Electronic Supplementary Information

From a mononuclear Ni^{II} precursor to antiferromagnetically coupled trinuclear double-stranded helicates

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Physical measurements

Infrared spectra in KBr pellets were recorded with a FTIR-8400S SHIMADZU spectrophotometer in the range 400–3600 cm^{-1}. NMR spectra in $CDCl_3$ were obtained on a Bruker Avance 300 MHz spectrometer at 25 °C. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at 299.948, and 121.420 MHz, respectively. Chemical shifts are reported with reference to $SiMe_4$ (^{1}H) and 85% H_3PO_4 (^{31}P{^{1}H}). Diffuse reflectance spectra were obtained with a Varian Cary 5E spectrometer using polytetrafluoroethylene (PTFE) as a reference. Thermogravimetric (TGA) analyses were performed by a SDT 2960 Simultaneous DTA-TGA instrument in a dynamic air atmosphere (100 mL min^{-1}) from laboratory temperature to 1100 °C with a 10 °C min^{-1} heating rate. Electrospray ionization mass spectra were recorded on a Thermo Fisher Scientific LCQ mass spectrometer on a 10^{-6} M solution in MeOH (the spray voltage was 5 kV and the capillary temperature was 260 °C). Elemental analyses were performed on a Thermoquest Flash EA 1112 Analyzer from CE Instruments. Magnetic susceptibility measurements were obtained with the use of MPMS-XL Quantum Design SQUID magnetometer. The magnetometer operates between 1.8 and 400 K for dc applied fields of up to 70 kOe. Measurements were performed on polycrystalline samples (13.82, 14.59 and 13.39 mg for **1**, **2** and **3**, respectively) loaded into a polyethylene bag (3 × 0.5 × 0.02 cm). Prior to each experiment, the field-dependent magnetization is measured at 100 K in order to verify the absence of any bulk ferromagnetic impurities. For each compound, the ac susceptibility measurements were performed with an oscillating field of 3 Oe with an ac frequency of 1000 Hz but it is worth noting that no out-of- phase AC signal has been detected down to 1.8 K. The magnetic data were corrected for the sample holder and diamagnetic contributions.

Synthesis of complexes 1–3

[NiL$_2$] was prepared following a literature procedure.[1] A EtOH (10 mL) solution of salicylaldehyde or 5-chlorosalicylaldehyde or 5-bromosalicylaldehyde (0.4 mmol; 0.049, 0.063 or 0.081 g, respectively) was added dropwise under vigorous stirring to a suspension of **[NiL$_2$]** (0.2 mmol, 0.151 g) in EtOH (10 mL). The mixture was stirred at room temperature for a further 3 hours and left overnight. Green crystals suitable for single crystal X-ray analysis were obtained on standing after three days.

1. Yield 0.081 g (92%). IR, *v*: 602 (P=S), 996 (POC), 1564 (SCN), 1614 (C=N), 1685 (C=O), 3216 (NH) cm^{-1}. ^{1}H NMR, δ (CDCl$_3$): 0.3–2.9 (m, 34H, *i*C$_3$H$_7$ + C$_5$H$_3$N), 9.2–10.8 (m, 16H, C$_6$H$_4$), 18.8 (br. s, 2H, NH), 21.7 (s, 2H, CHN), 22.4 (s, 2H, CHO, aldehyde) ppm. ^{1}H NMR, δ (DMSO-d_6): 0.7–3.8 (m, 34H, *i*C$_3$H$_7$ + C$_5$H$_3$N), 9.1–10.6 (m, 16H, C$_6$H$_4$), 18.2 (br. s, 2H, NH), 22.4 (s, 2H, CHN), 23.5 (s, 2H, CHO, aldehyde) ppm. ^{31}P{^{1}H} NMR, δ (CDCl$_3$): –317.8 ppm. ^{31}P{^{1}H} NMR, δ (DMSO-d_6): –326.2 ppm. *Anal*. Calc. for $C_{52}H_{56}N_8Ni_3O_{10}P_2S_4$ (1319.34): C 47.34, H 4.28, N 8.49. Found: C 47.42, H 4.23, N 8.57%.

2. Yield 0.097 g (97%). IR, *v*: 598 (P=S), 1001 (POC), 1556 (SCN), 1619 (C=N), 1679 (C=O), 3228 (NH) cm^{-1}. ^{1}H NMR, δ (CDCl$_3$): 0.0–3.5 (m, 34H, *i*C$_3$H$_7$ + C$_5$H$_3$N), 9.7–11.9 (m, 12H, C$_6$H$_3$), 19.1 (br. s, 2H, NH), 22.9 (s, 2H, CHN), 23.6 (s, 2H, CHO, aldehyde) ppm. ^{1}H NMR, δ (DMSO-d_6): 0.4–3.7 (m, 34H, *i*C$_3$H$_7$ + C$_5$H$_3$N), 10.1–12.2 (m, 12H, C$_6$H$_3$), 17.4 (br. s, 2H, NH), 22.1 (s, 2H, CHN), 23.0 (s, 2H, CHO, aldehyde) ppm. ^{31}P{^{1}H} NMR, δ (CDCl$_3$): –309.4 ppm. ^{31}P{^{1}H} NMR, δ (DMSO-d_6): –321.7 ppm. *Anal*. Calc. for $C_{52}H_{56}Cl_4N_8Ni_3O_{12}P_2S_4$ (1493.15): C 41.83, H 3.78, N 7.50. Found: C 41.72, H 3.69, N 7.52%.

3. Yield 0.094 g (86%). IR, *v*: 601 (P=S), 998 (POC), 1560 (SCN), 1622 (C=N), 1682 (C=O), 3236 (NH) cm^{-1}. ^{1}H NMR, δ (CDCl$_3$): 0.6–4.0 (m, 34H, *i*C$_3$H$_7$ + C$_5$H$_3$N), 11.2–12.6 (m, 12H, C$_6$H$_3$), 19.7 (br. s, 2H, NH), 22.7 (s, 2H, CHN), 23.3 (s, 2H, CHO, aldehyde) ppm. ^{1}H NMR, δ (DMSO-d_6): 0.8–4.0 (m, 34H, *i*C$_3$H$_7$ + C$_5$H$_3$N), 10.7–12.4 (m, 12H, C$_6$H$_3$), 18.6 (br. s, 2H, NH), 22.0 (s, 2H, CHN), 23.2 (s, 2H, CHO, aldehyde) ppm. ^{31}P{^{1}H} NMR, δ (CDCl$_3$): –307.6 ppm. ^{31}P{^{1}H} NMR, δ (DMSO-d_6): –318.1 ppm. *Anal*. Calc. for $C_{52}H_{52}Br_4N_8Ni_3O_{10}P_2S_4$ (1634.92): C 38.20, H 3.21, N 6.85. Found: C 38.07, H 3.30, N 6.97%.

X-Ray crystallography

X-ray data collection was performed on a Mar345 image plate detector using Mo-K$_\alpha$ radiation (Zr-filter) at 150(2) K for **1**, 293(2) K for **2** and 160(2) K for **3**. The data were integrated with the crysAlisPro software.[2] The implemented empirical absorption correction was applied. The structures were solved by direct methods using the SHELXS-97 program[3] and refined by full-matrix least squares on $|F^2|$ using SHELXL-97.[3] Non-hydrogen atoms were anisotropically refined and the hydrogen atoms were placed on calculated positions in riding mode with temperature factors fixed at 1.2 times U_{eq} of the parent atoms. Figures were generated using the program Mercury.[4]

Crystal data for 1. $C_{52}H_{56}N_8Ni_3O_{10}P_2S_4$, M_r = 1319.36 g mol^{-1}, monoclinic, space group $C2/c$, a = 18.2300(18), b = 16.8816(11), c = 18.0042(10) Å, β = 92.007(7)°, V = 5537.4(7) Å^3, Z = 4, ρ = 1.583 g cm^{-3},

μ(Mo-Kα) = 1.284 mm^{-1}, reflections: 13484 collected, 5007 unique, R_{int} = 0.042, R_1(all) = 0.0817, wR_2(all) = 0.1840.

Crystal data for 2. $C_{52}H_{52}Cl_4N_8Ni_3O_{10}P_2S_4$, 2($H_2O$), M_r = 1493.16 g mol^{-1}, monoclinic, space group $C2/c$, a = 33.988(9), b = 10.7792(10), c = 23.245(6) Å, β = 130.83(4)°, V = 6444(5) Å^3, Z = 4, ρ = 1.539 g cm^{-3}, μ(Mo-Kα) = 1.276 mm^{-1}, reflections: 13902 collected, 3579 unique, R_{int} = 0.095, R_1(all) = 0.0870, wR_2(all) = 0.1804. The crystals of this compound were very thin and diffracted quite weakly (θ = 21.29°). Although not modeled there are indications of some disorder for the two isopropyl groups. This kind of rotational disorder is often observed and is generally more pronounced at ambient temperature conditions. The O101 atom, that, is in proximity of the isopropyl group, will move along with the isopropyl group. Also for the S14 atom and its parent atom C13, there is tendency to be disordered over two sites (one above the Ni1-N12-C13-N15-C16-N21 ring, the other below). No restraints were added to control the anisotropic displacement parameters of these “disordered atoms” as the elongated temperature factors represent the true nature of motion for these groups.

Crystal data for 3. $C_{52}H_{52}Br_4N_8Ni_3O_{10}P_2S_4$, M_r = 1634.97 g mol^{-1}, monoclinic, space group $C2/c$, a = 33.853(19), b = 10.6228(11), c = 23.605(13) Å, β = 130.11(9)°, V = 6492(10) Å^3, Z = 4, ρ = 1.673 g cm^{-3}, μ(Mo-Kα) = 3.559 mm^{-1}, reflections: 5550 collected, 1429 unique, R_{int} = 0.096, R_1(all) = 0.1087, wR_2(all) = 0.1969. It should be noted that the crystals of **3** diffracted only to 1.33 Å inducing a poor quality of the collected data. Therefore the structure should be regarded as a partial structure determination, for which only global features such as connectivity are accurately determined.

CCDC 905820 (**1**) 905821 (**2**) and 905822 (**3**) contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

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2 Oxford Diffraction Data collection and data reduction, Version 171.34.40.

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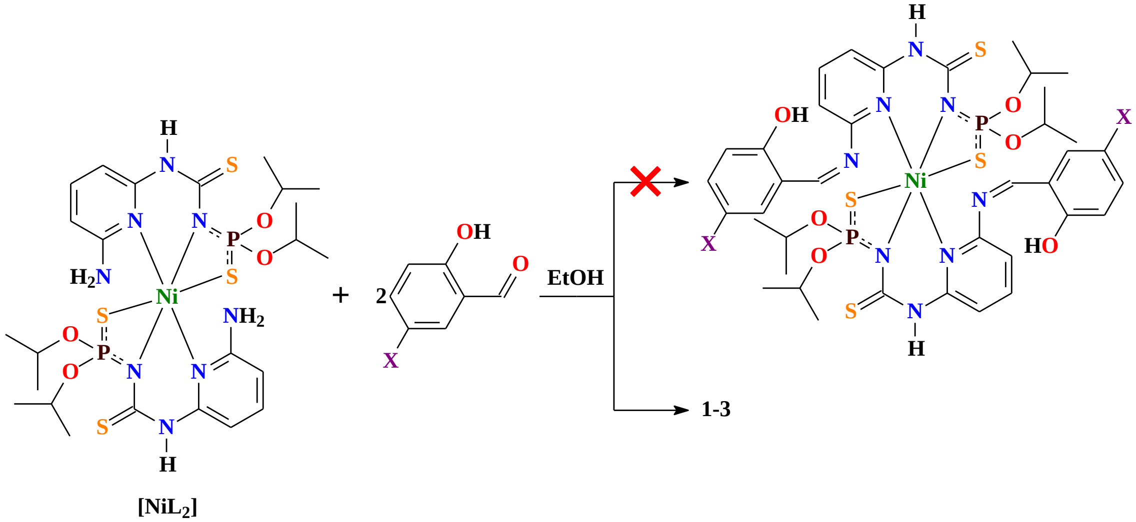
4 I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson and R. Taylor, *Acta Crystallogr.*, 2002, **B58**, 389.



Scheme S1. Preparation of **1** (X = H), **2** (X = Cl) and **3** (X = Br).

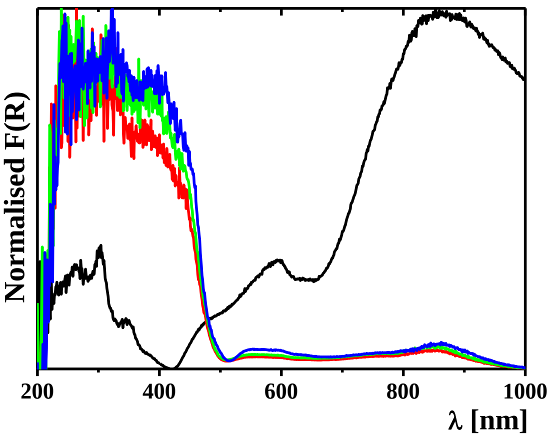


Fig. S1 Normalised Kubelka-Munk spectrum of **[NiL$_2$]** (black), **1** (red), **2** (green) and **3** (blue).

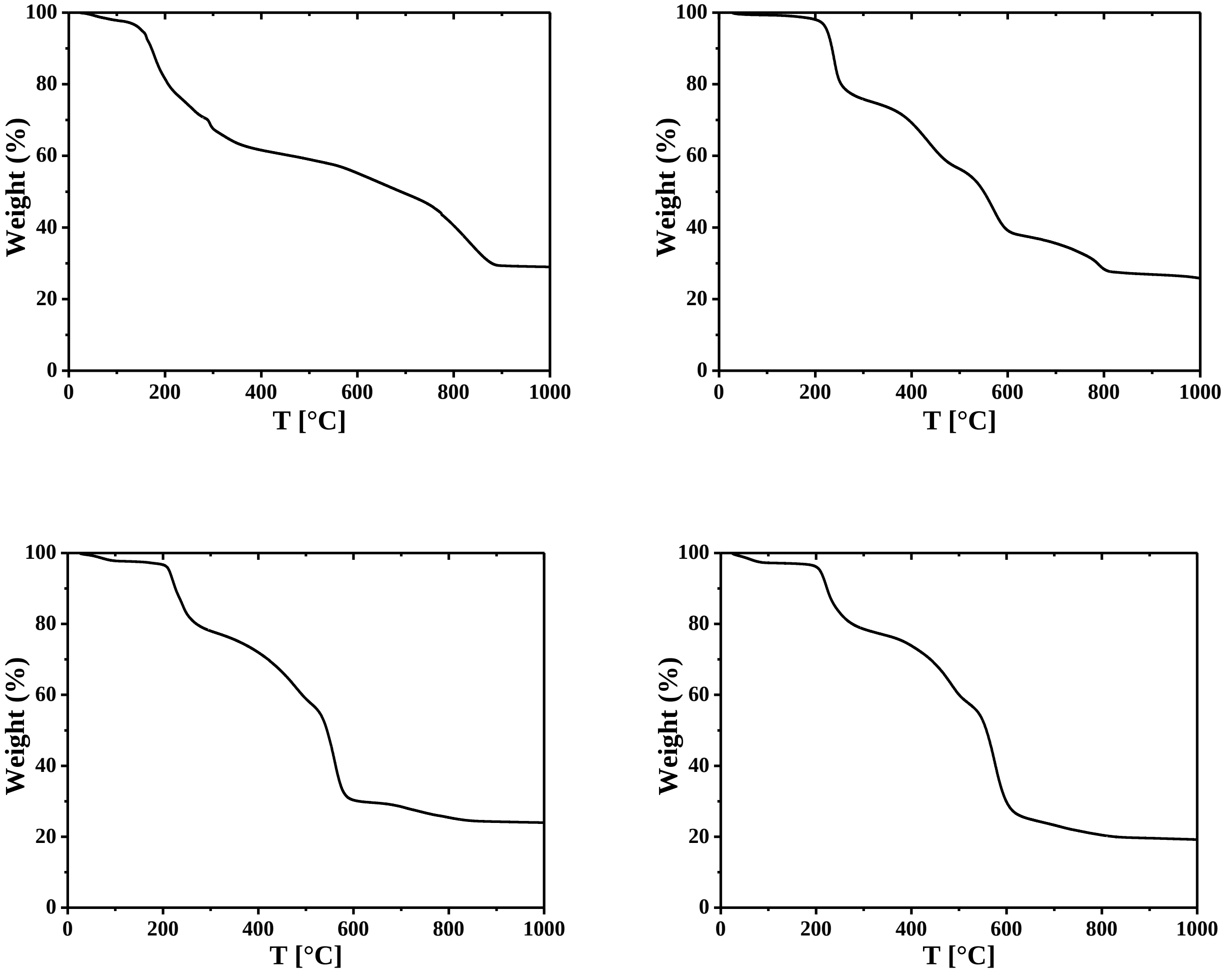


Fig. S2 Thermogravimetric analyses of **[NiL$_2$]** (top left) and **1** (top right), **2** (left bottom) and **3** (right bottom) performed in a dynamic air atmosphere.

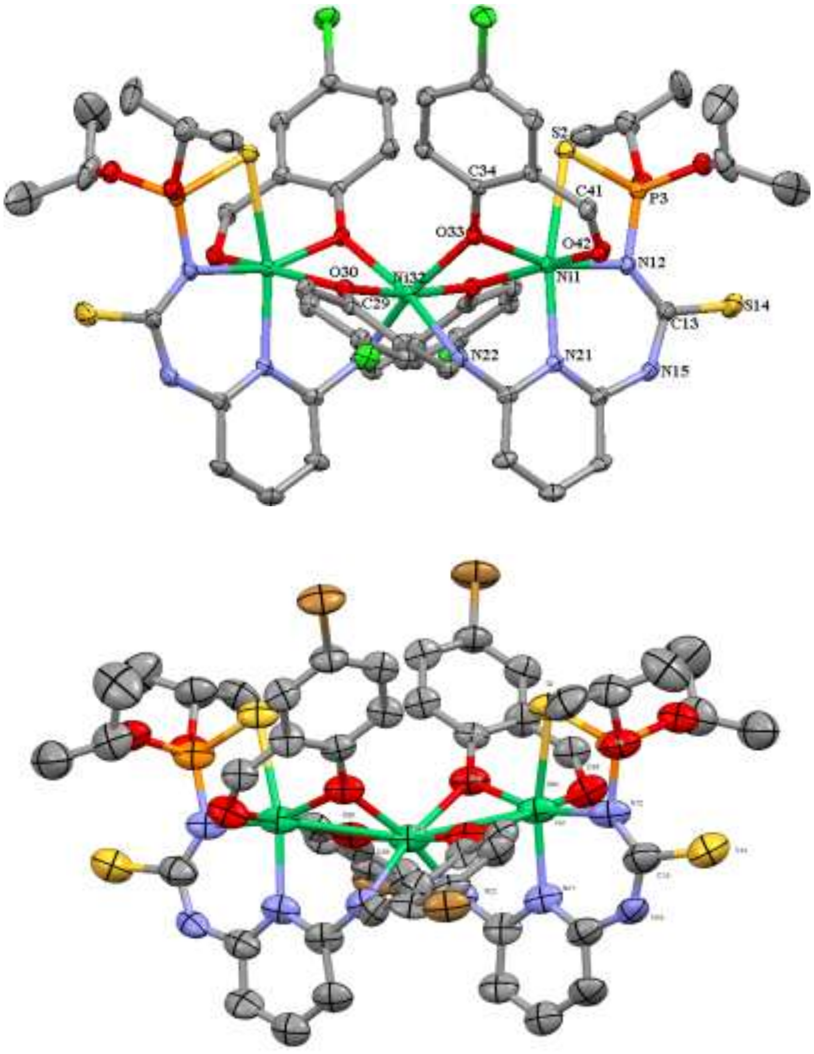


Fig. S3 Thermal ellipsoid (30%) plot of **2** (top) and **3** (bottom). H-atoms and water molecules for **2** were omitted for clarity.

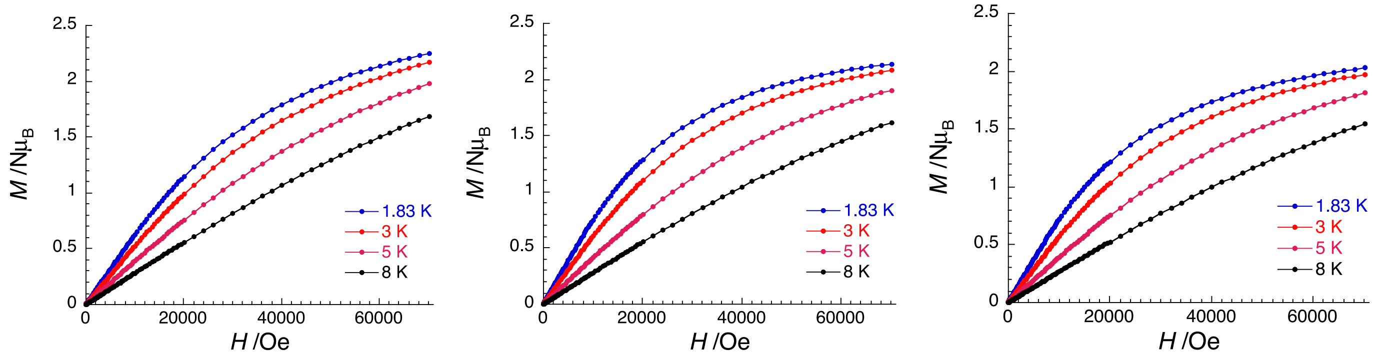


Fig. S4 *M* vs. *H* data for **1** (left), **2** (center) and **3** (right). A quasi-saturation of the magnetization is reached at 1.83 K and 7 T with value equals to 2.26 μ_B (**1**), 2.14 μ_B (**2**) and 2.03 μ_B (**3**), suggesting the presence of a significantly magnetic anisotropy of the $S_T = 1$ ground state.

Table S1. Selected bond lengths (Å) and angles (°) for **1**

Bond lengths			
Ni(1)···Ni(31)	3.0662(8)	Ni(31)–O(32)	2.043(4)
Ni(1)–N(12)	2.022(5)	N(12)–C(13)	1.323(8)
Ni(1)–N(21)	2.134(5)	N(15)–C(13)	1.375(8)
Ni(1)–O(32)	2.011(3)	O(30)–C(29)	1.301(6)
Ni(1)–O(40)	2.052(4)	O(32)–C(33)	1.289(6)
Ni(1)–O(30)a	2.094(3)	O(40)–C(39)	1.234(8)
Ni(1)–S(2)	2.5535(19)	P(3)–N(12)	1.653(5)
Ni(31)–N(22)	2.060(4)	S(2)–P(3)	1.940(2)
Ni(31)–O(30)	2.023(3)	S(14)–C(13)	1.693(6)
Bond angles			
Ni(1)···Ni(31)···Ni(1)a	153.62(4)	S(2)–Ni(1)–O(32)	89.08(11)
N(12)–Ni(1)–N(21)	89.88(18)	S(2)–Ni(1)–O(40)	92.45(15)
N(12)–Ni(1)–O(30)a	108.51(18)	N(22)–Ni(31)–N(22)a	93.91(14)
N(21)–Ni(1)–O(30)a	81.14(13)	N(22)–Ni(31)–O(30)a	94.59(14)
O(32)–Ni(1)–N(12)	163.54(18)	N(22)–Ni(31)–O(32)a	167.28(14)
O(32)–Ni(1)–N(21)	106.36(14)	O(30)–Ni(31)–N(22)	89.61(14)
O(32)–Ni(1)–O(30)a	77.40(14)	O(30)–Ni(31)–O(32)	97.77(14)
O(32)–Ni(1)–O(40)	88.00(15)	O(30)–Ni(31)–O(30)a	173.85(14)
O(40)–Ni(1)–N(12)	88.43(19)	O(30)–Ni(31)–O(32)a	78.31(14)
O(40)–Ni(1)–N(21)	93.16(17)	O(32)–Ni(31)–N(22)	83.22(14)
O(40)–Ni(1)–O(30)a	162.00(14)	O(32)–Ni(31)–N(22)a	167.28(14)
S(2)–Ni(1)–N(12)	75.03(15)	O(32)–Ni(31)–O(30)a	78.31(14)
S(2)–Ni(1)–N(21)	163.74(11)	O(32)–Ni(31)–O(32)a	102.20(14)
S(2)–Ni(1)–O(30)a	97.71(10)		

a = 1 – *x*, *y*, 1/2 – *z*

Table S2. Selected bond lengths (Å) and angles (°) for **2**

Bond lengths			
Ni(1)···Ni(32)	3.0546(14)	Ni(32)–O(32)	2.058(6)
Ni(1)–N(12)	2.021(7)	N(12)–C(13)	1.345(11)
Ni(1)–N(21)	2.112(7)	N(15)–C(13)	1.365(12)
Ni(1)–O(30)a	2.081(7)	O(30)–C(29)	1.309(14)
Ni(1)–O(33)	2.033(5)	O(33)–C(34)	1.311(10)
Ni(1)–O(42)	2.078(8)	O(42)–C(41)	1.253(11)
Ni(1)–S(2)	2.572(2)	P(3)–N(12)	1.646(6)
Ni(32)–N(22)	2.071(8)	S(2)–P(3)	1.956(3)
Ni(32)–O(30)	2.012(6)	S(14)–C(13)	1.679(9)
Bond angles			
Ni(1)···Ni(32)···Ni(1)a	157.54(6)	S(2)–Ni(1)–O(33)	87.39(15)
N(12)–Ni(1)–N(21)	89.9(3)	S(2)–Ni(1)–O(42)	91.45(18)
N(12)–Ni(1)–O(30)a	108.3(3)	N(22)–Ni(32)–N(22)a	95.1(3)
N(21)–Ni(1)–O(30)a	82.4(3)	N(22)–Ni(32)–O(30)a	95.6(3)
O(33)–Ni(1)–N(12)	162.0(2)	N(22)–Ni(32)–O(33)a	166.9(2)
O(33)–Ni(1)–N(21)	107.9(2)	O(30)–Ni(32)–N(22)	89.8(3)
O(33)–Ni(1)–O(30)a	77.3(2)	O(30)–Ni(32)–O(33)	96.8(2)
O(33)–Ni(1)–O(42)	85.3(3)	O(30)–Ni(32)–O(30)a	171.98(19)
O(42)–Ni(1)–N(12)	92.0(3)	O(30)–Ni(32)–O(33)a	78.3(2)
O(42)–Ni(1)–N(21)	91.6(3)	O(33)–Ni(32)–N(22)	81.0(3)
O(42)–Ni(1)–O(30)a	158.7(2)	O(33)–Ni(32)–N(22)a	166.9(2)
S(2)–Ni(1)–N(12)	74.90(17)	O(33)–Ni(32)–O(30)a	78.3(2)
S(2)–Ni(1)–N(21)	164.6(2)	O(33)–Ni(32)–O(33)a	105.4(2)
S(2)–Ni(1)–O(30)a	99.73(16)		

a = –*x*, *y*, 1/2 – *z*

Table S3. Selected bond lengths (Å) and angles (°) for **3**

Bond lengths			
Ni(1)···Ni(42)	3.062(5)	Ni(42)–O(40)	2100 (10)
Ni(1)–N(12)	2.076(11)	N(12)–C(13)	1.29(2)
Ni(1)–N(21)	2.098(11)	N(15)–C(13)	1.32(2)
Ni(1)–O(30)a	2.102(12)	O(30)–C(29)	1.349(15)
Ni(1)–O(32)	2.084(13)	O(32)–C(33)	1.234(22)
Ni(1)–O(40)	2.055(8)	O(40)–C(35)	1.306(12)
Ni(1)–S(2)	2.571(5)	P(3)–N(12)	1.661(14)
Ni(42)–N(22)a	2.081(13)	S(2)–P(3)	1.946(7)
Ni(42)–O(30)	2.002(9)	S(14)–C(13)	1.763 (19)
Bond angles			
Ni(1)···Ni(42)···Ni(1)a	159.5(1)	S(2)–Ni(1)–O(32)	90.7(3)
N(12)–Ni(1)–N(21)	89.2(4)	S(2)–Ni(1)–O(40)	87.6(3)
N(12)–Ni(1)–O(30)a	107.8(5)	N(22)–Ni(42)–N(22)a	94.3(5)
N(21)–Ni(1)–O(30)a	81.1(4)	N(22)–Ni(42)–O(30)a	93.3(4)
O(32)–Ni(1)–N(12)	91.2(5)	N(22)–Ni(42)–O(40)a	167.7(4)
O(32)–Ni(1)–N(21)	93.3(4)	O(30)–Ni(42)–N(22)	89.5(4)
O(32)–Ni(1)–O(30)a	159.9(4)	O(30)–Ni(42)–O(40)	97.8(4)
O(32)–Ni(1)–O(40)	84.8(4)	O(30)–Ni(42)–O(30)a	176.3(4)
O(40)–Ni(1)–N(12)	162.7(4)	O(30)–Ni(42)–O(40)a	79.9(4)
O(40)–Ni(1)–N(21)	107.8(4)	O(40)–Ni(42)–N(22)	80.2(5)
O(40)–Ni(1)–O(30)a	78.7(4)	O(40)–Ni(42)–N(22)a	167.7(4)
S(2)–Ni(1)–N(12)	75.6(4)	O(40)–Ni(42)–O(30)a	79.9(4)
S(2)–Ni(1)–N(21)	164.4(3)	O(40)–Ni(42)–O(40)a	107.3(4)
S(2)–Ni(1)–O(30)a	99.9(3)		

a = –*x*, *y*, 1/2 – *z*

Note: The data quality of **3** is low. The given bond lengths and angle values are only illustrative because their accuracy is an order of magnitude lower than for the structures of **1** and **2**.