Electronic Supporting Information

Thioether-terminated nickel(II) coordination clusters with {Ni_6} horseshoe- {Ni_8} and rollercoaster-shaped cores

Sebastian Schmitz,[a] Jan van Leusen,[a] Arkady Ellern,[b] Paul Kögerler[a,c,*] and Kirill Yu. Monakhov[a,*]

[a] Institut für Anorganische Chemie, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany

[b] Chemistry Department, Iowa State University, 1711 Gilman Hall, Ames, IA, 50011, USA

[c] Jülich-Aachen Research Alliance (JARA-FIT) and Peter Grünberg Institute (PGI-6), Forschungszentrum Jülich, 52425 Jülich, Germany

Contents:

1. Synthesis of the $H_3L{\cdot}SMe$ ligand

2-Hydroxy-5-(methylthio)isophthalaldehyde was prepared following a published procedure, *via* diformylation of 4-(methylthio)phenol (L. F. Lindoy, G. V. Meehan and N. Svenstrup, *Synthesis*, 1998, 1029). This compound was treated with two equivalents of 2-aminophenol and the reaction mixture was refluxed in MeOH over 3 Å molecular sieves for 2 h. For purification purposes, the product was re-crystallised from dichloromethane layered with pentane, by storing the solution at +3 °C overnight. C/H/N analysis, calculated for $C_{21}H_{18}N_2O_3S{\cdot}0.2(CH_2Cl_2){\cdot}0.3(C_5H_{12})$ (378.44 g mol^{-1}; 417.07 g mol^{-1} including solvent): C, 65.37; H, 5.32; N, 6.72%. Found: C, 65.31; H, 5.34; N, 6.72%. NMR (^1H, $CDCl_3$): δ = 8.99 (s, 2H, N=CH), 7.91 (s, 2H, Ar-H), 7.22 – 7.31 (m, 4H, Ar-H), 7.04 (dd, 2H, J_1 = 1.2 J_2 = 8.1, Ar-H), 6.97 (dt, 2H, J_1 = 7.8, J_2 = 1.2, Ar-H), 2.56 ppm (s, 3H, S-CH_3). IR (KBr pellet), ν_{max} / cm^{-1}: 3423 (s, br), 3042 (w), 2920 (w), 2852 (w), 1618 (s, -N=CH-), 1586 (m), 1522 (m), 1485 (m), 1466 (m), 1374 (m), 1332 (w), 1286 (m), 1220 (m), 1178 (m), 1148 (m), 1103 (w), 1032 (w), 1014 (m), 967 (w), 929 (w), 872 (w), 825 (w), 744 (s), 687 (w), 566 (m), 485 (m), 469 (m).

2. Possible oxidation of the $H_3L{\cdot}SMe$ ligand

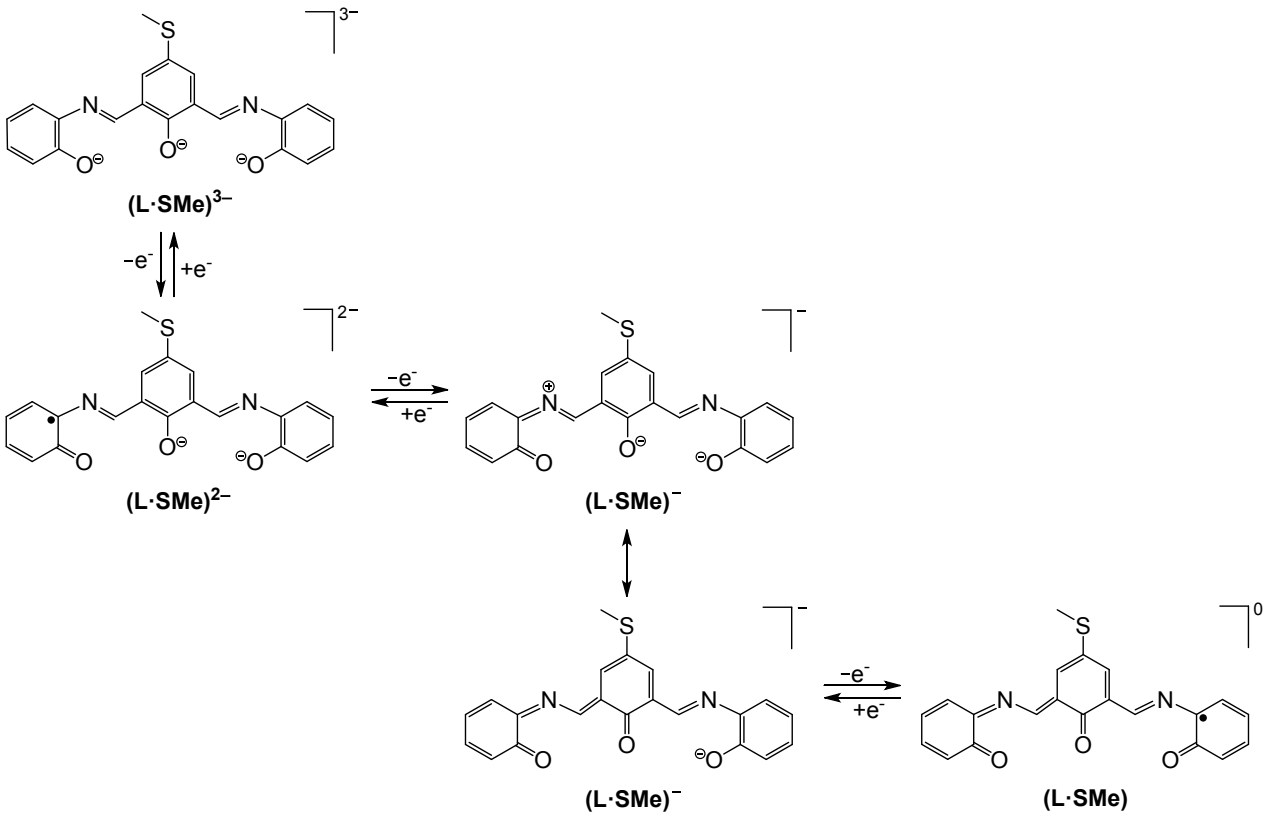


Figure S1. Stepwise oxidation of the fully deprotonated form of the $H_3L{\cdot}SMe$ ligand from $(L{\cdot}SMe)^{3-}$ to $(L{\cdot}SMe)^0$, including some resonance structures of $(L{\cdot}SMe)^-$.

3. Non-functionalised H_3L ligand

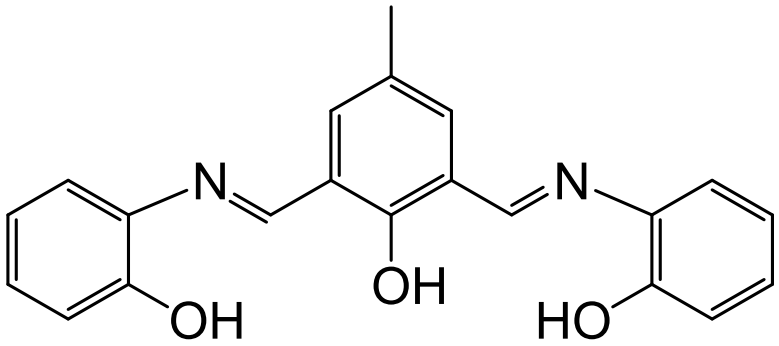
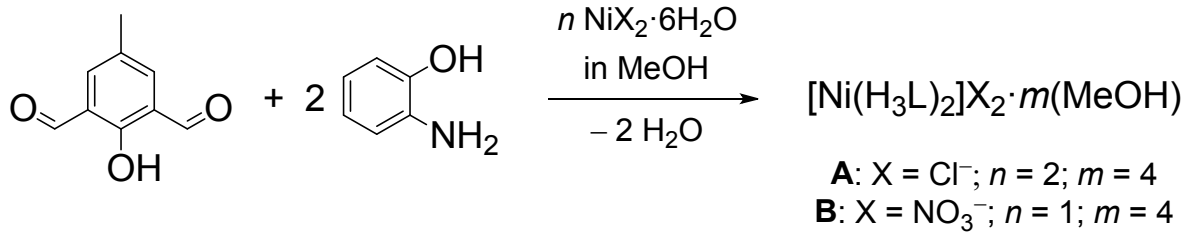


Figure S2. The pentadentate Schiff-base ligand $H_3L{\cdot}Me$ (= $C_{21}H_{18}N_2O_3$) used in this work.

4. Synthesis of the mononuclear nickel(II) Schiff-base complexes A and B



Scheme S1. Synthesis of $[Ni(H_3L)_2]Cl_2·4MeOH$ (**A**) and $[Ni(H_3L)_2](NO_3)_2·4MeOH$ (**B**). For the IR spectra of these compounds, see Figs. S5 and S6, respectively. According to TGA data, the $[Ni(H_3L)_2]^{2+}$ structural motif exhibits thermal stability up to *ca.* 200 °C under N_2.

Synthesis of $[Ni(H_3L)_2]Cl_2·4MeOH$ (A)

$NiCl_2·6H_2O$ (0.095 g, 0.4 mmol), 2-hydroxy-5-methylisophthalaldehyde (0.033 g, 0.2 mmol) and 2-aminophenol (0.044 g, 0.4 mmol) were dissolved in 5 mL methanol. The resulting red-coloured solution was stirred for 90 minutes under reflux. The MeOH solution was filtered off and the filtrate was kept in a capped vial at room temperature. Red single crystals of compound **A** were obtained via slow evaporation after *ca.* two weeks. Yield of the air-dried crystals: 0.065 g (79.0% based on H_3L). $C_{42}Cl_2H_{36}N_4NiO_6$ (822.36 g·mol^{-1}; disregarding solvent). IR (KBr pellet), ν_{max} / cm^{-1}: 3431 (br, m), 3224 (w), 2939 (br, m), 1639 (sh), 1623 (vs), 1525 (vs), 1510 (sh), 1470 (m), 1382 (w), 1333 (m), 1291 (m), 1271 (sh), 1228 (s), 1161 (w), 1109 (m), 1066 (w), 1047 (sh), 1017 (m), 993 (sh), 921 (w), 870 (w), 849 (sh), 771 (sh), 751 (m), 713 (w), 666 (w), 596 (w), 586 (w), 554 (w), 533 (sh), 483 (m), 469 (sh).

$[Ni(H_3L)_2](NO_3)_2·4MeOH$ (B)

$Ni(NO_3)_2·6H_2O$ (0.060 g, 0.2 mmol), 2-hydroxy-5-methylisophthalaldehyde (0.033 g, 0.2 mmol) and 2-aminophenol (0.044 g, 0.4 mmol) were dissolved in 10 mL methanol. The resulting red-coloured solution was stirred for 90 minutes under reflux. The MeOH solution was filtered off and the filtrate was kept in a capped vial at room temperature. Red single crystals of compound **B** were obtained via slow evaporation after *ca.* two weeks. Yield of the air-dried crystals: 0.010 g (11.4% based on H_3L). $C_{42}H_{36}N_6NiO_{12}$ (875.46 g mol^{-1}; disregarding solvent). IR (KBr pellet), ν_{max} / cm^{-1}: 3424 (br, s), 2923 (m), 1634 (s), 1534 (s), 1509 (sh), 1485 (w), 1467 (m), 1402 (m), 1385 (m), 1314 (m), 1274 (sh), 1233 (s), 1104 (m), 1068 (m), 1044 (sh), 995 (m), 873 (w), 802 (w), 753 (m), 677 (w), 590 (w), 578 (w), 557 (w), 505 (m), 448 (w), 405 (w).

5. IR spectra of compounds 1, 2, A and B

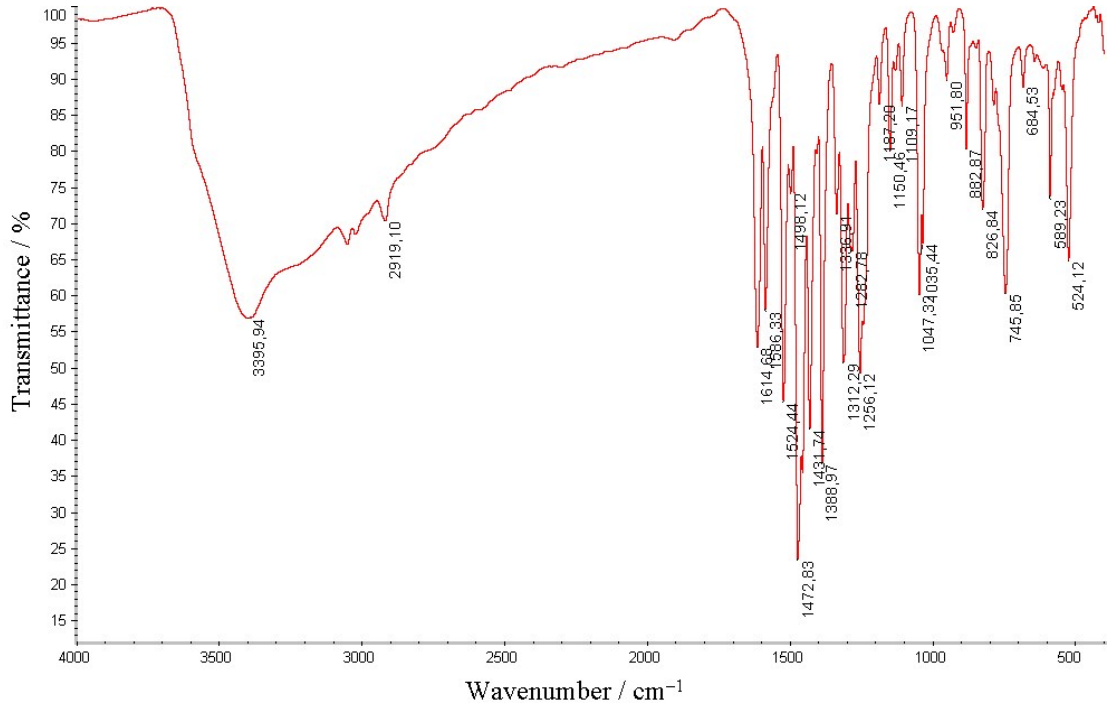


Figure S3. IR spectrum of $[Ni_6(L{\cdot}SMe)_3(CO_3)(MeOH)_6(THF)_2]Cl{\cdot}2MeOH$ (**1**) in the 4000–400 cm^{-1} region (KBr pellet).

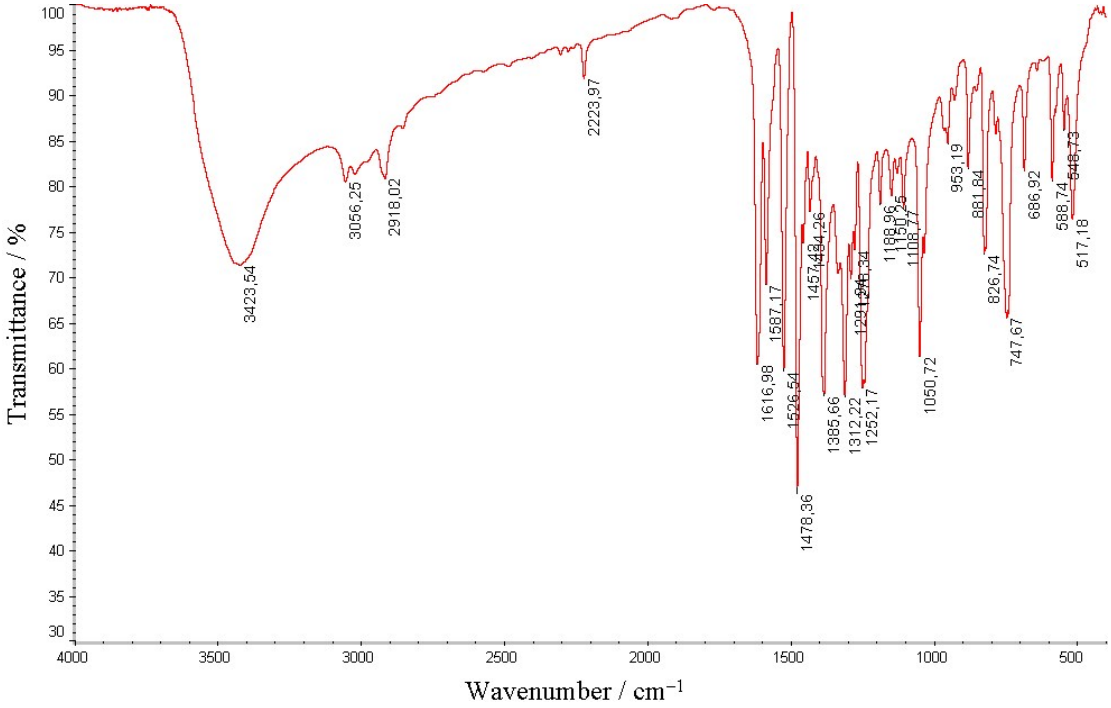


Figure S4. IR spectrum of $[Ni_8(HL{\cdot}SMe)_2(L{\cdot}SMe)_2(OH)_4(MeCN)_4(H_2O)_4](NO_3)_2{\cdot}11MeCN{\cdot}2PhCN$ (**2**) in the 4000–400 cm^{-1} region (KBr pellet).

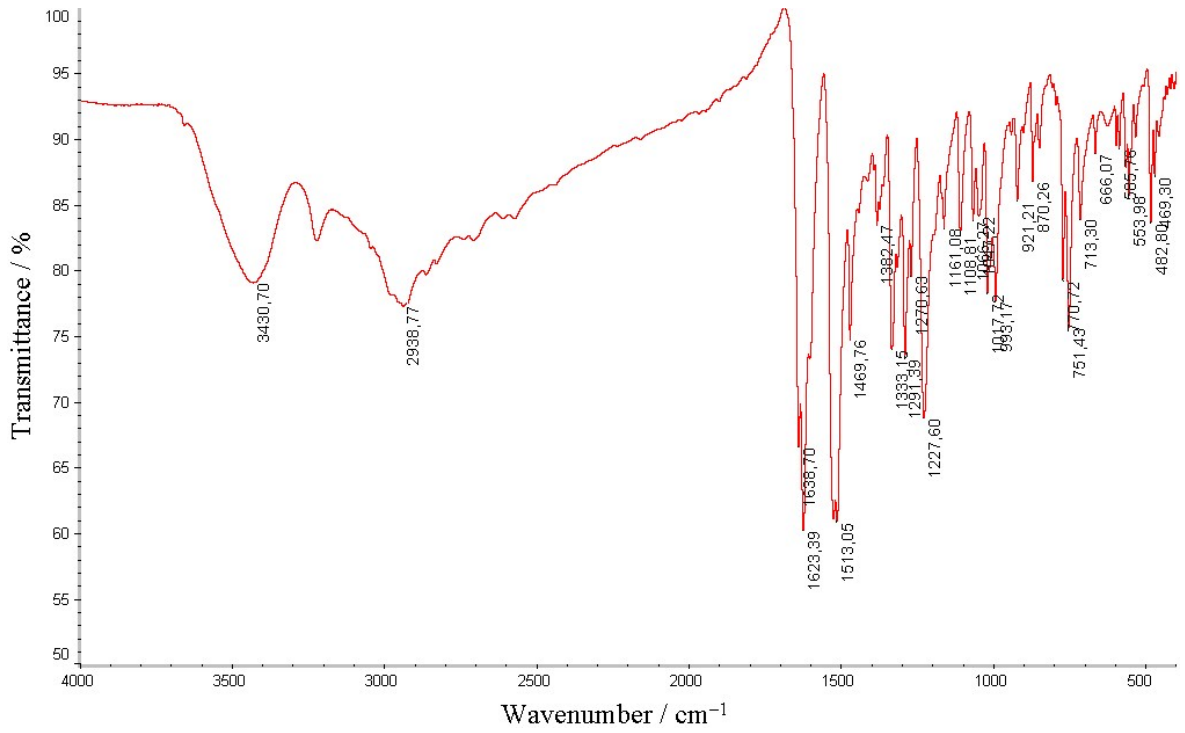


Figure S5. IR spectrum of $[Ni(H_3L)_2]Cl_2 \cdot 4MeOH$ (**A**) in the 4000–400 cm^{-1} region (KBr pellet).

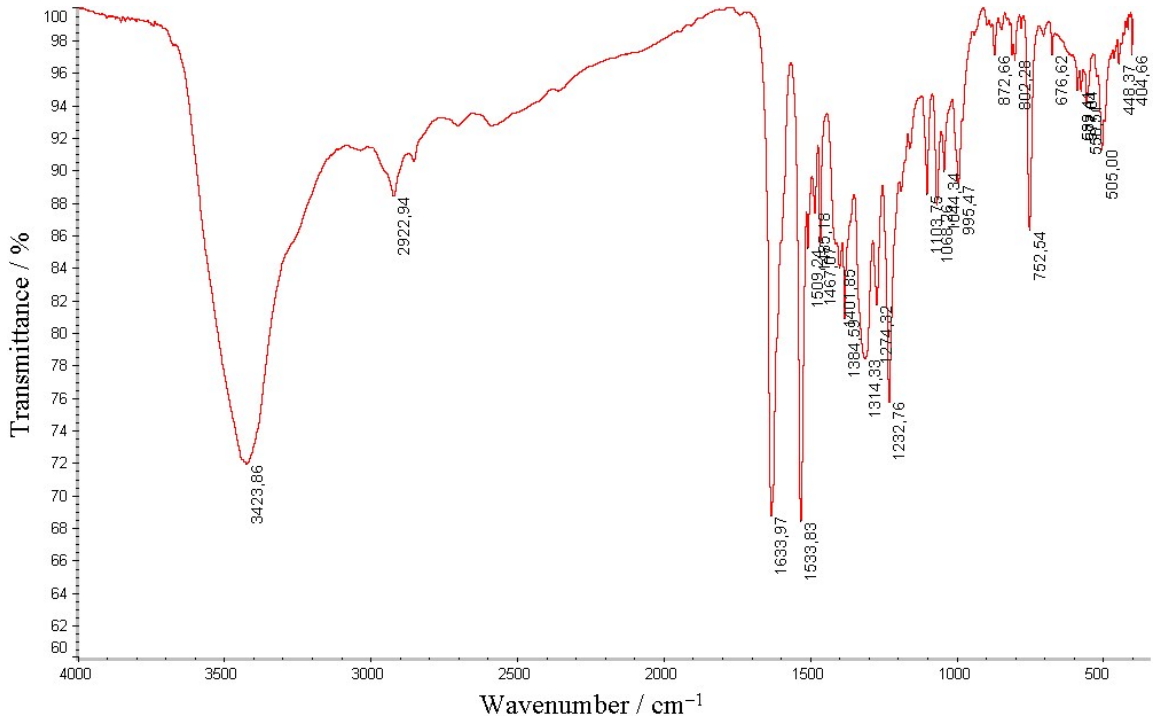


Figure S6. IR spectrum of $[Ni(H_3L)_2](NO_3)_2 \cdot 4MeOH$ (**B**) in the 4000–400 cm^{-1} region (KBr pellet).

6. Crystal data and structure refinement details for compounds 1, 2, A and B

Table S1. Crystallographic details of $[Ni_6(L{\cdot}SMe)_3(CO_3)(MeOH)_6(THF)_2]Cl{\cdot}2MeOH$ (**1**).

Chemical formula	$C_{78}H_{85}N_6Ni_6O_{20}S_3{\cdot}Cl{\cdot}2(CH_4O)$
M_r	1974.49 g mol^{-1}
Crystal system, space group	Monoclinic, *P*2/*c*
Temperature (K)	153
a, *b*, *c* (Å)	12.7711 (17), 21.197 (3), 15.366 (2)
β	97.636 (2)°
V (Å^3)	4122.9 (9)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	1.53
Crystal size (mm)	0.16 × 0.12 × 0.08
Diffractometer	Bruker *APEX*-II CCD diffractometer
Absorption correction	Multi-scan *SADABS* (Bruker, 2013)
T_{min}, T_{max}	0.59, 0.75
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	49431, 8544, 6612
R_{int}	0.074
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.628
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.094, 1.01
No. of reflections	8544
No. of parameters	556
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.59, −0.46

Table S2. Geometrical parameters for $[Ni_6(L{\cdot}SMe)_3(CO_3)(MeOH)_6(THF)_2]Cl{\cdot}2MeOH$ (**1**) (Å and °).

Ni1—N1	1.976 (2)	C21—C22	1.393 (4)
Ni1—O2	2.0010 (19)	C21—C26	1.414 (4)

Ni1—O3	2.046 (2)	C21—N2	1.421 (4)
Ni1—O1	2.0896 (19)	C22—C23	1.371 (4)
Ni1—O5	2.098 (2)	C23—C24	1.386 (5)
Ni1—O4	2.158 (2)	C24—C25	1.379 (4)
Ni1—Ni2	2.9708 (6)	C25—C26	1.389 (4)
Ni2—N2	1.963 (2)	C26—O4	1.353 (3)
Ni2—O7	1.9726 (18)	C27—O8	1.398 (4)
Ni2—O4	2.011 (2)	C28—O11	1.329 (3)
Ni2—O6	2.0306 (18)	C28—C29	1.400 (4)
Ni2—O8	2.119 (2)	C28—C33	1.421 (4)
Ni2—O3	2.143 (2)	C29—C30	1.371 (4)
Ni3—N3	1.995 (2)	C30—C31	1.398 (5)
Ni3—O11	2.000 (2)	C31—C32	1.368 (4)
Ni3—O2	2.0359 (19)	C32—C33	1.391 (4)
Ni3—O1	2.0856 (19)	C33—N3	1.425 (4)
Ni3—O9	2.095 (2)	C34—N3	1.283 (4)
Ni3—O10	2.112 (2)	C35—O6	1.278 (5)
S1—C19	1.731 (10)	C35—O1^{i}	1.284 (3)
S1—C19^{i}	1.732 (10)	C35—O1	1.284 (3)
S1—C18	1.764 (5)	C36—O10	1.422 (4)
S2—C4	1.769 (3)	C37—O9	1.447 (4)
S2—C5	1.794 (4)	C38—O5	1.415 (4)
C1—O2	1.316 (3)	C38—C39	1.528 (6)
C1—C7	1.424 (4)	C39—C40	1.550 (8)
C1—C2	1.435 (4)	C40—C41	1.413 (7)
C2—C3	1.403 (4)	C41—O5	1.433 (5)
C2—C34	1.447 (4)	C42—O67	1.386 (5)
C3—C4	1.386 (4)	O6—Ni2^{i}	2.0306 (18)
C4—C6	1.383 (4)	O7—Ni2^{i}	1.9726 (18)
C6—C7	1.406 (4)		
C7—C8	1.452 (4)		
C8—N1	1.283 (4)	C4—C6—C7	122.2 (3)
C9—C10	1.399 (4)	C6—C7—C1	120.3 (3)
C9—C14	1.409 (4)	C6—C7—C8	114.1 (3)
C9—N1	1.425 (4)	C1—C7—C8	125.5 (3)
C10—C11	1.378 (4)	N1—C8—C7	126.3 (3)
C11—C12	1.394 (4)	C10—C9—C14	120.6 (3)
C12—C13	1.383 (4)	C10—C9—N1	124.8 (3)
C13—C14	1.396 (4)	C14—C9—N1	114.6 (2)
C14—O3	1.353 (3)	C11—C10—C9	119.6 (3)
C15—O7	1.312 (5)	C10—C11—C12	120.3 (3)
C15—C16	1.421 (4)	C13—C12—C11	120.4 (3)
C15—C16^{i}	1.421 (4)	C12—C13—C14	120.5 (3)
C16—C17	1.403 (4)	O3—C14—C13	121.1 (3)
C16—C20	1.451 (4)	O3—C14—C9	120.2 (2)
C17—C18	1.385 (4)	C13—C14—C9	118.6 (3)
C18—C17^{i}	1.385 (4)	O7—C15—C16	120.64 (19)
C20—N2	1.285 (4)	O7—C15—C16^{i}	120.64 (19)
		C16—C15—C16^{i}	118.7 (4)
N1—Ni1—O2	92.56 (9)	C17—C16—C15	119.4 (3)
N1—Ni1—O3	83.79 (9)	C17—C16—C20	115.1 (3)

O2—Ni1—O3	173.92 (8)	C15—C16—C20	125.5 (3)
N1—Ni1—O1	172.55 (9)	C18—C17—C16	121.8 (3)
O2—Ni1—O1	80.59 (8)	C17^{i}—C18—C17	118.9 (4)
O3—Ni1—O1	103.28 (8)	C17^{i}—C18—S1	120.6 (2)
N1—Ni1—O5	91.36 (9)	C17—C18—S1	120.6 (2)
O2—Ni1—O5	91.81 (9)	N2—C20—C16	126.2 (3)
O3—Ni1—O5	93.13 (9)	C22—C21—C26	120.0 (3)
O1—Ni1—O5	85.96 (8)	C22—C21—N2	125.4 (3)
N1—Ni1—O4	93.61 (9)	C26—C21—N2	114.6 (3)
O2—Ni1—O4	92.94 (8)	C23—C22—C21	120.3 (3)
O3—Ni1—O4	82.47 (8)	C22—C23—C24	120.1 (3)
O1—Ni1—O4	89.70 (8)	C25—C24—C23	120.4 (3)
O5—Ni1—O4	172.96 (8)	C24—C25—C26	120.9 (3)
N1—Ni1—Ni2	106.46 (7)	O4—C26—C25	121.3 (3)
O2—Ni1—Ni2	131.19 (6)	O4—C26—C21	120.3 (3)
O3—Ni1—Ni2	46.15 (6)	C25—C26—C21	118.3 (3)
O1—Ni1—Ni2	80.45 (5)	O11—C28—C29	121.9 (3)
O5—Ni1—Ni2	130.92 (7)	O11—C28—C33	120.5 (3)
O4—Ni1—Ni2	42.59 (5)	C29—C28—C33	117.6 (3)
N2—Ni2—O7	92.11 (10)	C30—C29—C28	121.2 (3)
N2—Ni2—O4	85.23 (9)	C29—C30—C31	120.7 (3)
O7—Ni2—O4	177.34 (8)	C32—C31—C30	119.4 (3)
N2—Ni2—O6	173.20 (9)	C31—C32—C33	121.0 (3)
O7—Ni2—O6	81.47 (8)	C32—C33—C28	120.1 (3)
O4—Ni2—O6	101.19 (8)	C32—C33—N3	125.9 (3)
N2—Ni2—O8	96.43 (10)	C28—C33—N3	114.1 (3)
O7—Ni2—O8	81.85 (7)	N3—C34—C2	126.8 (3)
O4—Ni2—O8	98.52 (9)	O6—C35—O1^{i}	118.94 (18)
O6—Ni2—O8	84.92 (7)	O6—C35—O1	118.94 (18)
N2—Ni2—O3	97.63 (9)	O1^{i}—C35—O1	122.1 (4)
O7—Ni2—O3	96.60 (6)	O5—C38—C39	104.9 (4)
O4—Ni2—O3	83.69 (8)	C38—C39—C40	104.3 (4)
O6—Ni2—O3	81.00 (5)	C41—C40—C39	105.1 (4)
O8—Ni2—O3	165.91 (9)	C40—C41—O5	110.7 (4)
N2—Ni2—Ni1	110.42 (7)	C8—N1—C9	122.7 (2)
O7—Ni2—Ni1	134.79 (4)	C8—N1—Ni1	125.4 (2)
O4—Ni2—Ni1	46.58 (6)	C9—N1—Ni1	111.84 (18)
O6—Ni2—Ni1	73.18 (5)	C20—N2—C21	123.5 (3)
O8—Ni2—Ni1	130.74 (7)	C20—N2—Ni2	125.5 (2)
O3—Ni2—Ni1	43.53 (5)	C21—N2—Ni2	110.89 (18)
N3—Ni3—O11	84.32 (9)	C34—N3—C33	122.4 (3)
N3—Ni3—O2	89.78 (9)	C34—N3—Ni3	127.1 (2)
O11—Ni3—O2	173.04 (8)	C33—N3—Ni3	110.49 (18)
N3—Ni3—O1	169.55 (9)	C35—O1—Ni3	134.82 (16)
O11—Ni3—O1	105.88 (8)	C35—O1—Ni1	121.2 (2)
O2—Ni3—O1	79.89 (7)	Ni3—O1—Ni1	96.92 (8)
N3—Ni3—O9	93.64 (9)	C1—O2—Ni1	127.73 (17)
O11—Ni3—O9	90.51 (9)	C1—O2—Ni3	130.11 (18)
O2—Ni3—O9	93.56 (8)	Ni1—O2—Ni3	101.45 (8)
O1—Ni3—O9	88.63 (8)	C14—O3—Ni1	109.43 (17)
N3—Ni3—O10	94.40 (9)	C14—O3—Ni2	119.84 (17)

O11—Ni3—O10	87.74 (9)	Ni1—O3—Ni2	90.32 (8)
O2—Ni3—O10	89.04 (8)	C26—O4—Ni2	108.97 (17)
O1—Ni3—O10	83.91 (8)	C26—O4—Ni1	120.73 (17)
O9—Ni3—O10	171.56 (9)	Ni2—O4—Ni1	90.83 (8)
C19—S1—C19^{i}	152.2 (6)	C38—O5—C41	108.2 (3)
C19—S1—C18	103.9 (3)	C38—O5—Ni1	125.5 (2)
C19^{i}—S1—C18	103.9 (3)	C41—O5—Ni1	123.4 (2)
C4—S2—C5	102.99 (16)	C35—O6—Ni2	131.70 (6)
O2—C1—C7	121.9 (3)	C35—O6—Ni2^{i}	131.70 (6)
O2—C1—C2	121.0 (2)	Ni2—O6—Ni2^{i}	96.61 (11)
C7—C1—C2	117.1 (3)	C15—O7—Ni2	129.77 (6)
C3—C2—C1	119.7 (3)	C15—O7—Ni2^{i}	129.77 (6)
C3—C2—C34	115.3 (3)	Ni2—O7—Ni2^{i}	100.46 (12)
C1—C2—C34	125.0 (3)	C27—O8—Ni2	133.1 (2)
C4—C3—C2	122.6 (3)	C37—O9—Ni3	118.56 (18)
C6—C4—C3	117.9 (3)	C36—O10—Ni3	124.23 (19)
C6—C4—S2	124.7 (2)	C28—O11—Ni3	110.54 (17)
C3—C4—S2	117.4 (2)		

Symmetry code: (i) $-x+1, y, -z+3/2$.

Table S3. Crystallographical details of $[Ni_8(HL{\cdot}SMe)_2(L{\cdot}SMe)_2(OH)_4(MeCN)_4(H_2O)_4](NO_3)_2{\cdot}11MeCN{\cdot}2PhCN$ (**2**).

Chemical formula	$C_{92}H_{86}N_{12}Ni_8O_{20}S_4{\cdot}2(NO_3){\cdot}11(C_2H_3N){\cdot}2(C_7H_5N)$
M_r	2853.25 g mol^{-1}
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	153
a, *b*, *c* (Å)	17.742 (8), 18.183 (8), 20.695 (9)
α, *β*, *γ*	90.191 (8)°, 95.030 (9)°, 113.761 (8)°
V (Å^3)	6081 (5)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	1.36
Crystal size (mm)	0.14 × 0.14 × 0.08
Diffractometer	Bruker *APEX*-II CCD diffractometer
Absorption correction	Multi-scan
T_{min}, T_{max}	0.31, 0.74
No. of measured, independent and	73137, 25374, 11951

observed [$I > 2\sigma(I)$] reflections	
R_{int}	0.200
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.636
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.119, 0.357, 0.97
No. of reflections	25374
No. of parameters	1437
No. of restraints	797
H-atom treatment	H-atom parameters constrained
$(\Delta/\sigma)_{max}$	0.134
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.17, −2.11

Table S4. Geometrical parameters for $[Ni_8(HL{\cdot}SMe)_2(L{\cdot}SMe)_2(OH)_4(MeCN)_4(H_2O)_4](NO_3)_2{\cdot}11MeCN{\cdot}2PhCN$ (**2**) (Å and °).

Ni1—N10	2.013 (8)	C48—N4	1.427 (13)
Ni1—O10	2.027 (7)	C49—N4	1.277 (13)
Ni1—O16	2.048 (7)	C49—C50	1.452 (16)
Ni1—O6	2.071 (7)	C50—C51	1.385 (14)
Ni1—O8	2.087 (7)	C50—C56	1.442 (15)
Ni1—O15	2.093 (7)	C51—C52	1.415 (15)
Ni2—N1	1.980 (8)	C52—C54	1.355 (15)
Ni2—O11	1.990 (7)	C52—S1	1.775 (10)
Ni2—O17	2.026 (7)	C53—S1	1.758 (14)
Ni2—O14	2.045 (7)	C54—C55	1.427 (13)
Ni2—N6	2.091 (9)	C55—C56	1.407 (15)
Ni2—O3	2.151 (7)	C55—C57	1.414 (15)
Ni3—O12	1.973 (7)	C56—O12	1.331 (11)
Ni3—N4	1.992 (9)	C57—N7	1.313 (12)
Ni3—O18	2.030 (7)	C58—C59	1.397 (13)
Ni3—O19	2.061 (7)	C58—C63	1.415 (12)
Ni3—N3I	2.075 (10)	C58—N7	1.426 (13)
Ni3—O20	2.171 (7)	C59—C60	1.348 (15)
Ni4—N11	2.018 (9)	C60—C61	1.395 (14)

Ni4—O1	2.039 (7)	C61—C62	1.383 (14)
Ni4—O7	2.059 (7)	C62—C63	1.402 (14)
Ni4—O8	2.072 (7)	C63—O4	1.331 (11)
Ni4—O16	2.077 (7)	C64—O2	1.337 (12)
Ni4—O13	2.138 (6)	C64—C69	1.392 (15)
Ni5—N9	2.010 (8)	C64—C65	1.389 (13)
Ni5—O11	2.038 (7)	C65—C66	1.415 (14)
Ni5—O2	2.053 (7)	C66—C67	1.340 (15)
Ni5—O4	2.054 (7)	C67—C68	1.392 (14)
Ni5—O5	2.071 (7)	C68—C69	1.376 (14)
Ni5—O14	2.133 (7)	C69—N9	1.431 (12)
Ni6—O10	1.978 (7)	C70—N9	1.275 (13)
Ni6—N8	1.992 (8)	C70—C71	1.436 (13)
Ni6—O3	2.021 (7)	C71—C73	1.417 (15)
Ni6—O15	2.029 (7)	C71—C72	1.415 (13)
Ni6—N2	2.112 (9)	C72—O11	1.327 (12)
Ni6—O17	2.162 (7)	C72—C77	1.400 (14)
Ni7—N7	1.991 (8)	C73—C74	1.378 (14)
Ni7—O12	2.043 (7)	C74—C76	1.409 (14)
Ni7—O2	2.045 (7)	C74—S3	1.748 (12)
Ni7—O4	2.063 (7)	C75—S3	1.783 (16)
Ni7—O9	2.080 (8)	C76—C77	1.417 (15)
Ni7—O19	2.116 (7)	C77—C78	1.477 (13)
Ni8—N12	1.977 (9)	C78—N1	1.256 (13)
Ni8—O1	1.996 (7)	C79—C84	1.401 (15)
Ni8—O20	2.048 (7)	C79—C80	1.409 (14)
Ni8—O13	2.056 (7)	C79—N1	1.444 (12)
Ni8—N5	2.080 (10)	C80—C81	1.391 (14)
Ni8—O18	2.141 (7)	C81—C82	1.381 (16)
C1—O3	1.352 (12)	C82—C83	1.386 (15)
C1—C2	1.376 (14)	C83—C84	1.392 (13)
C1—C6	1.419 (13)	C84—O17	1.339 (12)
C2—C3	1.359 (15)	C85—N2	1.133 (13)
C3—C4	1.377 (15)	C85—C86	1.448 (16)
C4—C5	1.352 (14)	C87—N5	1.094 (14)
C5—C6	1.424 (14)	C87—C88	1.480 (18)
C6—N8	1.400 (13)	C89—N6	1.130 (15)
C7—N8	1.284 (12)	C89—C90	1.492 (19)
C7—C8	1.456 (15)	C91—N3I	1.153 (14)
C8—C9	1.407 (14)	C91—C92	1.439 (17)
C8—C14	1.416 (15)	C93—C94	1.3900
C9—C10	1.380 (15)	C93—C98	1.3900
C10—C12	1.381 (16)	C93—C99	1.55 (3)
C10—S4	1.769 (11)	C94—C95	1.3900
C11—S4	1.764 (17)	C95—C96	1.3900
C12—C13	1.414 (14)	C96—C97	1.3900
C13—C15	1.426 (15)	C97—C98	1.3900
C13—C14	1.439 (15)	C99—N13	1.13 (3)
C14—O10	1.320 (11)	C100—C101	1.3900
C15—N10	1.293 (12)	C100—C105	1.3900
C16—C17	1.380 (14)	C100—C106	1.424 (15)

C16—C21	1.407 (13)	C101—C102	1.3900
C16—N10	1.412 (14)	C102—C103	1.3900
C17—C18	1.371 (15)	C103—C104	1.3900
C18—C19	1.398 (14)	C104—C105	1.3900
C19—C20	1.387 (14)	C106—N14	1.125 (15)
C20—C21	1.372 (14)	C107—C108	1.47 (2)
C21—O16	1.364 (12)	C108—N15	1.13 (2)
C22—O8	1.357 (12)	N16—O23	1.226 (13)
C22—C27	1.388 (16)	N16—O21	1.232 (12)
C22—C23	1.389 (14)	N16—O22	1.265 (13)
C23—C24	1.384 (15)	N17—O26	1.246 (12)
C24—C25	1.369 (17)	N17—O25	1.236 (11)
C25—C26	1.420 (17)	N17—O24	1.249 (12)
C26—C27	1.365 (16)		
C27—N11	1.436 (13)		
C28—N11	1.269 (13)	C35—C29—C28	124.6 (11)
C28—C29	1.454 (15)	C31—C30—C29	122.6 (10)
C29—C30	1.387 (15)	C33—C31—C30	117.5 (11)
C29—C35	1.407 (15)	C33—C31—S2	124.6 (9)
C30—C31	1.384 (15)	C30—C31—S2	117.8 (9)
C31—C33	1.360 (15)	C31—C33—C34	121.8 (11)
C31—S2	1.760 (12)	C33—C34—C35	121.7 (10)
C32—S2	1.798 (13)	C33—C34—C36	114.1 (10)
C33—C34	1.380 (16)	C35—C34—C36	124.2 (10)
C34—C35	1.409 (15)	O1—C35—C34	123.0 (10)
C34—C36	1.509 (14)	O1—C35—C29	120.7 (10)
C35—O1	1.305 (13)	C34—C35—C29	116.3 (11)
C36—N12	1.286 (14)	N12—C36—C34	125.7 (11)
C37—C38	1.384 (17)	C38—C37—N12	125.7 (12)
C37—N12	1.405 (14)	C38—C37—C42	121.4 (11)
C37—C42	1.418 (18)	N12—C37—C42	112.8 (11)
C38—C39	1.442 (16)	C37—C38—C39	119.5 (13)
C39—C40	1.354 (19)	C40—C39—C38	117.7 (13)
C40—C41	1.411 (18)	C39—C40—C41	124.0 (13)
C41—C42	1.396 (16)	C42—C41—C40	118.4 (13)
C42—O20	1.342 (14)	O20—C42—C41	119.8 (12)
C43—O18	1.347 (12)	O20—C42—C37	121.4 (10)
C43—C44	1.379 (15)	C41—C42—C37	118.7 (12)
C43—C48	1.435 (14)	O18—C43—C44	122.1 (9)
C44—C45	1.386 (15)	O18—C43—C48	119.8 (9)
C45—C46	1.396 (15)	C44—C43—C48	118.1 (10)
C46—C47	1.386 (15)	C43—C44—C45	120.9 (10)
C47—C48	1.399 (14)	C44—C45—C46	121.9 (11)
		C47—C46—C45	117.9 (11)
N10—Ni1—O10	88.3 (3)	C46—C47—C48	121.4 (10)
N10—Ni1—O16	83.1 (3)	C47—C48—N4	125.5 (9)
O10—Ni1—O16	171.3 (3)	C47—C48—C43	119.8 (10)
N10—Ni1—O6	95.1 (3)	N4—C48—C43	114.7 (9)
O10—Ni1—O6	92.0 (3)	N4—C49—C50	126.1 (10)
O16—Ni1—O6	89.6 (3)	C51—C50—C56	120.4 (10)
N10—Ni1—O8	97.2 (3)	C51—C50—C49	114.0 (10)

O10—Ni1—O8	98.0 (3)	C56—C50—C49	125.5 (9)
O16—Ni1—O8	82.4 (3)	C50—C51—C52	120.8 (11)
O6—Ni1—O8	164.4 (3)	C54—C52—C51	118.7 (9)
N10—Ni1—O15	167.4 (3)	C54—C52—S1	124.6 (9)
O10—Ni1—O15	79.6 (3)	C51—C52—S1	116.7 (8)
O16—Ni1—O15	109.0 (3)	C52—C54—C55	123.0 (10)
O6—Ni1—O15	88.8 (3)	C56—C55—C57	125.9 (9)
O8—Ni1—O15	81.3 (3)	C56—C55—C54	118.5 (10)
N1—Ni2—O11	91.6 (3)	C57—C55—C54	115.3 (10)
N1—Ni2—O17	84.5 (3)	O12—C56—C55	120.6 (9)
O11—Ni2—O17	170.5 (3)	O12—C56—C50	120.9 (9)
N1—Ni2—O14	174.4 (3)	C55—C56—C50	118.4 (9)
O11—Ni2—O14	83.3 (3)	N7—C57—C55	126.3 (10)
O17—Ni2—O14	100.9 (3)	C59—C58—C63	120.2 (10)
N1—Ni2—N6	89.5 (3)	C59—C58—N7	125.2 (9)
O11—Ni2—N6	95.4 (3)	C63—C58—N7	114.4 (8)
O17—Ni2—N6	93.2 (3)	C60—C59—C58	120.0 (10)
O14—Ni2—N6	88.6 (3)	C59—C60—C61	120.3 (10)
N1—Ni2—O3	95.3 (3)	C62—C61—C60	121.7 (11)
O11—Ni2—O3	91.5 (3)	C61—C62—C63	118.4 (10)
O17—Ni2—O3	80.3 (3)	O4—C63—C62	122.0 (8)
O14—Ni2—O3	87.2 (3)	O4—C63—C58	119.0 (9)
N6—Ni2—O3	171.4 (3)	C62—C63—C58	119.1 (9)
O12—Ni3—N4	92.3 (3)	O2—C64—C69	120.7 (9)
O12—Ni3—O18	171.2 (3)	O2—C64—C65	119.3 (10)
N4—Ni3—O18	84.5 (3)	C69—C64—C65	120.0 (10)
O12—Ni3—O19	82.7 (3)	C64—C65—C66	118.3 (11)
N4—Ni3—O19	175.0 (3)	C67—C66—C65	121.2 (10)
O18—Ni3—O19	100.3 (3)	C66—C67—C68	120.6 (10)
O12—Ni3—N3I	96.0 (3)	C69—C68—C67	119.7 (11)
N4—Ni3—N3I	90.6 (4)	C68—C69—C64	120.3 (10)
O18—Ni3—N3I	92.2 (3)	C68—C69—N9	124.2 (10)
O19—Ni3—N3I	90.6 (3)	C64—C69—N9	115.4 (9)
O12—Ni3—O20	91.4 (3)	N9—C70—C71	126.6 (10)
N4—Ni3—O20	92.4 (3)	C73—C71—C72	116.8 (9)
O18—Ni3—O20	80.6 (3)	C73—C71—C70	116.8 (9)
O19—Ni3—O20	87.0 (3)	C72—C71—C70	126.1 (10)
N3I—Ni3—O20	171.8 (3)	O11—C72—C77	121.2 (9)
N11—Ni4—O1	87.5 (3)	O11—C72—C71	118.3 (9)
N11—Ni4—O7	95.5 (3)	C77—C72—C71	120.5 (10)
O1—Ni4—O7	90.2 (3)	C74—C73—C71	125.2 (10)
N11—Ni4—O8	82.5 (3)	C73—C74—C76	115.6 (10)
O1—Ni4—O8	170.0 (3)	C73—C74—S3	126.6 (8)
O7—Ni4—O8	90.2 (3)	C76—C74—S3	117.6 (8)
N11—Ni4—O16	97.2 (3)	C74—C76—C77	122.3 (10)
O1—Ni4—O16	99.8 (3)	C72—C77—C76	119.2 (9)
O7—Ni4—O16	164.1 (3)	C72—C77—C78	126.2 (10)
O8—Ni4—O16	82.0 (3)	C76—C77—C78	114.4 (9)
N11—Ni4—O13	167.0 (3)	N1—C78—C77	124.3 (10)
O1—Ni4—O13	80.1 (3)	C84—C79—C80	121.9 (10)
O7—Ni4—O13	88.4 (3)	C84—C79—N1	115.5 (9)

O8—Ni4—O13	110.0 (3)	C80—C79—N1	122.6 (10)
O16—Ni4—O13	81.3 (3)	C81—C80—C79	119.0 (11)
N9—Ni5—O11	87.8 (3)	C82—C81—C80	119.3 (10)
N9—Ni5—O2	83.0 (3)	C81—C82—C83	121.5 (10)
O11—Ni5—O2	170.5 (3)	C82—C83—C84	120.8 (11)
N9—Ni5—O4	102.4 (3)	O17—C84—C83	122.5 (10)
O11—Ni5—O4	98.6 (3)	O17—C84—C79	119.9 (9)
O2—Ni5—O4	81.2 (3)	C83—C84—C79	117.5 (10)
N9—Ni5—O5	92.0 (3)	N2—C85—C86	176.2 (15)
O11—Ni5—O5	93.9 (3)	N5—C87—C88	179.8 (15)
O2—Ni5—O5	88.7 (3)	N6—C89—C90	176.0 (17)
O4—Ni5—O5	161.2 (3)	N3I—C91—C92	178.4 (12)
N9—Ni5—O14	167.8 (3)	C94—C93—C98	120.0
O11—Ni5—O14	80.0 (3)	C94—C93—C99	123.0 (12)
O2—Ni5—O14	109.2 (3)	C98—C93—C99	116.9 (12)
O4—Ni5—O14	80.0 (3)	C93—C94—C95	120.0
O5—Ni5—O14	88.4 (3)	C96—C95—C94	120.0
O10—Ni6—N8	92.6 (3)	C97—C96—C95	120.0
O10—Ni6—O3	170.7 (3)	C96—C97—C98	120.0
N8—Ni6—O3	83.5 (3)	C97—C98—C93	120.0
O10—Ni6—O15	82.3 (3)	N13—C99—C93	178 (3)
N8—Ni6—O15	174.8 (3)	C101—C100—C105	120.0
O3—Ni6—O15	101.7 (3)	C101—C100—C106	120.8 (8)
O10—Ni6—N2	94.0 (3)	C105—C100—C106	119.1 (8)
N8—Ni6—N2	90.5 (3)	C102—C101—C100	120.0
O3—Ni6—N2	94.5 (3)	C101—C102—C103	120.0
O15—Ni6—N2	88.9 (3)	C104—C103—C102	120.0
O10—Ni6—O17	91.9 (3)	C103—C104—C105	120.0
N8—Ni6—O17	94.9 (3)	C104—C105—C100	120.0
O3—Ni6—O17	80.1 (3)	N14—C106—C100	174.9 (14)
O15—Ni6—O17	86.3 (3)	N15—C108—C107	177 (2)
N2—Ni6—O17	171.8 (3)	C78—N1—C79	123.5 (9)
N7—Ni7—O12	88.6 (3)	C78—N1—Ni2	125.7 (7)
N7—Ni7—O2	101.4 (3)	C79—N1—Ni2	109.9 (6)
O12—Ni7—O2	99.0 (3)	C85—N2—Ni6	172.7 (10)
N7—Ni7—O4	81.7 (3)	C49—N4—C48	123.4 (9)
O12—Ni7—O4	170.2 (3)	C49—N4—Ni3	125.7 (8)
O2—Ni7—O4	81.2 (3)	C48—N4—Ni3	110.8 (6)
N7—Ni7—O9	93.2 (3)	C87—N5—Ni8	172.4 (11)
O12—Ni7—O9	93.1 (3)	C89—N6—Ni2	177.4 (11)
O2—Ni7—O9	161.2 (3)	C57—N7—C58	121.6 (9)
O4—Ni7—O9	89.3 (3)	C57—N7—Ni7	126.6 (8)
N7—Ni7—O19	168.3 (3)	C58—N7—Ni7	111.7 (6)
O12—Ni7—O19	79.7 (3)	C7—N8—C6	124.3 (9)
O2—Ni7—O19	80.4 (3)	C7—N8—Ni6	124.1 (8)
O4—Ni7—O19	110.0 (2)	C6—N8—Ni6	111.0 (6)
O9—Ni7—O19	87.7 (3)	C70—N9—C69	123.1 (9)
N12—Ni8—O1	92.6 (3)	C70—N9—Ni5	127.3 (7)
N12—Ni8—O20	83.0 (3)	C69—N9—Ni5	109.4 (7)
O1—Ni8—O20	171.1 (3)	C15—N10—C16	122.6 (9)
N12—Ni8—O13	175.2 (3)	C15—N10—Ni1	125.8 (8)

O1—Ni8—O13	83.1 (3)	C16—N10—Ni1	111.3 (6)
O20—Ni8—O13	101.5 (3)	C28—N11—C27	121.6 (9)
N12—Ni8—N5	88.6 (4)	C28—N11—Ni4	126.8 (7)
O1—Ni8—N5	94.1 (3)	C27—N11—Ni4	111.3 (7)
O20—Ni8—N5	93.6 (3)	C36—N12—C37	121.4 (10)
O13—Ni8—N5	89.5 (3)	C36—N12—Ni8	124.5 (8)
N12—Ni8—O18	94.7 (3)	C37—N12—Ni8	113.6 (8)
O1—Ni8—O18	91.8 (3)	O23—N16—O21	119.5 (12)
O20—Ni8—O18	80.9 (3)	O23—N16—O22	123.1 (11)
O13—Ni8—O18	87.6 (3)	O21—N16—O22	117.3 (11)
N5—Ni8—O18	173.1 (3)	O26—N17—O25	120.2 (10)
O3—C1—C2	123.0 (9)	O26—N17—O24	119.6 (10)
O3—C1—C6	118.0 (9)	O25—N17—O24	120.2 (11)
C2—C1—C6	119.0 (10)	C91—N3I—Ni3	178.0 (9)
C3—C2—C1	121.6 (10)	C35—O1—Ni8	127.7 (6)
C2—C3—C4	120.9 (11)	C35—O1—Ni4	131.4 (6)
C5—C4—C3	119.4 (11)	Ni8—O1—Ni4	100.4 (3)
C4—C5—C6	121.8 (10)	C64—O2—Ni7	127.5 (6)
N8—C6—C1	116.2 (9)	C64—O2—Ni5	108.8 (6)
N8—C6—C5	126.6 (9)	Ni7—O2—Ni5	96.8 (3)
C1—C6—C5	117.2 (10)	C1—O3—Ni6	110.9 (6)
N8—C7—C8	127.0 (10)	C1—O3—Ni2	119.6 (6)
C9—C8—C14	120.9 (11)	Ni6—O3—Ni2	95.2 (3)
C9—C8—C7	114.9 (10)	C63—O4—Ni5	125.1 (7)
C14—C8—C7	124.2 (9)	C63—O4—Ni7	110.8 (6)
C10—C9—C8	121.4 (11)	Ni5—O4—Ni7	96.3 (3)
C9—C10—C12	119.4 (10)	C22—O8—Ni4	109.2 (6)
C9—C10—S4	118.5 (9)	C22—O8—Ni1	118.4 (6)
C12—C10—S4	122.1 (9)	Ni4—O8—Ni1	95.1 (3)
C10—C12—C13	121.2 (11)	C14—O10—Ni6	127.4 (7)
C12—C13—C15	115.6 (10)	C14—O10—Ni1	132.2 (7)
C12—C13—C14	120.1 (10)	Ni6—O10—Ni1	100.4 (3)
C15—C13—C14	124.2 (9)	C72—O11—Ni2	127.8 (6)
O10—C14—C8	123.3 (10)	C72—O11—Ni5	132.3 (6)
O10—C14—C13	119.7 (10)	Ni2—O11—Ni5	99.9 (3)
C8—C14—C13	116.9 (9)	C56—O12—Ni3	128.9 (7)
N10—C15—C13	128.3 (10)	C56—O12—Ni7	130.2 (7)
C17—C16—C21	119.7 (11)	Ni3—O12—Ni7	100.7 (3)
C17—C16—N10	125.1 (9)	Ni8—O13—Ni4	95.3 (3)
C21—C16—N10	115.1 (9)	Ni2—O14—Ni5	95.1 (3)
C18—C17—C16	121.6 (10)	Ni6—O15—Ni1	96.6 (3)
C17—C18—C19	118.8 (10)	C21—O16—Ni1	109.4 (6)
C20—C19—C18	120.0 (11)	C21—O16—Ni4	118.1 (6)
C21—C20—C19	121.3 (10)	Ni1—O16—Ni4	96.1 (3)
O16—C21—C20	121.1 (9)	C84—O17—Ni2	110.1 (6)
O16—C21—C16	120.2 (10)	C84—O17—Ni6	116.8 (6)
C20—C21—C16	118.7 (10)	Ni2—O17—Ni6	94.6 (3)
O8—C22—C27	121.2 (9)	C43—O18—Ni3	109.9 (6)
O8—C22—C23	119.2 (10)	C43—O18—Ni8	117.3 (7)
C27—C22—C23	119.6 (10)	Ni3—O18—Ni8	94.9 (3)
C24—C23—C22	120.3 (12)	Ni3—O19—Ni7	95.5 (3)

C25—C24—C23	119.9 (12)	C42—O20—Ni8	109.1 (7)
C24—C25—C26	120.1 (12)	C42—O20—Ni3	116.8 (8)
C27—C26—C25	119.3 (13)	Ni8—O20—Ni3	93.5 (3)
C26—C27—C22	120.7 (11)	C53—S1—C52	102.1 (6)
C26—C27—N11	124.6 (11)	C31—S2—C32	103.0 (6)
C22—C27—N11	114.7 (10)	C74—S3—C75	105.8 (7)
N11—C28—C29	126.7 (10)	C10—S4—C11	102.2 (7)
C30—C29—C35	120.0 (10)		
C30—C29—C28	115.3 (10)		

Table S5. Crystallographical details of $[Ni(H_3L)_2]Cl_2 \cdot 4MeOH$ (**A**).

Chemical formula	$C_{42}H_{36}N_4NiO_6 \cdot 2Cl \cdot 4(CH_4O)$

M_r	886.44 g mol^{-1}
Crystal system, space group	Triclinic, *P*1
Temperature (K)	173
a, *b*, *c* (Å)	13.394 (2), 18.546 (3), 20.152 (3)
α, *β*, *γ*	108.266 (2)°, 104.850 (2)°, 105.348 (2)°
V (Å^3)	4257.7 (11)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.64
Crystal size (mm)	0.21 × 0.16 × 0.14
Diffractometer	Bruker *APEX*-II CCD diffractometer
Absorption correction	Multi-scan Bruker *SADABS*
T_{min}, T_{max}	0.64, 0.75
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	61658, 21986, 16415
R_{int}	0.184
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.678
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.064, 0.192, 0.75
No. of reflections	21986
No. of parameters	1049
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.77, −0.96

Table S6. Geometrical parameters for $[Ni(H_3L)_2]Cl_2 \cdot 4MeOH$ (**A**) (Å and °).

Ni1—O1	1.998 (2)	C48—C49	1.388 (4)
Ni1—O4	2.010 (2)	C49—C51	1.373 (4)
Ni1—N2	2.013 (2)	C49—C50	1.512 (4)

Ni1—N1	2.014 (2)	C52—C57	1.405 (4)
Ni1—O2	2.115 (2)	C52—C53	1.397 (4)
Ni1—O3	2.151 (2)	C52—N8	1.411 (4)
Ni2—N6	2.004 (2)	C53—C54	1.384 (4)
Ni2—O7	2.003 (2)	C54—C55	1.393 (4)
Ni2—N5	2.014 (2)	C55—C56	1.392 (5)
Ni2—O9	2.023 (2)	C56—C57	1.388 (4)
Ni2—O10	2.084 (2)	C57—O11	1.355 (4)
Ni2—O8	2.127 (2)	C58—O8	1.377 (3)
C1—O1	1.303 (3)	C58—C59	1.387 (4)
C1—C8	1.433 (4)	C58—C63	1.398 (4)
C1—C2	1.439 (4)	C59—C60	1.390 (4)
C2—C3	1.413 (4)	C60—C61	1.391 (5)
C2—C4	1.411 (4)	C61—C62	1.378 (4)
C3—N4	1.312 (4)	C62—C63	1.404 (4)
C4—C5	1.381 (4)	C63—N5	1.429 (4)
C5—C7	1.395 (4)	C64—N5	1.287 (4)
C5—C6	1.512 (4)	C64—C65	1.446 (4)
C7—C8	1.397 (4)	C65—C66	1.398 (4)
C8—C9	1.442 (4)	C65—C71	1.438 (4)
C9—N1	1.292 (4)	C66—C67	1.397 (4)
C10—C11	1.398 (4)	C67—C69	1.374 (4)
C10—C15	1.401 (4)	C67—C68	1.506 (4)
C10—N1	1.415 (4)	C69—C70	1.415 (4)
C11—C12	1.396 (4)	C70—C72	1.412 (4)
C12—C13	1.379 (4)	C70—C71	1.437 (4)
C13—C14	1.392 (4)	C71—O9	1.288 (3)
C14—C15	1.381 (4)	C72—N7	1.314 (4)
C15—O2	1.374 (3)	C73—C74	1.392 (4)
C16—O3	1.377 (3)	C73—C78	1.402 (4)
C16—C17	1.379 (4)	C73—N7	1.424 (4)
C16—C21	1.403 (4)	C74—C75	1.386 (4)
C17—C18	1.394 (4)	C75—C76	1.385 (4)
C18—C19	1.380 (4)	C76—C77	1.384 (4)
C19—C20	1.389 (4)	C77—C78	1.397 (4)
C20—C21	1.398 (4)	C78—O12	1.361 (4)
C21—N2	1.417 (4)	C79—C80	1.400 (4)
C22—N2	1.288 (4)	C79—C84	1.408 (4)
C22—C23	1.451 (4)	C79—N6	1.421 (4)
C23—C24	1.392 (4)	C80—C81	1.386 (5)
C23—C29	1.436 (4)	C81—C82	1.393 (5)
C24—C25	1.394 (4)	C82—C83	1.390 (5)
C25—C27	1.387 (4)	C83—C84	1.376 (5)
C25—C26	1.505 (4)	C84—O10	1.369 (4)
C27—C28	1.404 (4)	C90—O13	1.406 (5)
C28—C30	1.427 (4)	C91—O14	1.425 (4)
C28—C29	1.436 (4)	C92—O15	1.386 (5)
C29—O4	1.297 (3)	C93—O16	1.346 (6)
C30—N3	1.300 (4)		
C31—C32	1.389 (4)	C34—C33—C32	120.5 (3)
C31—C36	1.391 (4)	C33—C34—C35	120.4 (3)

C31—N3	1.424 (3)	C36—C35—C34	119.7 (3)
C32—C33	1.388 (4)	O5—C36—C35	123.6 (3)
C33—C34	1.382 (5)	O5—C36—C31	117.3 (3)
C34—C35	1.392 (5)	C35—C36—C31	119.1 (3)
C35—C36	1.396 (4)	C38—C37—C42	120.7 (3)
C36—O5	1.357 (4)	C38—C37—N4	122.9 (3)
C37—C38	1.385 (5)	C42—C37—N4	116.4 (3)
C37—C42	1.394 (4)	C37—C38—C39	119.4 (3)
C37—N4	1.412 (4)	C40—C39—C38	120.1 (3)
C38—C39	1.393 (5)	C39—C40—C41	120.6 (3)
C39—C40	1.378 (5)	C40—C41—C42	119.9 (3)
C40—C41	1.383 (5)	O6—C42—C41	124.4 (3)
C41—C42	1.391 (4)	O6—C42—C37	116.3 (3)
C42—O6	1.353 (4)	C41—C42—C37	119.3 (3)
C43—N8	1.301 (4)	N8—C43—C44	125.2 (3)
C43—C44	1.425 (4)	C43—C44—C51	116.8 (3)
C44—C51	1.415 (4)	C43—C44—C45	121.8 (3)
C44—C45	1.433 (4)	C51—C44—C45	121.4 (3)
C45—O7	1.300 (3)	O7—C45—C46	124.6 (3)
C45—C46	1.430 (4)	O7—C45—C44	119.1 (3)
C46—C48	1.408 (4)	C46—C45—C44	116.3 (2)
C46—C47	1.440 (4)	C48—C46—C45	119.3 (3)
C47—N6	1.295 (4)	C48—C46—C47	115.2 (3)
		C45—C46—C47	125.5 (3)
O1—Ni1—O4	93.61 (9)	N6—C47—C46	125.9 (3)
O1—Ni1—N2	97.26 (9)	C49—C48—C46	123.8 (3)
O4—Ni1—N2	91.68 (9)	C51—C49—C48	117.5 (3)
O1—Ni1—N1	92.28 (9)	C51—C49—C50	121.0 (3)
O4—Ni1—N1	99.96 (9)	C48—C49—C50	121.5 (3)
N2—Ni1—N1	164.47 (10)	C49—C51—C44	121.6 (3)
O1—Ni1—O2	171.05 (8)	C57—C52—C53	120.3 (3)
O4—Ni1—O2	87.17 (9)	C57—C52—N8	117.2 (3)
N2—Ni1—O2	91.63 (9)	C53—C52—N8	122.5 (3)
N1—Ni1—O2	78.81 (9)	C54—C53—C52	120.0 (3)
O1—Ni1—O3	91.53 (9)	C55—C54—C53	119.7 (3)
O4—Ni1—O3	168.63 (8)	C54—C55—C56	120.5 (3)
N2—Ni1—O3	77.61 (9)	C55—C56—C57	120.3 (3)
N1—Ni1—O3	89.95 (9)	O11—C57—C56	123.9 (3)
O2—Ni1—O3	89.33 (8)	O11—C57—C52	117.0 (3)
N6—Ni2—O7	93.28 (9)	C56—C57—C52	119.1 (3)
N6—Ni2—N5	168.52 (10)	O8—C58—C59	121.1 (3)
O7—Ni2—N5	97.74 (9)	O8—C58—C63	117.9 (3)
N6—Ni2—O9	89.83 (9)	C59—C58—C63	121.0 (3)
O7—Ni2—O9	93.15 (8)	C58—C59—C60	120.1 (3)
N5—Ni2—O9	92.75 (9)	C59—C60—C61	119.3 (3)
N6—Ni2—O10	79.25 (9)	C62—C61—C60	120.9 (3)
O7—Ni2—O10	170.51 (9)	C61—C62—C63	120.4 (3)
N5—Ni2—O10	89.45 (9)	C58—C63—C62	118.3 (3)
O9—Ni2—O10	92.67 (9)	C58—C63—N5	115.7 (3)
N6—Ni2—O8	97.63 (9)	C62—C63—N5	126.0 (3)
O7—Ni2—O8	86.32 (8)	N5—C64—C65	126.3 (3)

N5—Ni2—O8	79.95 (9)	C66—C65—C71	119.4 (3)
O9—Ni2—O8	172.53 (8)	C66—C65—C64	115.4 (3)
O10—Ni2—O8	88.88 (9)	C71—C65—C64	125.2 (3)
O1—C1—C8	123.8 (3)	C65—C66—C67	124.1 (3)
O1—C1—C2	119.5 (2)	C69—C67—C66	117.0 (3)
C8—C1—C2	116.6 (2)	C69—C67—C68	122.4 (3)
C3—C2—C4	116.9 (3)	C66—C67—C68	120.6 (3)
C3—C2—C1	122.0 (3)	C67—C69—C70	122.2 (3)
C4—C2—C1	121.1 (3)	C69—C70—C72	116.3 (3)
N4—C3—C2	123.2 (3)	C69—C70—C71	121.0 (3)
C5—C4—C2	121.5 (3)	C72—C70—C71	122.7 (3)
C4—C5—C7	117.3 (3)	O9—C71—C65	124.5 (3)
C4—C5—C6	122.6 (3)	O9—C71—C70	119.2 (2)
C7—C5—C6	120.1 (3)	C65—C71—C70	116.3 (3)
C5—C7—C8	124.1 (3)	N7—C72—C70	126.3 (3)
C7—C8—C1	119.0 (3)	C74—C73—C78	120.2 (3)
C7—C8—C9	115.9 (2)	C74—C73—N7	121.8 (3)
C1—C8—C9	125.0 (2)	C78—C73—N7	118.0 (3)
N1—C9—C8	126.1 (3)	C73—C74—C75	120.0 (3)
C11—C10—C15	118.5 (3)	C76—C75—C74	119.9 (3)
C11—C10—N1	125.1 (2)	C75—C76—C77	120.7 (3)
C15—C10—N1	116.4 (2)	C76—C77—C78	120.0 (3)
C12—C11—C10	119.5 (3)	O12—C78—C77	123.3 (3)
C13—C12—C11	121.0 (3)	O12—C78—C73	117.5 (3)
C12—C13—C14	120.0 (3)	C77—C78—C73	119.1 (3)
C15—C14—C13	119.3 (3)	C80—C79—C84	118.3 (3)
O2—C15—C14	122.8 (2)	C80—C79—N6	126.4 (3)
O2—C15—C10	115.5 (2)	C84—C79—N6	115.2 (3)
C14—C15—C10	121.6 (2)	C81—C80—C79	120.3 (3)
O3—C16—C17	123.8 (3)	C80—C81—C82	120.2 (3)
O3—C16—C21	115.1 (2)	C83—C82—C81	120.2 (3)
C17—C16—C21	121.1 (2)	C84—C83—C82	119.5 (3)
C18—C17—C16	119.2 (3)	O10—C84—C83	122.9 (3)
C17—C18—C19	120.7 (3)	O10—C84—C79	115.7 (3)
C20—C19—C18	120.3 (3)	C83—C84—C79	121.4 (3)
C19—C20—C21	119.9 (3)	C9—N1—C10	120.7 (2)
C16—C21—C20	118.9 (3)	C9—N1—Ni1	123.2 (2)
C16—C21—N2	116.1 (2)	C10—N1—Ni1	114.96 (18)
C20—C21—N2	125.0 (3)	C22—N2—C21	120.9 (2)
N2—C22—C23	125.5 (2)	C22—N2—Ni1	123.3 (2)
C24—C23—C29	119.6 (3)	C21—N2—Ni1	114.81 (18)
C24—C23—C22	115.7 (2)	C30—N3—C31	127.0 (3)
C29—C23—C22	124.6 (3)	C3—N4—C37	126.5 (3)
C23—C24—C25	124.4 (3)	C64—N5—C63	120.4 (2)
C27—C25—C24	116.4 (3)	C64—N5—Ni2	124.7 (2)
C27—C25—C26	123.0 (3)	C63—N5—Ni2	114.64 (19)
C24—C25—C26	120.5 (3)	C47—N6—C79	121.0 (3)
C25—C27—C28	122.0 (3)	C47—N6—Ni2	124.7 (2)
C27—C28—C30	117.2 (3)	C79—N6—Ni2	114.19 (19)
C27—C28—C29	121.6 (3)	C72—N7—C73	125.0 (3)
C30—C28—C29	121.2 (3)	C43—N8—C52	126.5 (3)

O4—C29—C28	119.8 (2)	C1—O1—Ni1	126.23 (18)
O4—C29—C23	124.4 (3)	C15—O2—Ni1	113.52 (16)
C28—C29—C23	115.9 (3)	C16—O3—Ni1	111.95 (17)
N3—C30—C28	124.0 (3)	C29—O4—Ni1	124.47 (18)
C32—C31—C36	121.2 (3)	C45—O7—Ni2	125.86 (18)
C32—C31—N3	122.9 (3)	C58—O8—Ni2	111.77 (17)
C36—C31—N3	115.9 (3)	C71—O9—Ni2	126.24 (18)
C31—C32—C33	119.0 (3)	C84—O10—Ni2	113.20 (17)

Table S7. Crystallographical details of $[Ni(H_3L)_2](NO_3)_2 \cdot 4MeOH$ (**B**).

Chemical formula	$C_{42}H_{36}N_4NiO_6 \cdot 2(NO_3) \cdot 4(CH_4O)$
M_r	939.56 g mol^{-1}
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	173
a, b, c (Å)	13.6631 (8), 55.396 (3), 17.4219 (10)
β	101.750 (2)°
V (Å^3)	12910.1 (13)
Z	12
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.53
Crystal size (mm)	0.19 × 0.15 × 0.10
Diffractometer	Bruker *APEX*-II CCD diffractometer
Absorption correction	Multi-scan Bruker *SADABS*
T_{min}, T_{max}	0.61, 0.74
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	63976, 13531, 10525
R_{int}	0.151
θ_{max} (°)	20.8
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.500
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.117, 0.302, 1.02
No. of reflections	13531

No. of parameters	1774
No. of restraints	1614
H-atom treatment	H-atom parameters constrained $w = 1/[\sigma^2(F_o^2) + (0.1201P)^2 + 216.9637P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.25, −1.41

Table S8. Geometrical parameters for $[Ni(H_3L)_2](NO_3)_2 \cdot 4MeOH$ (**B**) (Å and °).

Ni1—N2A	1.993 (10)	C34B—C36B	1.390 (15)
Ni1—O5A	2.001 (7)	C34B—C35B	1.428 (16)
Ni1—N4A	2.001 (10)	C35B—O5B	1.288 (13)
Ni1—O2A	2.021 (7)	C36B—N4B	1.322 (14)
Ni1—O6A	2.079 (8)	C37B—C38B	1.375 (16)
Ni1—O3A	2.093 (8)	C37B—C42B	1.391 (16)
C1A—O1A	1.356 (15)	C37B—N4B	1.416 (15)
C1A—C6A	1.410 (18)	C38B—C39B	1.367 (17)
C1A—C2A	1.378 (18)	C39B—C40B	1.396 (17)
C2A—C3A	1.365 (19)	C40B—C41B	1.350 (17)
C3A—C4A	1.335 (19)	C41B—C42B	1.353 (16)
C4A—C5A	1.397 (18)	C42B—O6B	1.344 (14)
C5A—C6A	1.419 (18)	Ni3—N1C	2.010 (10)
C6A—N1A	1.429 (16)	Ni3—N4C	2.008 (10)
C7A—N1A	1.293 (15)	Ni3—O5C	2.035 (8)
C7A—C8A	1.416 (17)	Ni3—O2C	2.039 (8)
C8A—C9A	1.405 (17)	Ni3—O6C	2.051 (8)
C8A—C14A	1.433 (17)	Ni3—O1C	2.122 (9)
C9A—C10A	1.385 (17)	C1C—O1C	1.330 (16)
C10A—C12A	1.404 (17)	C1C—C2C	1.371 (19)
C10A—C11A	1.494 (17)	C1C—C6C	1.436 (19)
C12A—C13A	1.361 (16)	C2C—C3C	1.42 (2)
C13A—C14A	1.438 (17)	C3C—C4C	1.38 (2)
C13A—C15A	1.443 (17)	C4C—C5C	1.40 (2)

C14A—O2A	1.298 (13)	C5C—C6C	1.41 (2)
C15A—N2A	1.296 (15)	C6C—N1C	1.409 (17)
C16A—C17A	1.398 (17)	C7C—N1C	1.295 (15)
C16A—C21A	1.384 (17)	C7C—C8C	1.454 (18)
C16A—N2A	1.436 (15)	C8C—C9C	1.411 (17)
C17A—C18A	1.383 (18)	C8C—C14C	1.433 (17)
C18A—C19A	1.348 (18)	C9C—C10C	1.377 (18)
C19A—C20A	1.341 (18)	C10C—C12C	1.368 (18)
C20A—C21A	1.401 (18)	C10C—C11C	1.523 (17)
C21A—O3A	1.352 (15)	C12C—C13C	1.439 (17)
C22A—O4A	1.380 (15)	C13C—C15C	1.401 (18)
C22A—C27A	1.346 (17)	C13C—C14C	1.423 (17)
C22A—C23A	1.397 (17)	C14C—O2C	1.293 (13)
C23A—C24A	1.377 (17)	C15C—N2C	1.323 (15)
C24A—C25A	1.393 (17)	C16C—C17C	1.387 (18)
C25A—C26A	1.388 (17)	C16C—C21C	1.381 (17)
C26A—C27A	1.370 (17)	C16C—N2C	1.409 (16)
C27A—N3A	1.434 (15)	C17C—C18C	1.352 (18)
C28A—N3A	1.338 (14)	C18C—C19C	1.367 (18)
C28A—C29A	1.381 (16)	C19C—C20C	1.416 (18)
C29A—C30A	1.416 (16)	C20C—C21C	1.382 (18)
C29A—C35A	1.453 (16)	C21C—O3C	1.372 (15)
C30A—C31A	1.376 (16)	C22C—O4C	1.348 (18)
C31A—C33A	1.412 (16)	C22C—C27C	1.39 (2)
C31A—C32A	1.478 (16)	C22C—C23C	1.41 (2)
C33A—C34A	1.399 (16)	C23C—C24C	1.39 (2)
C34A—C36A	1.451 (16)	C24C—C25C	1.37 (2)
C34A—C35A	1.459 (16)	C25C—C26C	1.36 (2)
C35A—O5A	1.293 (13)	C26C—C27C	1.39 (2)
C36A—N4A	1.276 (14)	C27C—N3C	1.413 (17)
C37A—C38A	1.373 (17)	C28C—N3C	1.305 (16)
C37A—C42A	1.405 (17)	C28C—C29C	1.414 (17)
C37A—N4A	1.439 (15)	C29C—C30C	1.407 (18)
C38A—C39A	1.399 (17)	C29C—C35C	1.401 (18)
C39A—C40A	1.367 (18)	C30C—C31C	1.355 (18)
C40A—C41A	1.378 (18)	C31C—C33C	1.361 (18)
C41A—C42A	1.369 (17)	C31C—C32C	1.490 (19)
C42A—O6A	1.363 (15)	C33C—C34C	1.417 (18)
Ni2—N3B	1.988 (10)	C34C—C35C	1.436 (17)
Ni2—N2B	2.002 (10)	C34C—C36C	1.430 (17)
Ni2—O2B	2.048 (7)	C35C—O5C	1.311 (15)
Ni2—O4B	2.044 (8)	C36C—N4C	1.295 (16)
Ni2—O5B	2.070 (7)	C37C—C42C	1.397 (18)
Ni2—O3B	2.145 (8)	C37C—C38C	1.395 (17)
C1B—C2B	1.370 (17)	C37C—N4C	1.448 (16)
C1B—O1B	1.366 (15)	C38C—C39C	1.365 (18)
C1B—C6B	1.400 (18)	C39C—C40C	1.354 (19)
C2B—C3B	1.376 (18)	C40C—C41C	1.374 (18)
C3B—C4B	1.361 (18)	C41C—C42C	1.401 (18)
C4B—C5B	1.385 (17)	C42C—O6C	1.339 (14)
C5B—C6B	1.384 (17)	N1—O1	1.099 (17)

C6B—N1B	1.424 (15)	N1—O2	1.178 (19)
C7B—N1B	1.310 (14)	N1—O3	1.31 (2)
C7B—C8B	1.404 (16)	N2—O6	1.219 (19)
C8B—C14B	1.413 (16)	N2—O4	1.245 (19)
C8B—C9B	1.419 (16)	N2—O5	1.307 (18)
C9B—C10B	1.384 (16)	N3—O7	1.26 (3)
C10B—C12B	1.390 (16)	N3—O8	1.25 (3)
C10B—C11B	1.493 (16)	N3—O9	1.35 (3)
C12B—C13B	1.386 (16)	N4—O11	1.14 (2)
C13B—C14B	1.443 (16)	N4—O10	1.21 (2)
C13B—C15B	1.439 (16)	N4—O12	1.21 (2)
C14B—O2B	1.296 (13)	N5—O13	1.181 (15)
C15B—N2B	1.282 (15)	N5—O15	1.202 (16)
C16B—C21B	1.389 (18)	N5—O14	1.229 (17)
C16B—C17B	1.386 (18)	N6—O18	1.09 (2)
C16B—N2B	1.415 (15)	N6—O16	1.14 (3)
C17B—C18B	1.392 (18)	N6—O17	1.29 (3)
C18B—C19B	1.337 (19)	O20—C20	1.400 (2)
C19B—C20B	1.364 (19)	O21—C21	1.400 (2)
C20B—C21B	1.404 (17)	O22—C22	1.400 (2)
C21B—O3B	1.363 (15)	O23—C23	1.400 (2)
C22B—O4B	1.331 (15)	O24—C24	1.401 (2)
C22B—C27B	1.393 (19)	O25—C25	1.400 (2)
C22B—C23B	1.400 (19)		
C23B—C24B	1.36 (2)		
C24B—C25B	1.41 (2)	C22B—C27B—N3B	112.0 (12)
C25B—C26B	1.41 (2)	N3B—C28B—C29B	123.1 (12)
C26B—C27B	1.335 (19)	C30B—C29B—C35B	119.1 (11)
C27B—N3B	1.439 (17)	C30B—C29B—C28B	117.0 (11)
C28B—N3B	1.301 (15)	C35B—C29B—C28B	123.8 (11)
C28B—C29B	1.467 (17)	C29B—C30B—C31B	125.7 (11)
C29B—C30B	1.367 (16)	C33B—C31B—C30B	115.5 (11)
C29B—C35B	1.430 (16)	C33B—C31B—C32B	122.6 (10)
C30B—C31B	1.392 (16)	C30B—C31B—C32B	121.9 (10)
C31B—C33B	1.363 (16)	C31B—C33B—C34B	123.0 (11)
C31B—C32B	1.517 (16)	C36B—C34B—C33B	118.6 (10)
C33B—C34B	1.421 (16)	C36B—C34B—C35B	121.3 (10)
		C33B—C34B—C35B	120.0 (10)
N2A—Ni1—O5A	94.7 (3)	O5B—C35B—C34B	120.2 (10)
N2A—Ni1—N4A	169.2 (4)	O5B—C35B—C29B	123.1 (10)
O5A—Ni1—N4A	93.3 (3)	C34B—C35B—C29B	116.7 (10)
N2A—Ni1—O2A	93.7 (4)	N4B—C36B—C34B	124.1 (11)
O5A—Ni1—O2A	91.4 (3)	C38B—C37B—C42B	120.5 (11)
N4A—Ni1—O2A	93.5 (3)	C38B—C37B—N4B	122.5 (10)
N2A—Ni1—O6A	91.3 (4)	C42B—C37B—N4B	116.9 (10)
O5A—Ni1—O6A	172.5 (3)	C39B—C38B—C37B	119.9 (12)
N4A—Ni1—O6A	80.2 (4)	C38B—C39B—C40B	119.2 (12)
O2A—Ni1—O6A	92.7 (3)	C41B—C40B—C39B	119.5 (12)
N2A—Ni1—O3A	80.2 (4)	C42B—C41B—C40B	122.4 (12)
O5A—Ni1—O3A	89.8 (3)	C41B—C42B—O6B	124.4 (11)
N4A—Ni1—O3A	92.5 (3)	C41B—C42B—C37B	118.3 (11)

O2A—Ni1—O3A	173.8 (3)	O6B—C42B—C37B	117.3 (10)
O6A—Ni1—O3A	86.7 (3)	C14B—O2B—Ni2	121.6 (6)
O1A—C1A—C6A	115.8 (11)	C21B—O3B—Ni2	111.9 (7)
O1A—C1A—C2A	124.4 (12)	C22B—O4B—Ni2	111.6 (8)
C6A—C1A—C2A	119.8 (12)	C35B—O5B—Ni2	117.5 (7)
C3A—C2A—C1A	120.9 (14)	N1C—Ni3—N4C	169.8 (4)
C4A—C3A—C2A	120.7 (14)	N1C—Ni3—O5C	96.9 (4)
C3A—C4A—C5A	121.7 (13)	N4C—Ni3—O5C	89.3 (4)
C4A—C5A—C6A	118.6 (13)	N1C—Ni3—O2C	90.8 (4)
C1A—C6A—N1A	118.1 (11)	N4C—Ni3—O2C	97.8 (4)
C1A—C6A—C5A	118.2 (12)	O5C—Ni3—O2C	84.7 (3)
N1A—C6A—C5A	123.7 (12)	N1C—Ni3—O6C	92.3 (4)
N1A—C7A—C8A	124.3 (12)	N4C—Ni3—O6C	81.2 (4)
C9A—C8A—C7A	117.3 (11)	O5C—Ni3—O6C	170.3 (3)
C9A—C8A—C14A	120.8 (11)	O2C—Ni3—O6C	98.3 (3)
C7A—C8A—C14A	121.9 (11)	N1C—Ni3—O1C	77.9 (4)
C10A—C9A—C8A	123.1 (12)	N4C—Ni3—O1C	93.9 (4)
C9A—C10A—C12A	114.5 (11)	O5C—Ni3—O1C	91.7 (3)
C9A—C10A—C11A	124.5 (11)	O2C—Ni3—O1C	167.7 (3)
C12A—C10A—C11A	120.9 (12)	O6C—Ni3—O1C	87.2 (3)
C13A—C12A—C10A	126.1 (12)	O1C—C1C—C2C	125.5 (13)
C12A—C13A—C14A	119.4 (11)	O1C—C1C—C6C	115.8 (12)
C12A—C13A—C15A	115.7 (11)	C2C—C1C—C6C	118.7 (14)
C14A—C13A—C15A	124.9 (11)	C1C—C2C—C3C	120.4 (15)
O2A—C14A—C8A	119.4 (11)	C4C—C3C—C2C	121.3 (15)
O2A—C14A—C13A	124.5 (10)	C3C—C4C—C5C	119.5 (15)
C8A—C14A—C13A	116.0 (11)	C6C—C5C—C4C	119.5 (15)
N2A—C15A—C13A	126.9 (12)	N1C—C6C—C5C	125.1 (13)
C17A—C16A—C21A	120.2 (12)	N1C—C6C—C1C	114.4 (12)
C17A—C16A—N2A	125.1 (11)	C5C—C6C—C1C	120.5 (13)
C21A—C16A—N2A	114.7 (11)	N1C—C7C—C8C	122.7 (12)
C16A—C17A—C18A	119.0 (12)	C9C—C8C—C14C	118.6 (12)
C19A—C18A—C17A	120.8 (13)	C9C—C8C—C7C	115.5 (11)
C20A—C19A—C18A	120.6 (13)	C14C—C8C—C7C	125.6 (11)
C19A—C20A—C21A	121.6 (13)	C10C—C9C—C8C	124.6 (13)
O3A—C21A—C16A	118.5 (11)	C9C—C10C—C12C	117.9 (12)
O3A—C21A—C20A	123.7 (12)	C9C—C10C—C11C	119.8 (13)
C16A—C21A—C20A	117.8 (12)	C12C—C10C—C11C	122.2 (13)
O4A—C22A—C27A	119.6 (11)	C10C—C12C—C13C	120.7 (13)
O4A—C22A—C23A	120.2 (11)	C15C—C13C—C14C	122.2 (11)
C27A—C22A—C23A	120.2 (12)	C15C—C13C—C12C	116.3 (12)
C24A—C23A—C22A	118.9 (12)	C14C—C13C—C12C	121.4 (12)
C23A—C24A—C25A	120.2 (13)	O2C—C14C—C13C	120.1 (11)
C26A—C25A—C24A	119.8 (12)	O2C—C14C—C8C	123.1 (11)
C27A—C26A—C25A	118.8 (12)	C13C—C14C—C8C	116.8 (11)
C22A—C27A—C26A	122.0 (12)	N2C—C15C—C13C	123.9 (12)
C22A—C27A—N3A	116.9 (11)	C17C—C16C—C21C	119.5 (13)
C26A—C27A—N3A	120.9 (11)	C17C—C16C—N2C	123.8 (11)
N3A—C28A—C29A	125.8 (11)	C21C—C16C—N2C	116.4 (12)
C28A—C29A—C30A	117.7 (11)	C18C—C17C—C16C	121.9 (13)
C28A—C29A—C35A	122.2 (10)	C17C—C18C—C19C	118.8 (14)

C30A—C29A—C35A	120.0 (11)	C18C—C19C—C20C	121.4 (13)
C31A—C30A—C29A	123.1 (11)	C21C—C20C—C19C	118.3 (12)
C30A—C31A—C33A	117.8 (11)	C20C—C21C—O3C	121.9 (11)
C30A—C31A—C32A	122.6 (11)	C20C—C21C—C16C	120.0 (13)
C33A—C31A—C32A	119.6 (11)	O3C—C21C—C16C	118.0 (12)
C34A—C33A—C31A	122.5 (11)	O4C—C22C—C27C	117.3 (13)
C33A—C34A—C36A	114.9 (10)	O4C—C22C—C23C	123.9 (16)
C33A—C34A—C35A	120.3 (11)	C27C—C22C—C23C	118.8 (16)
C36A—C34A—C35A	124.7 (10)	C24C—C23C—C22C	117.0 (17)
O5A—C35A—C29A	119.2 (10)	C25C—C24C—C23C	124.0 (16)
O5A—C35A—C34A	124.6 (10)	C26C—C25C—C24C	117.9 (17)
C29A—C35A—C34A	116.1 (10)	C25C—C26C—C27C	120.9 (17)
N4A—C36A—C34A	125.6 (11)	C22C—C27C—C26C	120.9 (14)
C38A—C37A—C42A	117.8 (11)	C22C—C27C—N3C	117.6 (14)
C38A—C37A—N4A	126.0 (11)	C26C—C27C—N3C	121.5 (15)
C42A—C37A—N4A	116.1 (11)	N3C—C28C—C29C	125.7 (13)
C37A—C38A—C39A	120.6 (12)	C30C—C29C—C28C	116.5 (12)
C40A—C39A—C38A	119.2 (13)	C30C—C29C—C35C	121.7 (12)
C39A—C40A—C41A	122.3 (13)	C28C—C29C—C35C	121.9 (13)
C40A—C41A—C42A	117.5 (12)	C31C—C30C—C29C	122.5 (13)
O6A—C42A—C41A	121.7 (11)	C30C—C31C—C33C	117.2 (13)
O6A—C42A—C37A	115.6 (11)	C30C—C31C—C32C	121.9 (13)
C41A—C42A—C37A	122.6 (12)	C33C—C31C—C32C	120.9 (13)
C14A—O2A—Ni1	125.3 (7)	C31C—C33C—C34C	123.7 (13)
C21A—O3A—Ni1	112.0 (7)	C33C—C34C—C35C	119.1 (12)
C35A—O5A—Ni1	125.9 (7)	C33C—C34C—C36C	116.3 (11)
C42A—O6A—Ni1	114.1 (7)	C35C—C34C—C36C	124.6 (12)
N3B—Ni2—N2B	170.3 (4)	O5C—C35C—C29C	120.8 (11)
N3B—Ni2—O2B	97.6 (4)	O5C—C35C—C34C	123.4 (11)
N2B—Ni2—O2B	91.0 (3)	C29C—C35C—C34C	115.8 (12)
N3B—Ni2—O4B	79.9 (4)	N4C—C36C—C34C	124.3 (12)
N2B—Ni2—O4B	94.8 (4)	C42C—C37C—C38C	120.9 (12)
O2B—Ni2—O4B	97.5 (3)	C42C—C37C—N4C	114.2 (11)
N3B—Ni2—O5B	88.6 (4)	C38C—C37C—N4C	124.8 (12)
N2B—Ni2—O5B	96.5 (3)	C39C—C38C—C37C	118.8 (14)
O2B—Ni2—O5B	85.0 (3)	C40C—C39C—C38C	120.7 (13)
O4B—Ni2—O5B	168.4 (3)	C39C—C40C—C41C	122.2 (13)
N3B—Ni2—O3B	93.5 (4)	C40C—C41C—C42C	118.8 (14)
N2B—Ni2—O3B	78.2 (4)	O6C—C42C—C41C	122.7 (12)
O2B—Ni2—O3B	168.3 (3)	O6C—C42C—C37C	118.8 (11)
O4B—Ni2—O3B	88.0 (3)	C41C—C42C—C37C	118.5 (12)
O5B—Ni2—O3B	91.7 (3)	C7A—N1A—C6A	125.2 (11)
C2B—C1B—O1B	125.1 (12)	C15A—N2A—C16A	121.9 (11)
C2B—C1B—C6B	119.4 (12)	C15A—N2A—Ni1	124.0 (8)
O1B—C1B—C6B	115.5 (11)	C16A—N2A—Ni1	114.1 (8)
C1B—C2B—C3B	120.3 (13)	C28A—N3A—C27A	126.6 (10)
C4B—C3B—C2B	120.7 (12)	C36A—N4A—C37A	120.6 (10)
C3B—C4B—C5B	120.3 (13)	C36A—N4A—Ni1	125.8 (8)
C6B—C5B—C4B	119.4 (12)	C37A—N4A—Ni1	113.5 (7)
C5B—C6B—C1B	119.9 (11)	C7B—N1B—C6B	126.2 (10)
C5B—C6B—N1B	122.5 (11)	C15B—N2B—C16B	120.4 (11)

C1B—C6B—N1B	117.5 (11)	C15B—N2B—Ni2	125.1 (8)
N1B—C7B—C8B	124.3 (11)	C16B—N2B—Ni2	114.0 (8)
C14B—C8B—C7B	122.3 (11)	C28B—N3B—C27B	120.5 (11)
C14B—C8B—C9B	121.6 (10)	C28B—N3B—Ni2	125.1 (9)
C7B—C8B—C9B	116.0 (10)	C27B—N3B—Ni2	113.4 (8)
C10B—C9B—C8B	121.7 (10)	C36B—N4B—C37B	127.0 (10)
C9B—C10B—C12B	115.9 (11)	C7C—N1C—C6C	121.0 (11)
C9B—C10B—C11B	122.4 (11)	C7C—N1C—Ni3	125.0 (9)
C12B—C10B—C11B	121.7 (11)	C6C—N1C—Ni3	113.8 (8)
C13B—C12B—C10B	125.6 (11)	C15C—N2C—C16C	125.6 (11)
C12B—C13B—C14B	118.5 (10)	C28C—N3C—C27C	127.0 (13)
C12B—C13B—C15B	116.3 (11)	C36C—N4C—C37C	122.4 (11)
C14B—C13B—C15B	125.2 (11)	C36C—N4C—Ni3	126.1 (8)
O2B—C14B—C8B	120.0 (10)	C37C—N4C—Ni3	111.2 (8)
O2B—C14B—C13B	123.5 (10)	C1C—O1C—Ni3	112.5 (8)
C8B—C14B—C13B	116.6 (10)	C14C—O2C—Ni3	118.4 (7)
N2B—C15B—C13B	124.9 (11)	C35C—O5C—Ni3	122.3 (7)
C21B—C16B—C17B	118.8 (11)	C42C—O6C—Ni3	111.7 (8)
C21B—C16B—N2B	116.6 (11)	O1—N1—O2	143 (2)
C17B—C16B—N2B	124.6 (12)	O1—N1—O3	109 (2)
C18B—C17B—C16B	120.6 (14)	O2—N1—O3	108.0 (17)
C19B—C18B—C17B	118.4 (14)	O6—N2—O4	128.1 (16)
C18B—C19B—C20B	124.3 (13)	O6—N2—O5	116.0 (18)
C19B—C20B—C21B	117.2 (14)	O4—N2—O5	115.9 (17)
O3B—C21B—C16B	115.8 (10)	O7—N3—O8	118 (3)
O3B—C21B—C20B	123.6 (12)	O7—N3—O9	115 (3)
C16B—C21B—C20B	120.6 (13)	O8—N3—O9	127 (3)
O4B—C22B—C27B	119.2 (12)	O11—N4—O10	124 (3)
O4B—C22B—C23B	122.1 (13)	O11—N4—O12	127 (3)
C27B—C22B—C23B	118.6 (13)	O10—N4—O12	109 (2)
C24B—C23B—C22B	120.2 (15)	O13—N5—O15	124.3 (15)
C23B—C24B—C25B	121.0 (15)	O13—N5—O14	125.3 (15)
C26B—C25B—C24B	117.2 (15)	O15—N5—O14	109.9 (13)
C27B—C26B—C25B	121.6 (15)	O18—N6—O16	129 (3)
C26B—C27B—C22B	121.1 (13)	O18—N6—O17	121 (3)
C26B—C27B—N3B	126.7 (13)	O16—N6—O17	109 (3)

7. Electrospray ionisation mass spectrum of compound 1

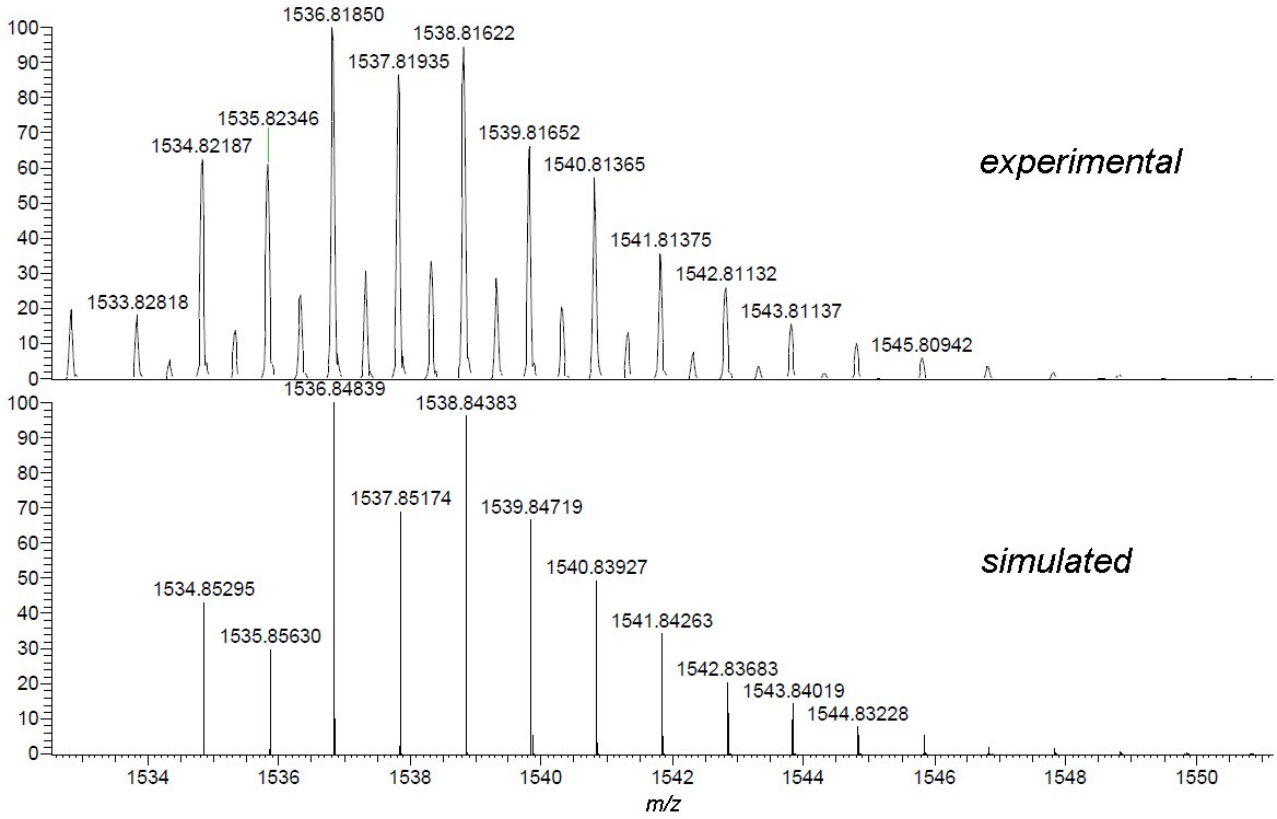


Figure S7. Top: The experimental molecular ion peak of $[Ni_6(L{\cdot}SMe)_3(CO_3)H_2]^+$ (–2 THF, –5 MeOH, –1 CH_2=O) in compound **1** obtained in positive ion mode using ESI mass spectrometry. Bottom: The simulated molecular ion peak of $[Ni_6(L{\cdot}SMe)_3(CO_3)H_2]^+$ in compound **1**. The experimentally detected minor peaks possibly stem from $^{58/60}$Ni isotope combinations in dimeric $[Ni_6(L{\cdot}SMe)_3(CO_3)H_2]_2^{2+}$ aggregates.

8. Solid-state molecular structures of compounds A and B

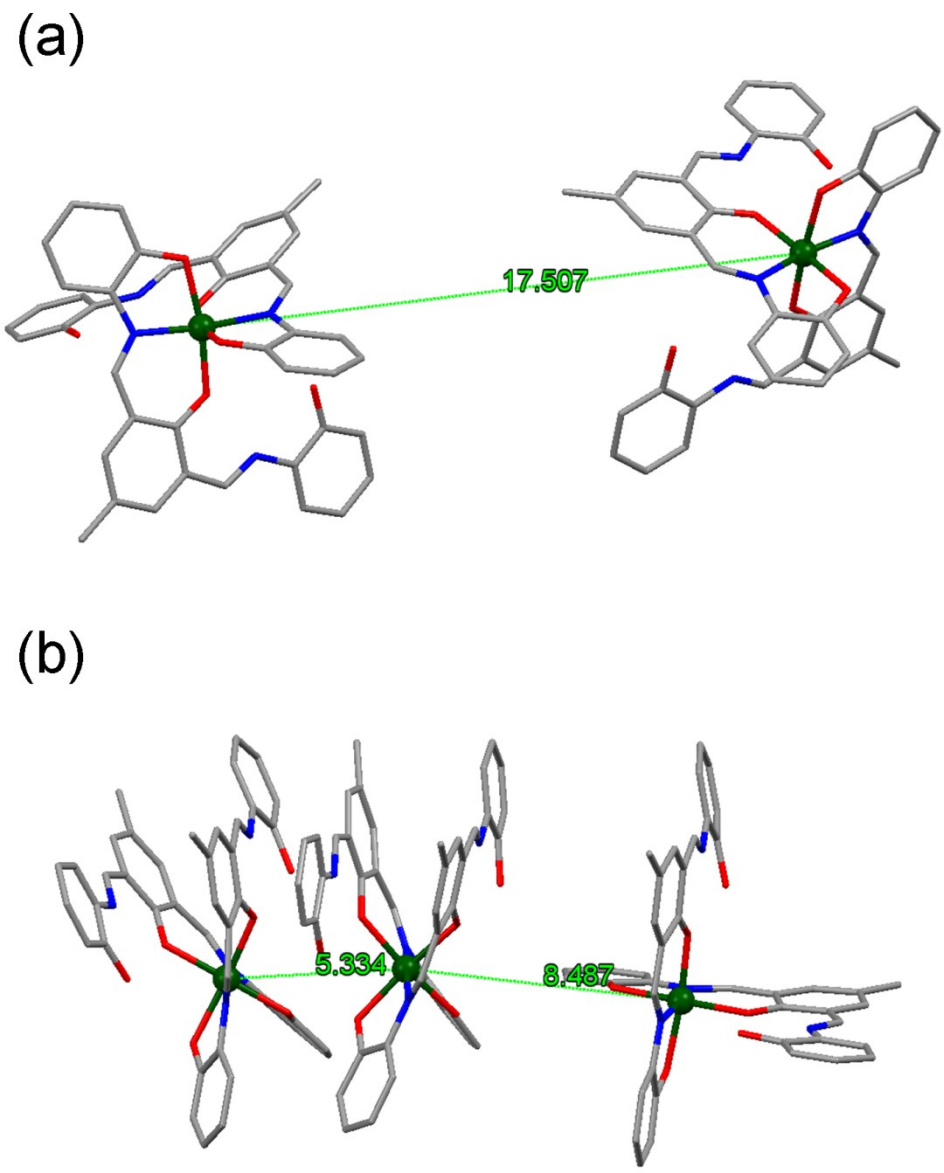


Figure S8. Asymmetric units of mononuclear nickel(II) complexes **A** (a) and **B** (b) with depiction of distances between $[Ni(H_3L)_2]^{2+}$ units. Hydrogen atoms and solvent molecules are omitted for clarity. Colour code: C = grey; N = blue; O = red; Ni = dark green. The nickel atoms are represented as ball-and-stick models. All bond lengths and angles are reported in Tables S6 and S8, respectively.

Each of the $[Ni(H_3L)_2]^{2+}$ structures (Figure S8) consists of an octahedrally coordinated Ni(II) ion ligated by N_2O_4 chelates of the two fully-protonated, thioether-free H_3L Schiff bases. In compound **A**, the Ni–O distances range from 1.998(2) Å to 2.151(2) Å and the Ni–N distances from 2.004(2) Å to 2.014(2) Å. The Ni–O and Ni–N bond lengths in compound **B** lie in the range of 2.001(7) Å – 2.145(8) Å and 1.988(10) Å – 2.010(10) Å, respectively.