(5)	29(5)	-10(4)	-1(4)	-10(4)
C(6)	32(9)	42(10)	28(8)	-3(7)	-10(7)	-11(8)
C(7)	15(5)	26(5)	22(5)	5(4)	-3(4)	-8(4)
C(8)	38(9)	32(10)	49(10)	-1(8)	-22(8)	-11(8)
C(9)	46(10)	32(11)	93(14)	22(9)	-52(10)	-15(9)
C(10)	67(11)	37(10)	90(12)	-9(9)	-45(9)	-23(8)
C(11)	41(10)	48(12)	79(13)	22(10)	-36(10)	-23(9)
C(21)	30(8)	33(9)	13(7)	-2(6)	-7(6)	-15(7)
C(22)	36(9)	32(9)	25(8)	-7(7)	-10(7)	-11(7)
C(23)	17(8)	56(12)	37(9)	-27(8)	-4(7)	4(8)
C(24)	37(10)	40(11)	61(11)	-25(9)	-19(9)	3(9)
C(25)	44(10)	47(11)	67(12)	-23(9)	-23(10)	-19(9)
C(26)	43(10)	45(11)	24(8)	-7(7)	0(7)	-18(9)
C(27)	30(8)	32(9)	18(7)	0(7)	-11(6)	-9(7)
C(28)	22(8)	36(10)	35(9)	2(7)	2(7)	-9(7)
C(29)	35(9)	41(11)	44(9)	10(8)	-16(8)	-13(8)
C(30)	37(9)	60(12)	47(10)	-14(9)	0(8)	-27(9)
C(31)	47(9)	42(10)	63(10)	14(8)	9(8)	-25(8)
C(41)	20(7)	18(8)	24(7)	2(6)	6(6)	-4(6)
C(42)	30(8)	14(8)	34(8)	-7(6)	-7(6)	-6(6)
C(43)	36(9)	36(10)	40(9)	2(7)	-10(8)	-13(8)
C(44)	53(11)	35(11)	36(9)	3(7)	-24(8)	-6(9)
C(45)	18(8)	44(11)	52(10)	-15(8)	-8(7)	2(8)
C(46)	17(7)	28(9)	53(9)	-16(7)	-7(7)	-6(7)
C(47)	34(7)	13(6)	24(6)	2(5)	-4(5)	-13(5)
C(48)	48(9)	18(8)	33(8)	-12(6)	-12(7)	-14(7)
C(49)	34(9)	27(9)	55(10)	-15(8)	-3(8)	-10(7)

C(50)	27(8)	35(9)	43(9)	0(7)	-8(7)	-17(7)
C(51)	46(9)	22(8)	41(9)	-14(7)	-3(7)	-19(7)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for complex 3.

	x	y	z	U(eq)
H(4A)	-487	5386	2652	21
H(1A)	388	3793	4326	24
H(1B)	238	3633	3570	24
H(21A)	-390	5036	1465	26
H(21B)	-301	5905	677	26
H(41A)	-2604	6709	3094	26
H(41B)	-3027	7577	3677	26
H(3)	4505	711	4497	41
H(4)	4172	-976	4294	42
H(5)	2334	-600	3823	36
H(6)	912	1519	3537	42
H(9A)	5190	3812	4567	66
H(9B)	3807	4205	5212	66
H(10A)	2300	6819	3866	85
H(10B)	3331	6571	4369	85
H(10C)	2129	6112	4785	85
H(11A)	5135	4178	3071	83
H(11B)	5160	5411	3267	83
H(11C)	4146	5569	2777	83
H(23)	3619	3293	-795	47
H(24)	3191	1455	-412	55

H(25)	1493	1264	641	56
H(26)	62	3044	1297	46
H(29A)	2909	7430	-1400	51
H(29B)	4342	6627	-1221	51
H(30A)	3655	6872	793	69
H(30B)	4411	7472	-36	69
H(30C)	4678	5980	150	69
H(31A)	1276	8633	-450	87
H(31B)	2489	9023	-572	87
H(31C)	1672	8696	318	87
H(43)	-4993	11524	2182	47
H(44)	-6185	10929	1637	53
H(45)	-5829	8782	1802	49
H(46)	-4219	7223	2442	38
H(49A)	-3065	11422	3961	47
H(49B)	-2598	12304	3147	47
H(50A)	186	9937	2219	52
H(50B)	-94	11213	2516	52
H(50C)	-985	11226	1986	52
H(51A)	-1326	9360	4318	51
H(51B)	-651	10386	4056	51
H(51C)	75	9078	3707	51

Table 6. Torsion angles [°] for complex 3.

Ni(2)-Br(1)-Ni(1)-O(4)		25.8(3)
Ni(2)-Br(1)-Ni(1)-N(2)	-154.2(3)	
Ni(2)-Br(1)-Ni(1)-N(1)	118.9(3)	
Ni(2)-Br(1)-Ni(1)-Br(3)	17.4(4)	
Ni(2)-Br(1)-Ni(1)-Br(4)	-48.66(7)	
Ni(3)-Br(3)-Ni(1)-O(4)	-27.2(3)	
Ni(3)-Br(3)-Ni(1)-N(2)	152.9(3)	
Ni(3)-Br(3)-Ni(1)-N(1)	-121.3(3)	
Ni(3)-Br(3)-Ni(1)-Br(1)	-18.7(4)	
Ni(3)-Br(3)-Ni(1)-Br(4)	47.57(7)	
Ni(3)-Br(4)-Ni(1)-O(4)	35.5(2)	
Ni(2)-Br(4)-Ni(1)-O(4)	-38.3(2)	
Ni(3)-Br(4)-Ni(1)-N(2)	-142.1(3)	
Ni(2)-Br(4)-Ni(1)-N(2)	144.2(3)	
Ni(3)-Br(4)-Ni(1)-N(1)	14.8(14)	
Ni(2)-Br(4)-Ni(1)-N(1)	-58.9(14)	
Ni(3)-Br(4)-Ni(1)-Br(1)	119.94(8)	
Ni(2)-Br(4)-Ni(1)-Br(1)	46.23(6)	
Ni(3)-Br(4)-Ni(1)-Br(3)	-45.32(6)	
Ni(2)-Br(4)-Ni(1)-Br(3)	-119.03(7)	
Ni(3)-Br(2)-Ni(2)-O(4)	23.5(3)	
Ni(3)-Br(2)-Ni(2)-N(22)	-158.8(4)	
Ni(3)-Br(2)-Ni(2)-N(21)	115.7(3)	
Ni(3)-Br(2)-Ni(2)-Br(1)	-4.4(4)	
Ni(3)-Br(2)-Ni(2)-Br(4)	-49.71(7)	
Ni(1)-Br(1)-Ni(2)-O(4)	-25.7(3)	

Ni(1)-Br(1)-Ni(2)-N(22)	156.8(4)
Ni(1)-Br(1)-Ni(2)-N(21)	-116.8(3)
Ni(1)-Br(1)-Ni(2)-Br(2)	2.3(4)
Ni(1)-Br(1)-Ni(2)-Br(4)	47.38(7)
Ni(1)-Br(4)-Ni(2)-O(4)	38.5(2)
Ni(3)-Br(4)-Ni(2)-O(4)	-38.4(2)
Ni(1)-Br(4)-Ni(2)-N(22)	-139.3(3)
Ni(3)-Br(4)-Ni(2)-N(22)	143.8(3)
Ni(1)-Br(4)-Ni(2)-N(21)	59.7(10)
Ni(3)-Br(4)-Ni(2)-N(21)	-17.2(10)
Ni(1)-Br(4)-Ni(2)-Br(2)	124.01(7)
Ni(3)-Br(4)-Ni(2)-Br(2)	47.14(6)
Ni(1)-Br(4)-Ni(2)-Br(1)	-45.91(6)
Ni(3)-Br(4)-Ni(2)-Br(1)	-122.78(8)
Ni(2)-Br(2)-Ni(3)-O(4)	-23.7(3)
Ni(2)-Br(2)-Ni(3)-N(42)	156.8(3)
Ni(2)-Br(2)-Ni(3)-N(41)	-117.7(3)
Ni(2)-Br(2)-Ni(3)-Br(3)	-3.9(4)
Ni(2)-Br(2)-Ni(3)-Br(4)	50.37(7)
Ni(1)-Br(3)-Ni(3)-O(4)	27.2(3)
Ni(1)-Br(3)-Ni(3)-N(42)	-153.3(3)
Ni(1)-Br(3)-Ni(3)-N(41)	121.8(3)
Ni(1)-Br(3)-Ni(3)-Br(2)	7.2(4)
Ni(1)-Br(3)-Ni(3)-Br(4)	-46.92(7)
Ni(1)-Br(4)-Ni(3)-O(4)	-35.8(2)
Ni(2)-Br(4)-Ni(3)-O(4)	38.6(2)
Ni(1)-Br(4)-Ni(3)-N(42)	143.9(3)

Ni(2)-Br(4)-Ni(3)-N(42)	-141.7(3)
Ni(1)-Br(4)-Ni(3)-N(41)	-22.9(14)
Ni(2)-Br(4)-Ni(3)-N(41)	51.5(14)
Ni(1)-Br(4)-Ni(3)-Br(2)	-122.30(8)
Ni(2)-Br(4)-Ni(3)-Br(2)	-47.91(6)
Ni(1)-Br(4)-Ni(3)-Br(3)	46.53(7)
Ni(2)-Br(4)-Ni(3)-Br(3)	120.92(7)
N(41)-Ni(3)-O(4)-Ni(1)	-126.0(4)
Br(2)-Ni(3)-O(4)-Ni(1)	138.0(3)
Br(3)-Ni(3)-O(4)-Ni(1)	-37.4(3)
Br(4)-Ni(3)-O(4)-Ni(1)	51.4(3)
N(41)-Ni(3)-O(4)-Ni(2)	127.0(4)
Br(2)-Ni(3)-O(4)-Ni(2)	30.9(3)
Br(3)-Ni(3)-O(4)-Ni(2)	-144.4(3)
Br(4)-Ni(3)-O(4)-Ni(2)	-55.7(3)
N(1)-Ni(1)-O(4)-Ni(3)	123.6(4)
Br(1)-Ni(1)-O(4)-Ni(3)	-141.0(3)
Br(3)-Ni(1)-O(4)-Ni(3)	36.6(3)
Br(4)-Ni(1)-O(4)-Ni(3)	-51.9(3)
N(1)-Ni(1)-O(4)-Ni(2)	-129.2(4)
Br(1)-Ni(1)-O(4)-Ni(2)	-33.8(3)
Br(3)-Ni(1)-O(4)-Ni(2)	143.9(4)
Br(4)-Ni(1)-O(4)-Ni(2)	55.3(3)
N(21)-Ni(2)-O(4)-Ni(3)	-119.0(4)
Br(2)-Ni(2)-O(4)-Ni(3)	-30.5(3)
Br(1)-Ni(2)-O(4)-Ni(3)	142.9(3)
Br(4)-Ni(2)-O(4)-Ni(3)	55.1(3)

N(21)-Ni(2)-O(4)-Ni(1)	131.6(4)
Br(2)-Ni(2)-O(4)-Ni(1)	-139.8(3)
Br(1)-Ni(2)-O(4)-Ni(1)	33.5(3)
Br(4)-Ni(2)-O(4)-Ni(1)	-54.2(3)
O(4)-Ni(1)-N(1)-C(1)	133.6(9)
N(2)-Ni(1)-N(1)-C(1)	-48.8(9)
Br(1)-Ni(1)-N(1)-C(1)	49.2(9)
Br(3)-Ni(1)-N(1)-C(1)	-146.6(9)
Br(4)-Ni(1)-N(1)-C(1)	153.5(10)
N(1)-Ni(1)-N(2)-C(7)	23.9(11)
Br(1)-Ni(1)-N(2)-C(7)	-71.4(10)
Br(3)-Ni(1)-N(2)-C(7)	111.0(10)
Br(4)-Ni(1)-N(2)-C(7)	-161.1(10)
N(1)-Ni(1)-N(2)-C(8)	-164.4(12)
Br(1)-Ni(1)-N(2)-C(8)	100.4(11)
Br(3)-Ni(1)-N(2)-C(8)	-77.3(11)
Br(4)-Ni(1)-N(2)-C(8)	10.6(12)
O(4)-Ni(2)-N(21)-C(21)	-123.8(8)
N(22)-Ni(2)-N(21)-C(21)	53.8(8)
Br(2)-Ni(2)-N(21)-C(21)	152.2(8)
Br(1)-Ni(2)-N(21)-C(21)	-40.2(8)
Br(4)-Ni(2)-N(21)-C(21)	-144.1(8)
N(21)-Ni(2)-N(22)-C(27)	-31.6(10)
Br(2)-Ni(2)-N(22)-C(27)	-119.7(9)
Br(1)-Ni(2)-N(22)-C(27)	66.4(10)
Br(4)-Ni(2)-N(22)-C(27)	153.7(9)
N(21)-Ni(2)-N(22)-C(28)	157.2(11)

Br(2)-Ni(2)-N(22)-C(28)	69.1(10)
Br(1)-Ni(2)-N(22)-C(28)	-104.8(10)
Br(4)-Ni(2)-N(22)-C(28)	-17.5(11)
O(4)-Ni(3)-N(41)-C(41)	-123.8(9)
N(42)-Ni(3)-N(41)-C(41)	56.5(9)
Br(2)-Ni(3)-N(41)-C(41)	-37.9(9)
Br(3)-Ni(3)-N(41)-C(41)	154.7(9)
Br(4)-Ni(3)-N(41)-C(41)	-136.2(12)
N(41)-Ni(3)-N(42)-C(47)	-33.7(10)
Br(2)-Ni(3)-N(42)-C(47)	62.4(10)
Br(3)-Ni(3)-N(42)-C(47)	-122.2(9)
Br(4)-Ni(3)-N(42)-C(47)	149.1(9)
N(41)-Ni(3)-N(42)-C(48)	156.9(11)
Br(2)-Ni(3)-N(42)-C(48)	-107.1(11)
Br(3)-Ni(3)-N(42)-C(48)	68.3(11)
Br(4)-Ni(3)-N(42)-C(48)	-20.4(11)
Ni(1)-N(1)-C(1)-C(6)	-132.5(12)
Ni(1)-N(1)-C(1)-C(2)	47.5(14)
C(6)-C(1)-C(2)-C(3)	-6(2)
N(1)-C(1)-C(2)-C(3)	173.5(11)
C(6)-C(1)-C(2)-C(7)	172.6(13)
N(1)-C(1)-C(2)-C(7)	-7.4(19)
C(1)-C(2)-C(3)-C(4)	4(2)
C(7)-C(2)-C(3)-C(4)	-175.4(13)
C(2)-C(3)-C(4)-C(5)	-1(2)
C(3)-C(4)-C(5)-C(6)	0(2)
C(2)-C(1)-C(6)-C(5)	6(2)

N(1)-C(1)-C(6)-C(5)	-173.7(11)
C(4)-C(5)-C(6)-C(1)	-3(2)
C(8)-N(2)-C(7)-O(1)	6.5(16)
Ni(1)-N(2)-C(7)-O(1)	179.7(8)
C(8)-N(2)-C(7)-C(2)	-168.0(13)
Ni(1)-N(2)-C(7)-C(2)	5.2(19)
C(9)-O(1)-C(7)-N(2)	6.6(17)
C(9)-O(1)-C(7)-C(2)	-178.2(13)
C(3)-C(2)-C(7)-N(2)	157.1(13)
C(1)-C(2)-C(7)-N(2)	-22(2)
C(3)-C(2)-C(7)-O(1)	-17.5(18)
C(1)-C(2)-C(7)-O(1)	163.5(12)
C(7)-N(2)-C(8)-C(11)	102.0(13)
Ni(1)-N(2)-C(8)-C(11)	-70.9(14)
C(7)-N(2)-C(8)-C(10)	-133.9(13)
Ni(1)-N(2)-C(8)-C(10)	53.3(17)
C(7)-N(2)-C(8)-C(9)	-15.3(15)
Ni(1)-N(2)-C(8)-C(9)	171.8(10)
C(7)-O(1)-C(9)-C(8)	-15.5(17)
N(2)-C(8)-C(9)-O(1)	18.4(16)
C(11)-C(8)-C(9)-O(1)	-95.5(16)
C(10)-C(8)-C(9)-O(1)	138.6(15)
Ni(2)-N(21)-C(21)-C(26)	130.0(12)
Ni(2)-N(21)-C(21)-C(22)	-49.3(13)
C(26)-C(21)-C(22)-C(23)	2.5(19)
N(21)-C(21)-C(22)-C(23)	-178.3(12)
C(26)-C(21)-C(22)-C(27)	-172.7(13)

N(21)-C(21)-C(22)-C(27)	6.6(18)
C(21)-C(22)-C(23)-C(24)	-2(2)
C(27)-C(22)-C(23)-C(24)	173.5(14)
C(22)-C(23)-C(24)-C(25)	-1(2)
C(23)-C(24)-C(25)-C(26)	2(2)
C(22)-C(21)-C(26)-C(25)	-1(2)
N(21)-C(21)-C(26)-C(25)	179.8(12)
C(24)-C(25)-C(26)-C(21)	-1(2)
C(28)-N(22)-C(27)-O(21)	-4.8(15)
Ni(2)-N(22)-C(27)-O(21)	-177.8(8)
C(28)-N(22)-C(27)-C(22)	174.0(14)
Ni(2)-N(22)-C(27)-C(22)	1.0(19)
C(29)-O(21)-C(27)-N(22)	-4.2(15)
C(29)-O(21)-C(27)-C(22)	176.8(12)
C(23)-C(22)-C(27)-N(22)	-153.0(14)
C(21)-C(22)-C(27)-N(22)	22(2)
C(23)-C(22)-C(27)-O(21)	25.7(18)
C(21)-C(22)-C(27)-O(21)	-159.2(11)
C(27)-N(22)-C(28)-C(29)	11.3(14)
Ni(2)-N(22)-C(28)-C(29)	-176.7(9)
C(27)-N(22)-C(28)-C(31)	129.2(14)
Ni(2)-N(22)-C(28)-C(31)	-58.8(17)
C(27)-N(22)-C(28)-C(30)	-109.0(14)
Ni(2)-N(22)-C(28)-C(30)	63.0(15)
C(27)-O(21)-C(29)-C(28)	11.2(14)
N(22)-C(28)-C(29)-O(21)	-13.3(14)
C(31)-C(28)-C(29)-O(21)	-132.0(13)

C(30)-C(28)-C(29)-O(21)	104.6(15)
Ni(3)-N(41)-C(41)-C(46)	129.9(11)
Ni(3)-N(41)-C(41)-C(42)	-50.9(14)
C(46)-C(41)-C(42)-C(43)	2(2)
N(41)-C(41)-C(42)-C(43)	-177.3(11)
C(46)-C(41)-C(42)-C(47)	-173.7(13)
N(41)-C(41)-C(42)-C(47)	7.1(19)
C(41)-C(42)-C(43)-C(44)	-2(2)
C(47)-C(42)-C(43)-C(44)	173.9(14)
C(42)-C(43)-C(44)-C(45)	2(2)
C(43)-C(44)-C(45)-C(46)	-1(2)
C(42)-C(41)-C(46)-C(45)	-2(2)
N(41)-C(41)-C(46)-C(45)	177.5(12)
C(44)-C(45)-C(46)-C(41)	1(2)
C(48)-N(42)-C(47)-O(41)	-4.2(15)
Ni(3)-N(42)-C(47)-O(41)	-175.8(8)
C(48)-N(42)-C(47)-C(42)	175.4(13)
Ni(3)-N(42)-C(47)-C(42)	3.8(19)
C(49)-O(41)-C(47)-N(42)	-10.5(15)
C(49)-O(41)-C(47)-C(42)	169.9(12)
C(41)-C(42)-C(47)-N(42)	20(2)
C(43)-C(42)-C(47)-N(42)	-155.3(13)
C(41)-C(42)-C(47)-O(41)	-160.0(12)
C(43)-C(42)-C(47)-O(41)	24.3(18)
C(47)-N(42)-C(48)-C(51)	135.8(12)
Ni(3)-N(42)-C(48)-C(51)	-53.7(15)
C(47)-N(42)-C(48)-C(50)	-102.2(12)

Ni(3)-N(42)-C(48)-C(50)	68.4(14)
C(47)-N(42)-C(48)-C(49)	16.0(14)
Ni(3)-N(42)-C(48)-C(49)	-173.5(9)
C(47)-O(41)-C(49)-C(48)	19.9(14)
N(42)-C(48)-C(49)-O(41)	-21.4(14)
C(51)-C(48)-C(49)-O(41)	-139.8(13)
C(50)-C(48)-C(49)-O(41)	92.3(14)

DFT calculations

All calculations were performed using the Spartan 8.0 and 10.0 suite of programs.[1] The Ni clusters were calculated using B3LYP at the 6-31 G* (H, C, N, O, Cl) and LANL2DZ (Ni) levels of theory on structures which had been pre-optimized using MM2 and PM3(tm) semi-empirical calculations. Establishment of the likely Cl atom for replacement by a methyl group of complex **1** was investigated using ethylenediamine (en) as the *N*-donor chelating ligand for reasons of computational simplicity. The resulting skeletal structure was then applied to a full optimization of this isomer only (Figure 3) containing the tmeda ligands. Full details of the optimization of the cation derived from **1,** and the relative energies of hypothetical mono-methylated forms incorporated en and the full optimization of the mono-methylated derivative are available from the authors.

[1] Spartan 8.0 and 10.0., Wavefunction Inc., CA, USA.

Polymerization Results / Characterization

Data Table T-1. Polymerization results using **1** and **2**.

Run[a]	Catalyst/monomer/solvent[b]	Time (days)	M_w (± 2) × 10^{-3} $gmol^{-1}$	PDI	Yield (± 2%)
1[c]	nil / Sty / tol	0.5	–	–	0
2[c,d]	nil / Sty / tol	0.5	n.d.[e]	n.d.	trace
3	nil / Sty / neat	8	4.2	6.0	4
4	**1** / Sty / neat	0.7	87	2.9	14
5	**1** / Sty / neat	8	191	1.7	62
6[f]	**1** / Sty / neat	8	220	4.6	75
7[f,g]	**2** / Sty / neat	8	55	3.6	14
8[g,h]	**2** / Sty / neat	8	246	2.4	24
9	**1** / Sty / tol	0.25	41	2.3	2
10-11	**1** / Sty / tol	8	88	2.2 (±0.1)	12
12[i]	**1** / Sty / tol	8	n.d.	n.d.	2
13[j]	nil / MMA / tol	0.21	–	–	0
15[k]	**1** / MMA / tol	1	290	2.3	n.d.
16[k]	**1** / MMA / tol	2	380	1.9	n.d.
17[k]	**1** / MMA / tol	3	580	1.9	37
18[k]	**1** / MMA / tol	4	660	2.2	n.d.
19[k]	**1** / MMA / tol	5	730	1.6	n.d.
20[f,k]	**1** / MMA / tol	5	204	1.8	48

[a] General Conditions useless otherwise stated: [Ni] / [MAO] = 1:1 (catalyst: 2.5 × 10^{-4} mol; MAO: 7.5 × 10^{-4} mol [0.5 mL: 10% wt. sol'n C_7H_8]); monomer = 5 mL. Run 10-11 are combined average values; PDI = polydispersity index.

[b] Sty = styrene; MMA = methyl methacrylate; tol = toluene (5 mL).

[c] toluene: 20 mL, temp.: 90°C; see: H. Gao, L. Pei, K. Song, Q. Wu, *Eur. Polym. J.* **2007**, *43*, 908–914.

[d] MAO: 250 mg (4 × 10^{-3} mol).

[e] n.d. = not determined.

[f] [Ni] / [MAO] = 1:3.

[g] 2 mL Sty.

[h] [Ni] / [MAO] = 1:6.

[i] monomer added after 2 hours;

[j] [MMA] = 1.9 M (tol), temp.: 30°C; see: K. Endo, Y. Yamanaka, *Macromol. Rapid Commun*. **2000**, *21*, 785–787;

[k] 2 mL monomer; 7 mL tol.

Polystyrene

Figure P-1 shows a GPC result of a typical PS sample catalyzed using **1**. All three detectors show a monomodal distribution of the polymer and an absolute M_w of about 3.0×10^5 Daltons with a PDI of 1.7.

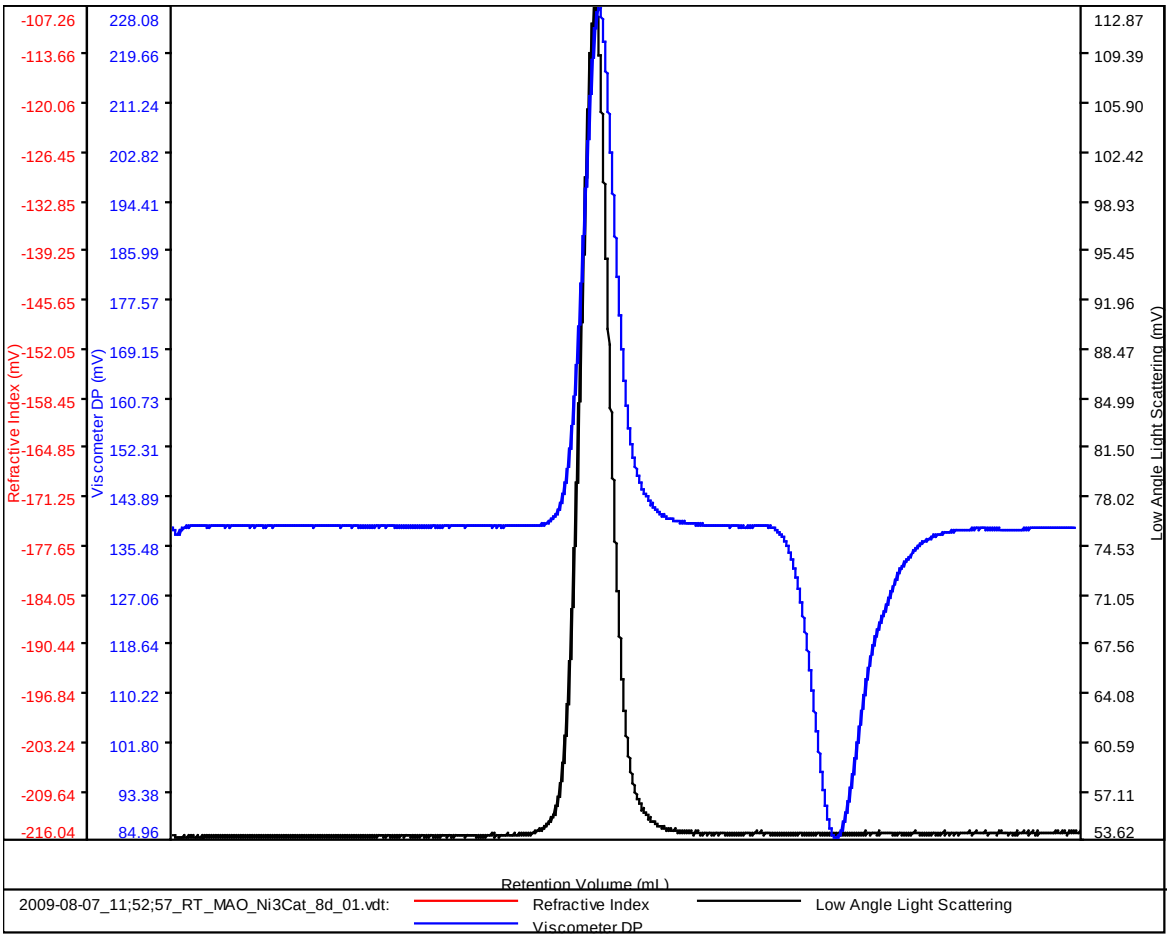


Figure P-1. The GPC results of **1** polymerized PS. Refractive index, viscometer and low angle light scattering peaks are shown.

The oxazoline analogue of **1** was also employed in the polymerization of styrene. The polymerization yielded 14% PS after 8 days. The M_w of the resulting PS was found to be 8.5×10^4 Daltons with a PDI of 3.5. The GPC peaks of this PS were much broader and less refined than

those of a **1** polymerized PS (Figure P-1). Compound **3** was found to be completely inactive in styrene polymerization.

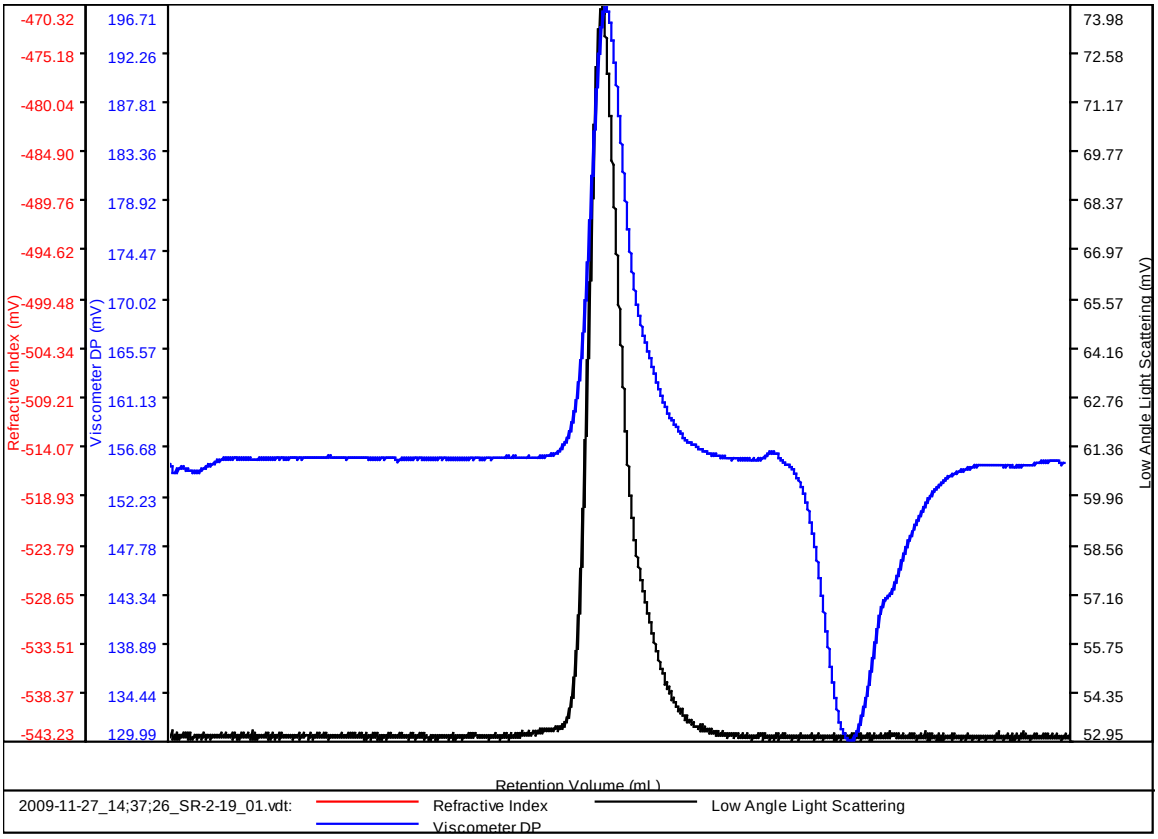


Figure P-2. The GPC results of **2** polymerized PS. Refractive index, viscometer and low angle light scattering peaks are shown.

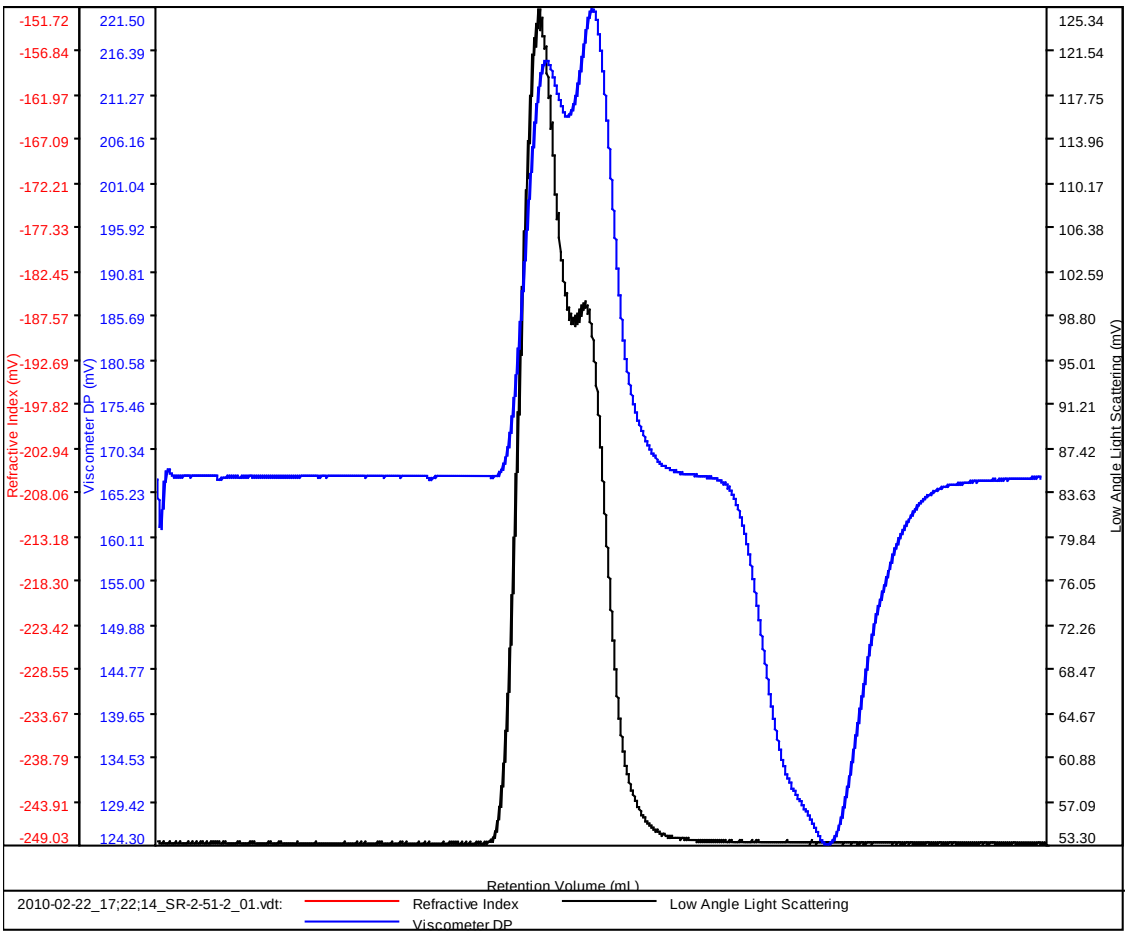


Figure 17. The GPC results of crystalline **1** polymerized PS (neat). Refractive index, viscometer and low angle light scattering peaks are shown.

Tacticity

The T_g, T_m, and ^{1}H-NMR of the PS were examined to determine the tacticity of the synthesized polymer. Figure P-3 shows a typical ^{1}H-NMR spectrum of the PS prepared using the crude catalyst **1**. In the 6.3–7.3 ppm range, the aromatic protons resonate and in the 2.0 to 1.2 ppm range the methine and methylene protons are identified. This information is important for determination of tacticity. For isotactic-PS, the shifts of the methylene and methine protons are

greater than 1.5 and 2.0 ppm, respectively. The experimental shift of the methylene protons is 1.44 ppm and of the methine proton 1.86 ppm, both indicative of a sPS. The peaks however, are not well-defined and exhibit broadness which suggests some atactic nature of this PS sample (Ishihara, N., Seimiya, T., Kuramoto, M., Uoi, M. *Polym. Prepr., Jpn.* **1986**, *35*, 240–241).

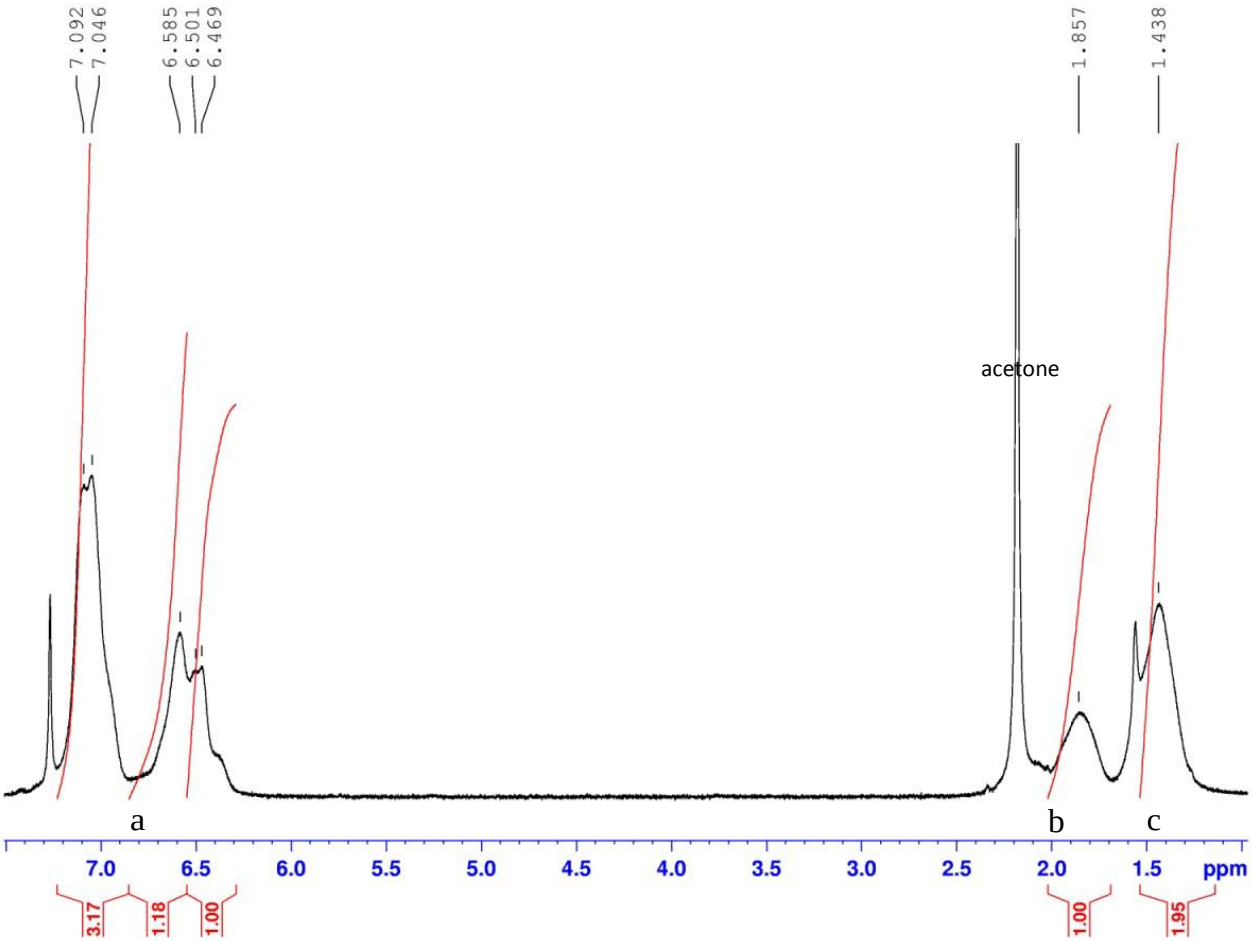


Figure P-3. ^{1}H-NMR spectrum of **1** polymerized PS.

The DSC results are also consistent with a largely *s*PS. The T_g values for both *s*PS and isotactic-PS are 101°C and the T_m 270°C and 240°C, respectively (Yu, S., Yu, X., Chen, Y., Liu, Y., Hong, S.,

Wu, Q., *J. Appl. Poyml. Sci.*, **2007**, *105*, 500–509). The experimental determined T_g value for the PS is 99°C with onsets at 96°C (Figure P-4). The T_m for this polymer was found to be 265°C (Figure P-5).

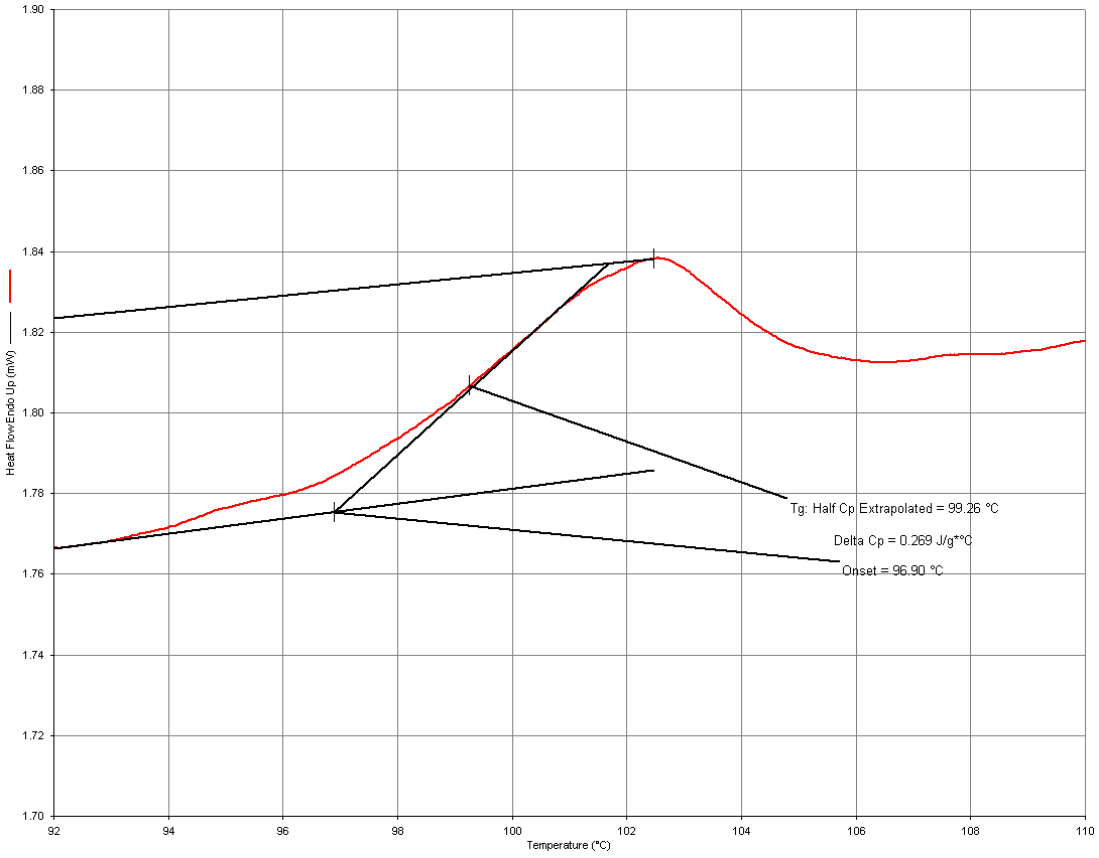


Figure P-4. The T_g of the polymerized PS initiated with **1**.

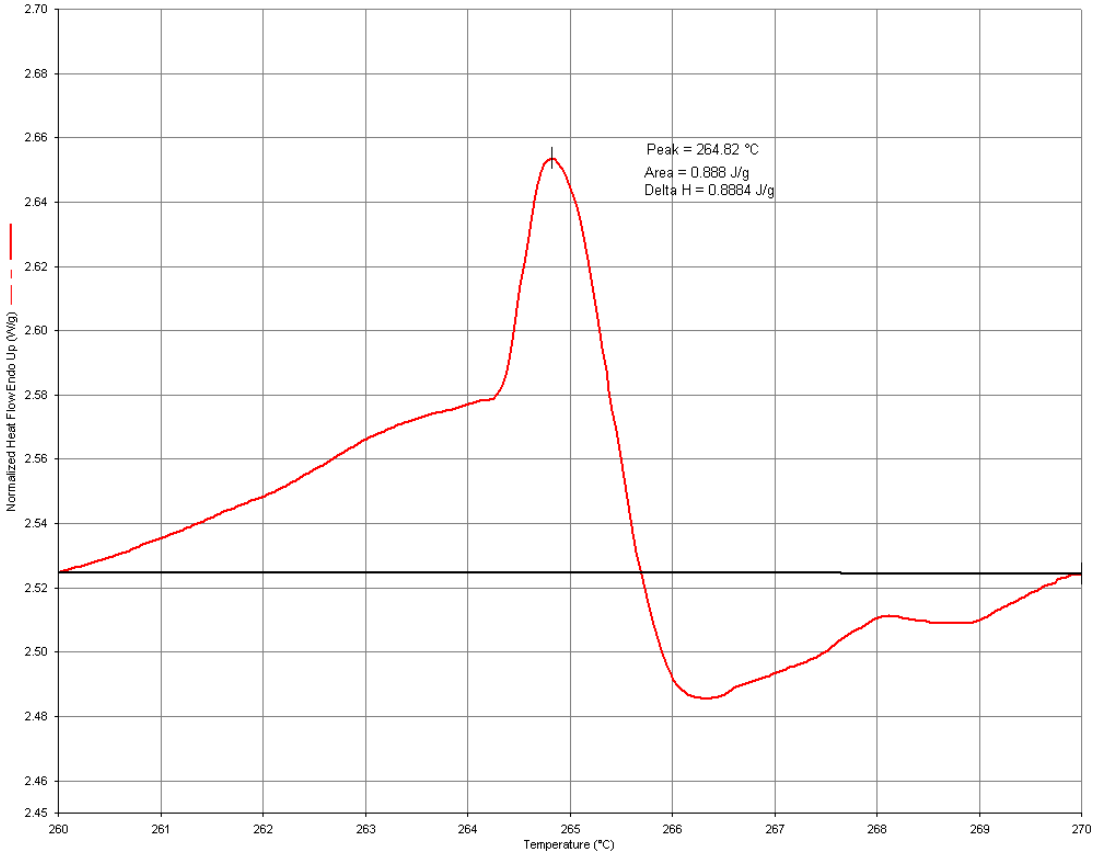


Figure P-5. The T_m of polymerized PS initiated with **1.**

Poly(methyl methacrylate)

n.b., The pMMA mixture becomes steadily more viscous as the reaction proceeds and thus the use of a solvent is desirable to reduce this viscosity. Toluene was chosen for this purpose due to literature precedence. The GPC results show clean monomodal peaks (Figure P-6).

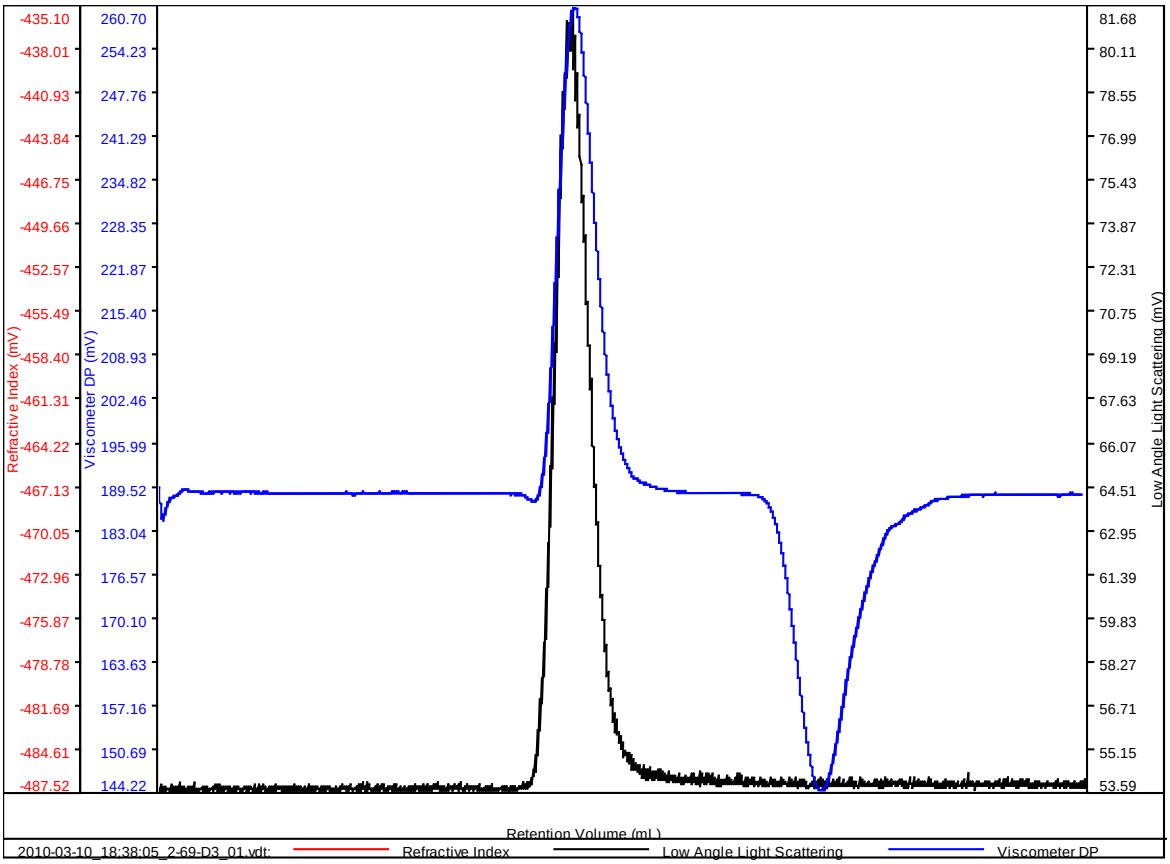


Figure P-6. The GPC results of **1** polymerized pMMA. Refractive index, viscometer and low angle light scattering peaks are shown.

The increasing molecular weight of the polymer can be seen in Figure P-7. A sample was extracted every 24 h for five consecutive days. The graph in Figure P-7 shows a steady increase in M_w with the allowed reaction time reaching about 7.3×10^5 Daltons by day 5 at which point the

high viscosity of the reaction mixture required additional toluene in order for a sample to be extracted.

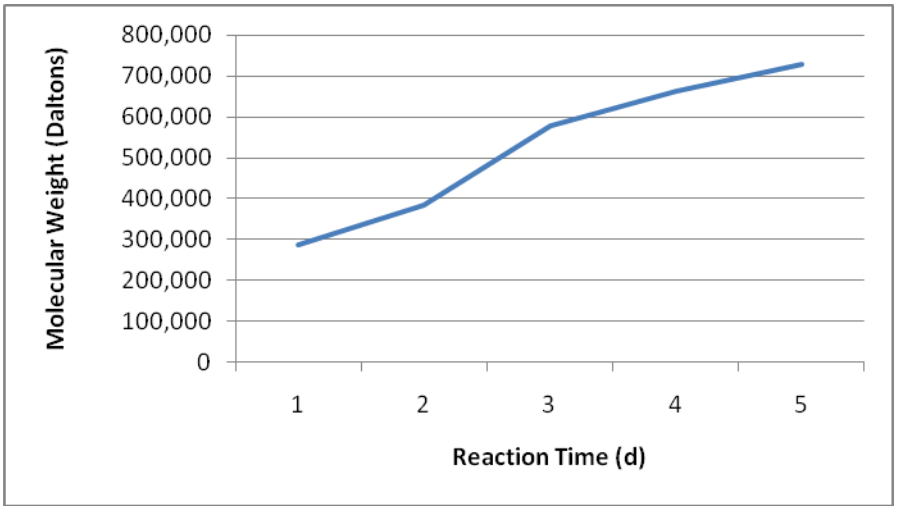


Figure P-7. The increase of the absolute M_w of **1** polymerized pMMA over a five day reaction time.

Tacticity

Poly(methyl methacrylate) tacticity can be determined by a collective examination of the ^{1}H-NMR, ^{13}C-NMR, T_g and T_m. As seen in Figure P-8, the typical pMMA product using **1**, there are three different groups of protons. At 3.61 ppm, a sharp singlet corresponding to the three methyl group protons directly connected to the methoxy group (H_a), can be seen. The α-methyl resonances (H_c) appear at 0.86 ppm and 1.03 ppm which correspond to syndiotactic and atactic pMMA respectively and are found in a ratio of 2.12 : 0.90 or about 70% syndiotactic. The methylene group protons (H_b) appear as a sharp singlet and as a cluster of smaller broader resonances. The singlet is centred at 1.82 ppm and integrates for approximately 1.14 protons while the broader area has δ_H values of 1.89, 1.91, 1.94 and 1.98 ppm with a combined integration of 0.63 protons. The methylene group signals therefore, suggest that the pMMA is

64% syndiotactic and the rest (36%) atactic (see: Braun, D., Cherdron, H., Rehahn, M., Ritter, H., Voit, B. *Polymer Synthesis Theory and Practice;* Springer-Verlag: Berlin, **2005**). The integrations of both H_b and H_c suggest 65-75% syndiotacticity.

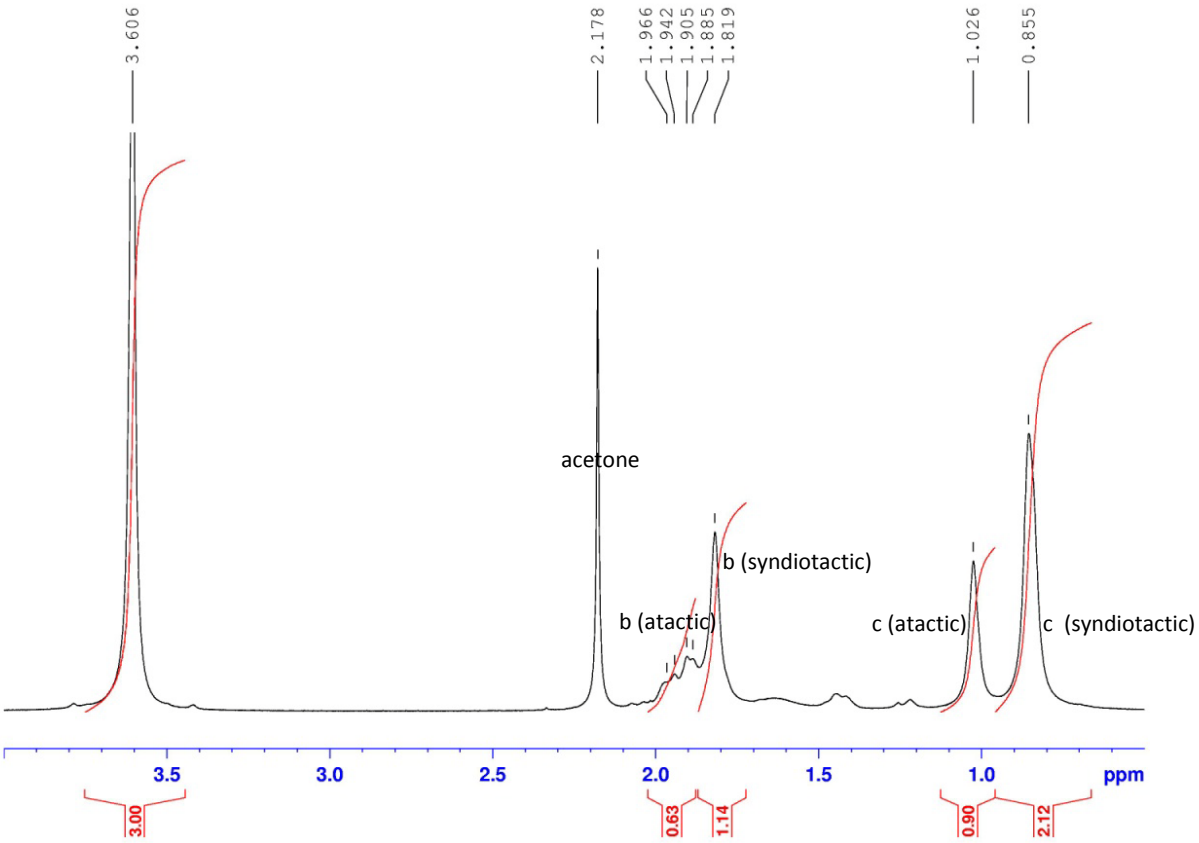


Figure P-8. ^{1}H-NMR spectrum of **1** polymerized pMMA.

The DSC T_g data for a **1** catalyzed pMMA sample is shown in Figure P-9. Predominantly isotactic pMMA (95%) has a T_g of 41.5°C and a more syndiotactic (81%) pMMA has a T_g of 134°C (W. Wunderlich, *Physical Constants of Poly(Methyl Methacrylate)* **2005**, 87–90). The experimental T_g was about 136°C indicating the presence of a highly syndiotactic (>60%) polymer. ^{1}H-NMR data suggests ~64% syndiotactic pMMA.

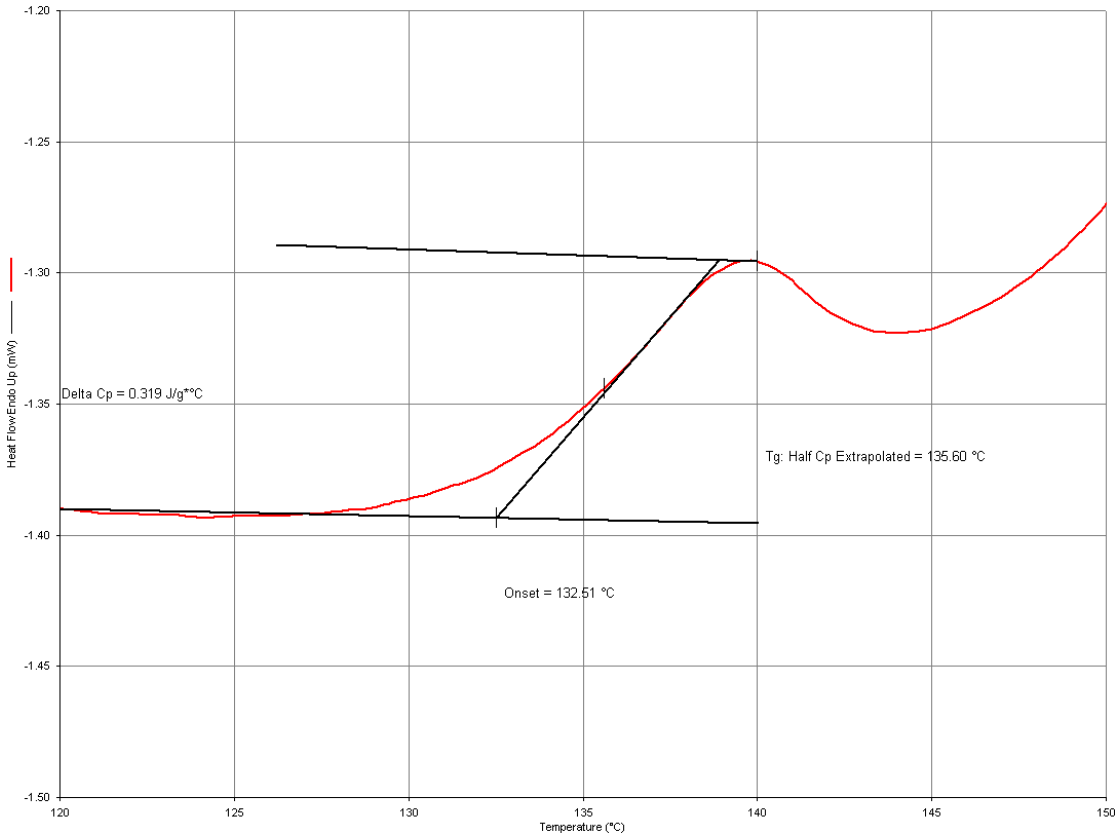


Figure P-9. The T_g close-up of **1** polymerized pMMA.

Figure S-1. A schematic representation of the Ni_3-core indicating the unique bridging-chlorido positions. The red-colored halogen "X" is predicted (DFT: Figure S-2) to be the favorable one for replacement by a methyl anion.

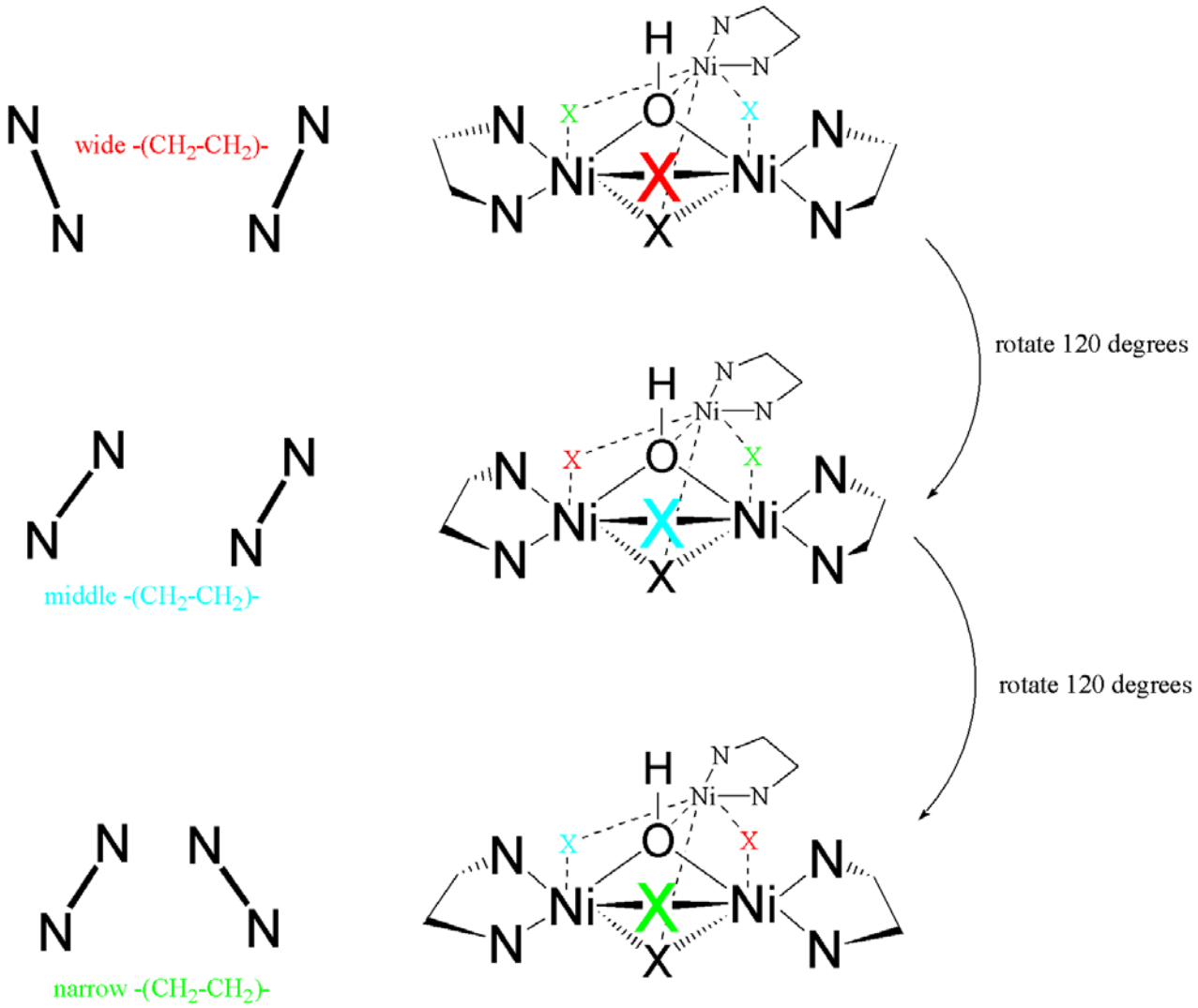


Figure S-2. Calculated (DFT) HOMO (left) and LUMO (right) of the cation of **1**. The energetically favorable substitution of a bridging Cl atom by a CH_3 group is that Cl atom located at the bottom of each diagram.

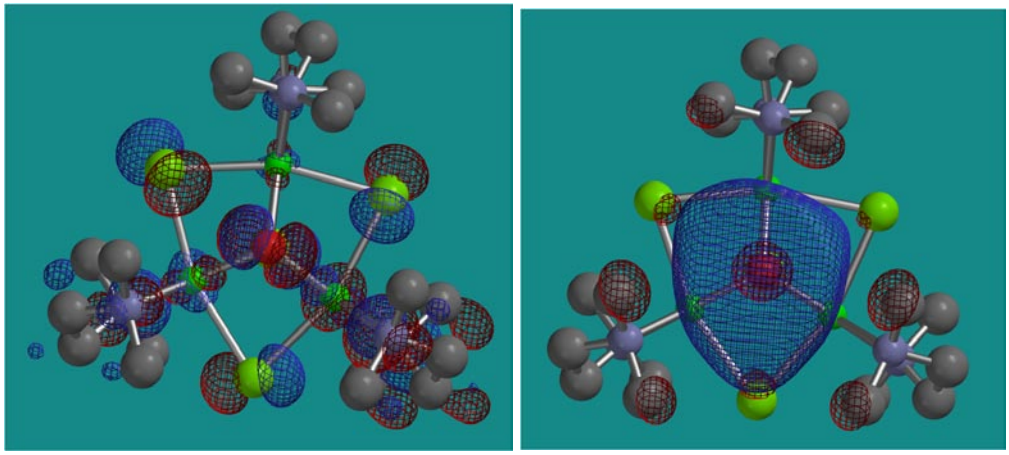


Figure S-3. The identity of the HOMO (right) and LUMO (left) of a hypothetical mono-methylated analogue of **1** (DFT). The methyl group is indicated by the red arrow.