Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Quenching of Tryptophan Fluorescence in Various Proteins by a Series of Small Nickel Complexes

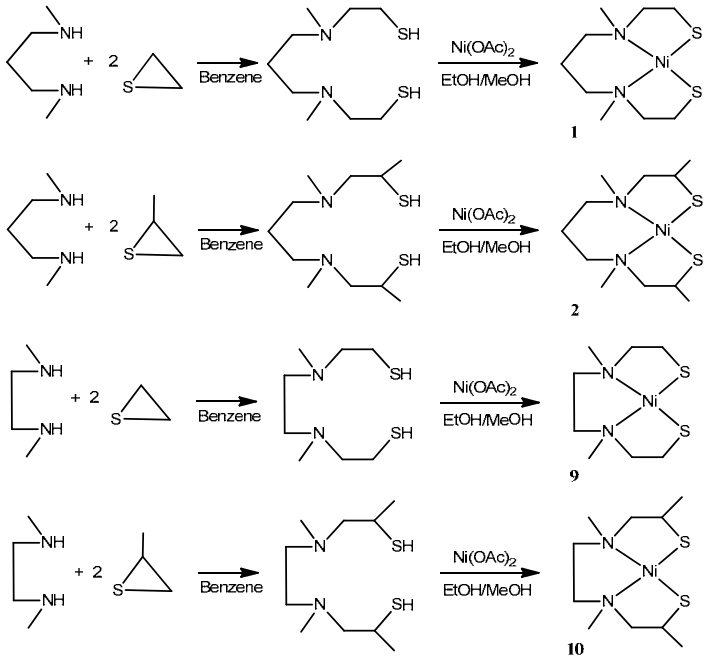
Heather F. Crouse[1], Julianne Potoma[1], Farhat Nejrabi[2], Deanna L. Snyder[1], Balwant S. Chohan[2] and Swarna Basu[1]

[1] Department of Chemistry, Susquehanna University, 514 University Avenue Selinsgrove, PA 17870

[2] Current address: Penn State Harrisburg, 777 West Harrisburg Pike, Middletown, PA 17057

Supplementary Information 1

Synthesis of Nickel Complexes & Characterization Data



Scheme 1: Synthesis of Complexes **1**, **2**, **9**, and **10**.

Complex 1: (Ni-Pr-Et). Synthesis of (N,N'-dimethyl-N-N'-bis(2-mecaptoethyl)-1,3-propanediaminato)-nickel(II).

The ligand N,N'-dimethyl-N, N'-bis (2-mercaptoethyl)-1,3-propanediamine was prepared by literature methods[100]. The red colored neutral monomeric nickel complex was synthesized (**Scheme 1, above**) by combining the ligand with $Ni(OAc)_2.4H_2O$ in a methanol/ethanol (1:1) solvent mix, according to published procedures[101]. ESI-MS(+) m/z (relative intensity), as shown in **SI (#7a)**, 447.0(12) isotopic cluster (tetranuclear species / 2, $((Ni_4C_{27}H_{60}N_6S_6) / 2)^+$ calculated mass = 446.0); 308.0(85) cluster (trinuclear species / 2, $((Ni_3C_{18}H_{40}N_4S_4) / 2)^+$ calculated mass = 307.0); 279.0(100) cluster (parent mononuclear complex, $(NiC_9H_{21}N_2S_2)^+$, calculated mass = 279.0). MS/MS of 447.0 cluster gives the 308.0(76) cluster and the 279.0(100) cluster. The ESI-MS spectra of **1** can be simulated well: Simulated MS for 447.0 is shown in **SI (#7b)**, for 308.0 in **SI (#7c)**, and for 279.0 in **SI (#7d).**

Complex 2: (Ni-Pr-Pr or Ni-dsppm).

(a) Synthesis of N,N'-dimethyl-N,N'-bis(2-sulfanylpropyl)propylenediamine) ligand.

A solution of N,N-dimethyl-1,3-propenediamine (5.5997 g, 53.16 mmol) in 5 mL benzene was placed in Schlenk reaction tube, and the temperature was raised to 40ºC. Propylene sulfide (8.2

mL, 111.64 mmol) in 5 mL benzene was then added dropwise, the temperature was raised to 80ºC. The mixture was stirred overnight at 80ºC (**Scheme 1, above**). The oily product was washed with 4 x 10 mL of distilled water in a 125 mL separatory funnel. The ligand solution was then dried over $MgSO_4$ and gravity filtered into a tarred 25 mL round-bottom flask. The benzene was removed to yield a colorless viscous liquid (4.4093 g, 17.64 mmol, 33.2% yield). NMR (400MHz Joel, in $CDCl_3$) produced a spectrum with the corresponding peaks: 2.25t (4H), 1.60q (3H), 2.19m (6H), 2.37m (4H), 3.20m (2H), 1.57d (2H), 1.19d (6H)

(b) Synthesis of N,N'-dimethyl-N-N'-bis(2-sulfanylpropyl)propylenediamine)-nickel(II).

The N,N'-dimethyl-N,N'-bis(2-sulfanylpropyl)propylenediamine ligand (3.983 g, 15.93 mmol) in 30 mL of 1:1, EtOH:MeOH was placed in a 250 mL round-bottom flask in an ice bath under an Ar atmosphere and stirred for 10 mins. $Ni(OAc)_2.4H_2O$ (3.2128 g, 13.27 mmol) was dissolved in ethanol (120 mL) under an Ar atmosphere, and then added drop wise to the ligand. The mixture was allowed to stir for 12 hrs (**Scheme 1, above**). The product was filtered, solvent removed under vacuum, and the solid material re-dissolved in minimum MeOH and purified using a silica gel column (20 mm x 300 mm; 60-200 mesh Aldrich grade 62 silica gel) with MeOH as the eluent. The purple-red colored fraction was reduced to 25 mL, and diethyl ether was layered onto the solution, and left in a refrigerator at 5ºC for eight days. The cubic shaped clear red-purple crystals of **2** were collected and analyzed by X-ray crystallography (**Figure 2**). CHN microanalysis, Anal Calcd for $NiC_{11}H_{24}N_2S_2$: C, 43.01; H, 7.88; N, 9.12. Found: C, 43.10; H, 8.07; N, 8.48. IR (KBr, cm^{-1}): 1652, 1467, 1456, 1442, 1410, 1364, 1297, 1143, 1046, 1009, 985, 827. UV-vis in MeOH, λ(nm)(ε ($M^{-1}cm^{-1}$)): 212 (8605), 244 (9105), 282(3835).

Complex 9: (Ni-Et-Et or Ni-dsdm). Synthesis of (N,N'-dimethyl-N-N'-bis(2-mecaptoethyl)-ethylenediaminato)-nickel(II).

The ligand and the neutral nickel complex, was synthesized in a manner similar to that reported for Complex **1**[100, 101]. The synthesis of the ligand[106,107] and the nickel complex was synthesized by modification of published procedures[108,109,y] (**Scheme 1, above**). CHN microanalysis, Anal Calcd (found) for $NiC_8H_{18}N_2S_2$: C, 36.25 (34.66); H, 6.85 (6.48); N, 10.57 (9.79). Slow evaporation of diethyl ether onto an ethanol solution of the product, yielded thin pink-red plates after 22 days, suitable for X-ray diffraction studies. The crystal structure of complex **9** was recently reported.[y]

Complex 10: (Ni-Et-Pr or Ni-dspem). The ligand and the neutral nickel complex, was synthesized in a manner *similar* to that reported for Complex **1**[100, 101].

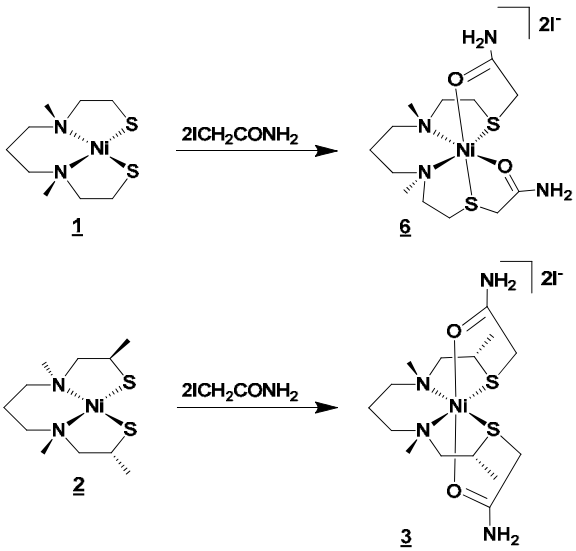
(a) Synthesis of ligand, N,N'-dimethyl-N, N'-bis(2-sulfanylpropyl)ethylenediamine)

A solution of N,N-dimethyl-1,2-ethylenediamine (5.344 g, 60.62 mmol) in 5 mL benzene was placed in Schlenk reaction tube, and the temperature was raised to 40ºC. Propylene sulfide (9.44 g, 9.98 ml, 127.33 mmol) in 5 mL benzene was then added dropwise. The reaction was allowed to stir overnight at 80ºC. The resulting solution was washed with 3 x 15 mL of distilled water in a 125 mL separatory funnel then dried over $MgSO_4$ and gravity filtered (**Scheme 1,**

above). The benzene was removed to yield the product as a colorless viscous liquid (9.72 g, 68% yield).

(b) Synthesis of N,N'-dimethyl-N-N'-bis(2-sulfanylpropyl) ethylenediamine nickel(II).

The N,N'-dimethyl-N,N'-bis(2-sulfanylpropyl)ethylenediamine ligand (5.33 g, 22.58 mmol) in 40 mL of 1:1, EtOH:MeOH was placed in a 250 mL round-bottom flask in an ice bath under an Ar atmosphere and left to stir for 15 mins. $Ni(OAc)_2$ (5.62 g, 22.58 mmol) was dissolved in ethanol (60 mL) under an inert atmosphere, and cooled on ice. The $Ni(OAc)_2$ solution was then added drop wise to the ligand, and the resulting red-brown colored mixture was left to stir for 14 hrs (**Scheme 1, above**). The nickel product was filtered, the solvent removed under vacuum, and the solid product re-dissolved in minimum MeOH and purified using a silica gel column (20 mm x 270 mm; 60-200 mesh Aldrich grade 62 silica gel), with MeOH as the eluent. The purple-red colored fraction was reduced to 25 mL, and diethyl ether was added to precipitate the product. CHN microanalysis, Anal Calcd (found) for $NiC_{10}H_{22}N_2S_2$: C, 40.98 (39.87); H, 7.57(7.41); N, 9.56(9.28). Slow evaporation of diethyl ether onto a (9:1) MeOH/MeCN solution of the product red plate shaped crystals after 3 days, suitable for X-ray diffraction studies (**Figure 3**).



Scheme 2: Di-alkylation of complex **1** and **2** with iodoacetamide to give **6** and **3**, respectively.

Complex 3: (Ni-Pr-Pr-Iodo). Synthesis of (N,N'-dimethyl-N-N'-bis(2-methyl-3-thiapentanamide)-1,3-propanediaminato)-nickel(II) iodide.

Alkylation of complex **2** with two equivalents of iodoacetamide yields a high spin blue-purple colored complex, with pseudo octahedral nickel centers and iodide counterions (**Scheme 2, above**). The iodoacetamide derivative was crystallized from MeOH/MeCN solutions as thin plates, which crumble when taken out of solvent. The complex is nevertheless stable in the solid state.

In a round bottomed 250 mL flask, 778 mg (2.53 mmol) of complex **2** was dissolved in 60 mL of a 1:1 mix of MeCN and MeOH. The flask was placed in an Ar environment and allowed to

stir for 15 minutes. Iodoacetamide (942 mg, 5.09 mmol) was placed in a small test tube along with 3 mL of MeOH/MeCN solution and dissolved. The iodoacetamide solution was then added to the solution of **2** using a 5 mL syringe. The solution immediately changed from a red-purple color to blue. The solution was left to stir overnight. The reaction mixture was then reduced by rotary evaporation to approximately 10 mL, and filtered through a fine glass frit funnel. The solution was placed into a test tube, and an equal amount of diethyl ether was carefully layered on to the top of the solution and left to stand for 4 days. Blue-purple crystals that appeared (**Figure 4**) were collected by filtration and dried under vacuum to give 878 mg (82% yield) of a blue colored powder. CHN microanalysis, Anal Calcd (found) for $NiC_{15}H_{32}N_4S_2O_2I_2$: C, 23.55 (23.23); H, 4.31 (4.22); N,4.99 (4.82). μ_{eff} = 2.82 (n=2). IR (cm^{-1}): ν(N-H) 3275s, ν(C-H) 3100s, ν(C=O) 1645s, ν(C-N) 1375s.

Complex 6: (Ni-Pr-Et-Iodo). Synthesis of (N,N'-dimethyl-N-N'-bis(3-thiapentanamide)-1,3-propanediaminato)-nickel(II) iodide.

The alkylation of Complex **1** with two equivalents of iodoacetamide yields a high spin blue colored complex, with pseudo octahedral nickel centers and iodide counterions (**Scheme 2, above**). The iodoacetamide derivative was readily crystallized from MeOH/MeCN solutions and is very stable in the solid state.

In a 250 mL flask, 813 mg (2.91 mmol) of complex **1** was dissolved in 120 mL of a 1:1 mix of MeCN and MeOH. To this was added 1.0776 g (5.83 mmol) of iodoacetamide dissolved in 30 mL of MeCN. The solution changed from red to green within 15 minutes and then to a blue color overnight. The resulting solution was reduced in volume to 60 mL and filtered. Slow addition of diethyl ether yielded blue colored crystals of diffraction quality within 8 days (**Figure 5**). Filtration and subsequent drying under vacuum gave 1.66 g (88% yield) of a light blue colored powder. CHN microanalysis, Anal Calcd (found) for $NiC_{13}H_{28}N_4S_2O_2I_2.CH_3OH$: C, 24.69 (24.97); H, 4.74 (4.60); N, 8.23 (8.18). μ_{eff} = 2.82 (n=2). IR (cm^{-1}): ν(N-H) 3280s, ν(C-H) 3100s, ν(C=O) 1650s, ν(C-N) 1380s. ESI-MS(+) m/z (relative intensity), as shown in **SI (#8a)**, 392.9(58) isotopic cluster (parent complex, $(NiC_{13}H_{27}N_4O_2S_2)^+$ calculated mass = 393.1); 335.9(100) cluster (loss of one acetamide, $(NiC_{11}H_{24}N_3OS_2)^+$ calculated mass = 336.1); 278.9(13) cluster (loss of both acetamides). ESI-MS(-) m/z (relative intensity): 127.0(100) (iodide counterion). The ESI-MS spectra of **6** can be simulated well: Simulated MS for 392.9 is shown in **SI (#8b)**.

Complex 4: ($Ni(pya_2tn)Cl_2 \cdot H_2O$). Synthesis of N,N'-bis(2-pyridylmethylene)-1,3-diaminopropyl nickel(II) chloride.

The complex was synthesized according to published procedures[102]. The Schiff base ligand (pya_2tn) was derived from pyridine-2-carboxaldehyde and 1,3-diamino-2-propanol in isopropyl alcohol. The nickel complex was made *in-situ* by addition of nickel (II) chloride hexahydrate dissolved in absolute ethanol to the Schiff base. Recrystallization from water gave dark olive green crystals, which when dried *in vacuo* gave the product in excellent yield.

Complex 7: ($Ni(pya_2tn\text{-}OH)Cl_2$). Synthesis of N,N'-Bis(2-pyridylmethylene)1,3-diamino-2-propanol nickel(II) chloride.

The ligand[104], and the nickel complex[102] were synthesized according to modification of published procedures. The Schiff base ligand (pya_2tn) is derived from pyridine-2-carboxaldehyde and 1,3-diamino-2-propanol. The resulting yellow colored oil was crystallized (only once) by addition of absolute ethanol to the neat oil. The nickel complex is made by addition of the Schiff base dissolved in absolute ethanol to a refluxing solution of nickel(II) chloride hexahydrate and 2,2-dimethoxypropane. The solution was slowly cooled yielding green colored crystals, which were dried *in vacuo* to give an excellent yield.

Complex 5: ($Ni\text{-}(en)_2Cl_2$). Synthesis of bis(ethylenediamine)-nickel(II) chloride

Bis(ethylenediamine)-nickel(II) chloride was synthesized according to published procedures from tris(ethylenediamine)nickel(II) chloride via redistribution of ligands in methanol[103].

$$[Ni(H_2O)_6]Cl_2 + 2[Ni(en)_3]Cl_2.2H_2O \rightarrow [Ni(en)_2]Cl_2 + 4H_2O$$

In a 250 mL round bottomed flask, 10 g (42.1 mmol) of nickel (II) chloride hexahydrate, 24.1 g (84.3 mmol) of tris(ethylenediamine)-nickel(II) chloride dihydrate, 80 mL of MeOH, and 2 mL of water was gently refluxed for 10 minutes. The dark blue solution was filtered through a fine frit funnel whilst still warm. The filtrate was cooled, and 110 mL of acetone was added, forming a blue-purple colored product. The precipitate was filtered, and washed with 10 mL of acetone, and further dried in an oven at 105°C for 50 min. Yield was 8.60 g (82%).

Complex 11: ($Ni(en)_3Cl_2.2H_2O$). Tris(ethylenediamine)-nickel(II) chloride dihydrate was synthesized from the nickel(II) chloride salt:

$$[Ni(H_2O)_6]Cl_2 + 3\ en \rightarrow [Ni(en)_3]Cl_2.2H_2O + 4H_2O$$

In a 125 mL Erlenmeyer flask, 11.8 g (49.6 mmol) of was dissolved in 20 mL of warm deionized water. The mixture was cooled in an ice bath, and to this was added 10 mL of (150 mmol) ethylenediamine. Cooled 95% ethanol (15 mL) was then slowly added to the solution to form a purple colored precipitate. The precipitate was filtered, wash with two 10 mL volumes of cold 95% ethanol, 10 mL of acetone, and air dried to yield 15.40 g (90%) of product.

Complex 12: ($Ni(NH_3)_6Cl_2$). Hexaammine nickel(II) chloride was synthesized from the nickel(II) chloride salt:

$$[Ni(H_2O)_6]Cl_2(aq) + 6\ NH_3(aq) \rightarrow [Ni(NH_3)_6]Cl_2(aq) + 6\ H_2O\ (l)$$

In a 125 mL Erlenmeyer flask, 6 g (25.2mmol) of nickel(II) chloride hexahydrate was dissolved in 10 mL of warm deionized water. To this was slowly added 20 mL of concentrated NH_3 solution. The mixture was cooled in an ice bath, and then 15 mL of cold 95% ethanol was added to precipitate a lavender colored product. The solid was vacuum filtered, washed with two 5 mL volumes of cold 95 % ethanol, 10 mL of acetone, and air dried to give 5.52 g (94%) of product.

Complex 8: ($Ni(EDTA)\text{-}H_2O.Na$). Synthesis of the nickel(II) salt of ethylenediamine-tetraacetate.

Nickel (II) carbonate was made by reacting sodium carbonate (20 g, 84 mmol) with nickel chloride (8.92 g, 84 mmol) in water. The solution was stirred and heated at 90°C for 30mins. The

green solution was cooled, and ethanol was added to precipitate light green colored $NiCO_3$ (9.88 g, 99% yield):

$$Ni^{2+} + Na_2CO_3 \rightarrow NiCO_3 + 2\ Na^+$$

The H_4EDTA ligand was prepared by acidification of an aqueous solution of reagent grade $Na_2H_2EDTA.2H_2O$ with concentrated HCl. Powdered nickel (II) carbonate was added in small increments, totaling 8.00 g (67 mmol) to 19.58 g (67 mmol) of H_4EDTA partially dissolved in 120 mL of water. This slurry was warmed and stirred to generate a uniform product. The solution was adjusted to pH 2 with HCl, concentrated to about 40 mL in a crystallizing dish, and left to stand in the open air for 8 days to yield blue colored plate and rod-like crystals. (**Figure 6**). The product was further dried in a vacuum desiccator to give a yield of 22.24 g (86%), based on the $Na[Ni\text{-}EDTA.H_2O]$ crystal structure. The crystal structure shows the EDTA is functioning as a quinquedentate ligand. The structure is similar, with minor differences, to that reported in literature[105].

Supplementary Information 2

Table 1. Crystal data and structure refinement for bsc1a (**Complex 2**).

Identification code	bsc1a
Empirical formula	C11 H24 N2 Ni S2
Formula weight	307.15
Temperature	200(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 10.5547(10)Å alpha = 90° B = 12.3943(11)Å beta = 111.126(5)° C = 11.5831(11)Å gamma = 90°
Volume	1413.4(2) A^3
Z, Calculated density	4, 1.443 Mg/m^3
Absorption coefficient	1.646 mm^-1
F(000)	656
Crystal size	0.20 x 0.20 x 0.02 mm
Theta range for data collection	2.50 to 43.94 deg.
Limiting indices	-20<=h<=20, -22<=k<=24, -22<=l<=21
Reflections collected / unique	39600 / 10794 [R(int) = 0.0866]
Completeness to theta = 43.94	97.9 %
Absorption correction	psi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10794 / 0 / 149
Goodness-of-fit on F^2	0.956
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.1022
R indices (all data)	R1 = 0.0829, wR2 = 0.1180
Largest diff. peak and hole	2.049 and -0.882 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for bsc1a.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ni(1)	1023(1)	6323(1)	1701(1)	20(1)
C(1)	4854(1)	6058(1)	1164(2)	42(1)
C(2)	3315(1)	6063(1)	667(1)	31(1)
C(3)	2785(1)	7208(1)	625(1)	31(1)
C(4)	547(1)	6787(1)	-856(1)	36(1)
C(5)	942(1)	8381(1)	463(1)	36(1)
C(6)	-563(2)	8589(1)	208(2)	43(1)
C(7)	-1322(1)	7712(1)	628(1)	33(1)
C(8)	-54(1)	7983(1)	2828(1)	35(1)
C(9)	-1441(1)	6395(1)	2092(1)	28(1)
C(10)	-721(1)	5745(1)	3245(1)	29(1)
C(11)	-1599(1)	4801(1)	3343(1)	39(1)
N(1)	1308(1)	7228(1)	398(1)	23(1)
N(2)	-517(1)	7179(1)	1815(1)	25(1)
S(1)	2622(1)	5268(1)	1629(1)	37(1)
S(2)	900(1)	5305(1)	3180(1)	29(1)

Table 3. Bond lengths [A] and angles [deg] for bsc1a.

Ni(1)-N(2)	1.9844(9)
Ni(1)-N(1)	1.9888(9)
Ni(1)-S(1)	2.1605(3)
Ni(1)-S(2)	2.1692(3)
C(1)-C(2)	1.5149(18)
C(2)-C(3)	1.5194(18)
C(2)-S(1)	1.8260(13)
C(3)-N(1)	1.4848(15)
C(4)-N(1)	1.4871(16)
C(5)-N(1)	1.4886(16)
C(5)-C(6)	1.530(2)
C(6)-C(7)	1.529(2)
C(7)-N(2)	1.4855(16)
C(8)-N(2)	1.4819(15)
C(9)-N(2)	1.4911(15)
C(9)-C(10)	1.5093(18)
C(10)-C(11)	1.5223(18)
C(10)-S(2)	1.8228(12)
N(2)-Ni(1)-N(1)	95.77(4)
N(2)-Ni(1)-S(1)	174.90(3)
N(1)-Ni(1)-S(1)	88.72(3)
N(2)-Ni(1)-S(2)	88.57(3)
N(1)-Ni(1)-S(2)	175.00(3)
S(1)-Ni(1)-S(2)	87.044(14)
C(1)-C(2)-C(3)	110.39(12)
C(1)-C(2)-S(1)	112.07(10)
C(3)-C(2)-S(1)	107.42(8)
N(1)-C(3)-C(2)	111.86(10)
N(1)-C(5)-C(6)	114.96(11)
C(7)-C(6)-C(5)	116.46(11)
N(2)-C(7)-C(6)	114.83(11)
N(2)-C(9)-C(10)	112.25(9)
C(9)-C(10)-C(11)	110.52(10)
C(9)-C(10)-S(2)	107.69(8)
C(11)-C(10)-S(2)	112.25(10)
C(3)-N(1)-C(4)	109.29(9)
C(3)-N(1)-C(5)	106.36(9)
C(4)-N(1)-C(5)	110.10(10)
C(3)-N(1)-Ni(1)	106.99(7)
C(4)-N(1)-Ni(1)	110.95(8)
C(5)-N(1)-Ni(1)	112.95(8)
C(8)-N(2)-C(7)	110.44(10)
C(8)-N(2)-C(9)	108.84(9)
C(7)-N(2)-C(9)	106.79(9)
C(8)-N(2)-Ni(1)	111.57(7)
C(7)-N(2)-Ni(1)	112.65(8)
C(9)-N(2)-Ni(1)	106.28(7)
C(2)-S(1)-Ni(1)	100.81(4)
C(10)-S(2)-Ni(1)	100.51(4)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for bsc1a.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Ni(1)	18(1)	18(1)	23(1)	0(1)	6(1)	1(1)
C(1)	28(1)	52(1)	46(1)	-2(1)	14(1)	3(1)
C(2)	26(1)	35(1)	32(1)	-1(1)	13(1)	3(1)
C(3)	27(1)	29(1)	38(1)	0(1)	12(1)	-4(1)
C(4)	34(1)	42(1)	27(1)	0(1)	5(1)	0(1)
C(5)	38(1)	21(1)	50(1)	4(1)	17(1)	2(1)
C(6)	38(1)	31(1)	60(1)	18(1)	18(1)	13(1)
C(7)	24(1)	31(1)	42(1)	6(1)	8(1)	8(1)
C(8)	32(1)	27(1)	47(1)	-14(1)	15(1)	-3(1)
C(9)	19(1)	31(1)	34(1)	-3(1)	9(1)	-2(1)
C(10)	24(1)	35(1)	29(1)	-3(1)	11(1)	-4(1)
C(11)	34(1)	47(1)	40(1)	5(1)	17(1)	-9(1)
N(1)	23(1)	20(1)	26(1)	0(1)	7(1)	-1(1)
N(2)	19(1)	22(1)	33(1)	-4(1)	7(1)	0(1)
S(1)	37(1)	31(1)	50(1)	14(1)	26(1)	16(1)
S(2)	27(1)	32(1)	30(1)	7(1)	11(1)	3(1)

Supplementary Information 3

Crystal Structure Information for btw5s (Complex 3).

A blue block shaped crystal of btw5 (C15 H32 N4 Ni O4 S2, 2(C H4 O), 2(I)) with approximate dimensions 0.21 x 0.32 x 0.37 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 298(2) K, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal.

A total of 1850 frames were collected with a scan width of 0.3º in ω and an exposure time of 10 seconds/frame. The total data collection time was about 8 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Triclinic unit cell yielded a total of 14030 reflections to a maximum θ angle of 28.26° (0.90 Å resolution), of which 7086 were independent, completeness = 97.6%, R_{int} = 0.0130, R_{sig} = 0.0206 and 5972 were greater than 2σ(I). The final cell constants: a = 10.4046(12) Å, b = 10.9123(12)Å, c = 13.8838(16)Å, α = 87.671(2)°, β = 78.132(2)°, γ = 72.023(2)°, volume = 1466.9(3)$Å^3$, are based upon the refinement of the XYZ-centroids of 6974 reflections above 20σ(I) with 2.320° <θ <28.167°. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multi-scan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.5172.

The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group P-1, with Z = 2 for the formula unit, C17 H40 I2 N4 Ni O4 S2. The final anisotropic full-matrix least-squares refinement on F^2 with 279 variables converged at R1 = 4.90%, for the observed data and wR2 = 14.46% for all data. The goodness-of-fit was 1.036. The largest peak on the final difference map was 2.983 $e^-/Å^3$ and the largest hole was -1.825 $e^-/Å^3$. Based on the final model, the calculated density of the crystal is 1.678 g/cm^3 and F(000) amounts to 736 electrons.

Table 1. Sample and crystal data for btw5.

Identification code	btw5	
Empirical formula	C17 H40 I2 N4 Ni O4 S2	
Formula weight	741.16	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal size	0.37 x 0.32 x 0.21 mm	
Crystal habit	blue block	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.4046(12) Å	α= 87.671(2)°
	b = 10.9123(12) Å	β= 78.132(2)°
	c = 13.8838(16) Å	γ = 72.023(2)°
Volume	1466.9(3) $Å^3$	
Z	2	
Density (calculated)	1.678 g/cm^3	
Absorption coefficient	2.934 mm^{-1}	
F(000)	736	
Diffractometer	CCD area detector	
Radiation source	fine-focus sealed tube, MoKα	
Generator power	1600 watts (50 kV, 32mA)	
Detector distance	5.8 cm	
Data collection method	phi and omega scans	
Theta range for data collection	1.96 to 28.26°	
Index ranges	$-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $-18 \leq l \leq 18$	

Table 2. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for btw5.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C1	0.9792(5)	0.3248(5)	0.3857(4)	0.0522(11)
C2	0.9060(4)	0.2334(4)	0.4381(3)	0.0420(9)
C3	1.2033(6)	0.2523(7)	0.1245(5)	0.0731(16)
C4	1.0891(5)	0.2110(4)	0.1929(4)	0.0493(10)
C5	1.0189(5)	0.1471(4)	0.1335(3)	0.0466(9)
C6	0.9627(5)	-0.0022(4)	0.2558(4)	0.0533(11)
C7	0.8415(5)	0.0560(5)	0.1218(3)	0.0520(11)
C8	0.7127(5)	0.0204(5)	0.1672(4)	0.0548(11)
C9	0.5852(5)	0.1355(5)	0.1991(4)	0.0531(11)
C10	0.5719(6)	0.1310(5)	0.3768(4)	0.0562(11)
C11	0.4603(5)	0.3239(5)	0.2973(3)	0.0492(10)
C12	0.4512(5)	0.4237(5)	0.3730(3)	0.0492(10)
C13	0.3199(6)	0.5367(6)	0.3792(5)	0.0701(15)
C14	0.6036(5)	0.5622(4)	0.2410(3)	0.0498(10)
C15	0.6579(4)	0.4807(4)	0.1473(3)	0.0426(9)
C16	0.892(2)	0.3663(13)	0.8478(13)	0.263(12)
O3	0.7300(7)	0.4118(6)	0.8783(5)	0.1067(19)
O4	0.7594(7)	0.0785(9)	0.6562(4)	0.124(2)
C17	0.6479(15)	0.0752(15)	0.6201(7)	0.178(7)
I1	0.78886(4)	0.71976(4)	0.40706(3)	0.06209(13)
I3	0.60964(5)	0.14225(4)	0.90216(3)	0.07380(15)
N1	0.9039(4)	0.1062(3)	0.1936(3)	0.0416(7)
N2	0.5849(4)	0.2098(4)	0.2875(3)	0.0426(7)
N3	0.6364(5)	0.5419(4)	0.0649(3)	0.0613(11)
N4	0.9424(5)	0.1860(5)	0.5202(3)	0.0611(11)
Ni1	0.76266(5)	0.27167(5)	0.27326(3)	0.03544(13)
O1	0.7221(3)	0.3631(3)	0.1466(2)	0.0443(6)
O2	0.8128(3)	0.2089(3)	0.4068(2)	0.0445(6)
S1	0.96051(11)	0.35097(10)	0.26065(8)	0.0437(2)
S2	0.60645(12)	0.47247(10)	0.35245(7)	0.0435(2)

Table 3. Bond lengths (Å) for btw5.

C1-C2	1.512(6)	C1-S1	1.789(5)
C1-H1A	0.9700	C1-H1B	0.9700
C2-O2	1.243(5)	C2-N4	1.310(6)
C3-C4	1.532(7)	C3-H3C	0.9600
C3-H3D	0.9600	C3-H3E	0.9600
C4-C5	1.520(7)	C4-S1	1.830(5)
C4-H4	0.9800	C5-N1	1.487(6)
C5-H5A	0.9700	C5-H5B	0.9700
C6-N1	1.486(5)	C6-H6A	0.9600
C6-H6B	0.9600	C6-H6C	0.9600
C7-N1	1.498(6)	C7-C8	1.517(7)
C7-H7A	0.9700	C7-H7B	0.9700
C8-C9	1.520(7)	C8-H8A	0.9700
C8-H8B	0.9700	C9-N2	1.496(5)
C9-H9A	0.9700	C9-H9B	0.9700
C10-N2	1.488(6)	C10-H10A	0.9600
C10-H10B	0.9600	C10-H10C	0.9600
C11-N2	1.482(6)	C11-C12	1.513(6)
C11-H11A	0.9700	C11-H11B	0.9700
C12-C13	1.521(7)	C12-S2	1.817(5)
C12-H12	0.9800	C13-H13A	0.9600
C13-H13B	0.9600	C13-H13C	0.9600
C14-C15	1.511(6)	C14-S2	1.798(5)
C14-H14A	0.9700	C14-H14B	0.9700
C15-O1	1.250(5)	C15-N3	1.325(6)
C16-O3	1.571(18)	C16-H16A	0.9600
C16-H16B	0.9600	C16-H16C	0.9600
O3-H3	0.8200	O4-C17	1.365(11)
O4-H4O	0.8200	C17-H17A	0.9600
C17-H17B	0.9600	C17-H17C	0.9600
N1-Ni1	2.121(3)	N2-Ni1	2.128(4)
N3-H3A	0.8600	N3-H3B	0.8600
N4-H4A	0.8600	N4-H4B	0.8600
Ni1-O1	2.042(3)	Ni1-O2	2.063(3)
Ni1-S2	2.4319(11)	Ni1-S1	2.4406(12)

Symmetry transformations used to generate equivalent atoms (if any):

Table 4. Bond angles (°) for btw5.

C2-C1-S1	113.7(3)	C2-C1-H1A	108.8
S1-C1-H1A	108.8	C2-C1-H1B	108.8
S1-C1-H1B	108.8	H1A-C1-H1B	107.7
O2-C2-N4	122.1(4)	O2-C2-C1	121.5(4)
N4-C2-C1	116.3(4)	C4-C3-H3C	109.5
C4-C3-H3D	109.5	H3C-C3-H3D	109.5
C4-C3-H3E	109.5	H3C-C3-H3E	109.5
H3D-C3-H3E	109.5	C5-C4-C3	110.2(4)
C5-C4-S1	109.1(3)	C3-C4-S1	110.3(4)
C5-C4-H4	109.1	C3-C4-H4	109.1
S1-C4-H4	109.1	N1-C5-C4	114.2(4)
N1-C5-H5A	108.7	C4-C5-H5A	108.7
N1-C5-H5B	108.7	C4-C5-H5B	108.7
H5A-C5-H5B	107.6	N1-C6-H6A	109.5
N1-C6-H6B	109.5	H6A-C6-H6B	109.5
N1-C6-H6C	109.5	H6A-C6-H6C	109.5
H6B-C6-H6C	109.5	N1-C7-C8	114.8(4)
N1-C7-H7A	108.6	C8-C7-H7A	108.6
N1-C7-H7B	108.6	C8-C7-H7B	108.6
H7A-C7-H7B	107.5	C7-C8-C9	114.0(4)
C7-C8-H8A	108.7	C9-C8-H8A	108.7
C7-C8-H8B	108.7	C9-C8-H8B	108.7
H8A-C8-H8B	107.6	N2-C9-C8	115.4(4)
N2-C9-H9A	108.4	C8-C9-H9A	108.4
N2-C9-H9B	108.4	C8-C9-H9B	108.4
H9A-C9-H9B	107.5	N2-C10-H10A	109.5
N2-C10-H10B	109.5	H10A-C10-H10B	109.5
N2-C10-H10C	109.5	H10A-C10-H10C	109.5
H10B-C10-H10C	109.5	N2-C11-C12	114.4(4)
N2-C11-H11A	108.7	C12-C11-H11A	108.7
N2-C11-H11B	108.7	C12-C11-H11B	108.7
H11A-C11-H11B	107.6	C11-C12-C13	111.1(4)
C11-C12-S2	111.8(3)	C13-C12-S2	113.2(4)
C11-C12-H12	106.8	C13-C12-H12	106.8
S2-C12-H12	106.8	C12-C13-H13A	109.5
C12-C13-H13B	109.5	H13A-C13-H13B	109.5
C12-C13-H13C	109.5	H13A-C13-H13C	109.5
H13B-C13-H13C	109.5	C15-C14-S2	114.7(3)
C15-C14-H14A	108.6	S2-C14-H14A	108.6
C15-C14-H14B	108.6	S2-C14-H14B	108.6
H14A-C14-H14B	107.6	O1-C15-N3	121.5(4)
O1-C15-C14	122.4(4)	N3-C15-C14	116.0(4)
O3-C16-H16A	109.5	O3-C16-H16B	109.5
H16A-C16-H16B	109.5	O3-C16-H16C	109.5
H16A-C16-H16C	109.5	H16B-C16-H16C	109.5
C16-O3-H3	109.5	C17-O4-H4O	109.5
O4-C17-H17A	109.5	O4-C17-H17B	109.5
H17A-C17-H17B	109.5	O4-C17-H17C	109.5
H17A-C17-H17C	109.5	H17B-C17-H17C	109.5
C6-N1-C5	108.6(4)	C6-N1-C7	108.0(4)
C5-N1-C7	106.0(3)	C6-N1-Ni1	114.6(3)
C5-N1-Ni1	107.1(2)	C7-N1-Ni1	112.1(3)
C11-N2-C10	108.8(4)	C11-N2-C9	105.6(3)
C10-N2-C9	109.9(4)	C11-N2-Ni1	109.4(3)

C10-N2-Ni1	109.8(3)	C9-N2-Ni1	113.2(3)
C15-N3-H3A	120.0	C15-N3-H3B	120.0
H3A-N3-H3B	120.0	C2-N4-H4A	120.0
C2-N4-H4B	120.0	H4A-N4-H4B	120.0
O1-Ni1-O2	169.46(12)	O1-Ni1-N1	91.84(12)
O2-Ni1-N1	94.12(13)	O1-Ni1-N2	90.19(13)
O2-Ni1-N2	97.78(13)	N1-Ni1-N2	96.32(14)
O1-Ni1-S2	83.83(9)	O2-Ni1-S2	89.78(9)
N1-Ni1-S2	174.96(10)	N2-Ni1-S2	86.30(10)
O1-Ni1-S1	89.69(10)	O2-Ni1-S1	82.06(9)
N1-Ni1-S1	86.06(10)	N2-Ni1-S1	177.61(10)
S2-Ni1-S1	91.32(4)	C15-O1-Ni1	121.2(3)
C2-O2-Ni1	122.9(3)	C1-S1-C4	104.2(2)
C1-S1-Ni1	96.71(16)	C4-S1-Ni1	96.64(16)
C14-S2-C12	104.9(2)	C14-S2-Ni1	95.22(15)
C12-S2-Ni1	96.35(15)		

Symmetry transformations used to generate equivalent atoms (if any):

Table 5. Torsion angles (°) for btw5.

S1-C1-C2-O2	-18.8(6)	S1-C1-C2-N4	164.0(4)
C3-C4-C5-N1	-178.7(4)	S1-C4-C5-N1	-57.4(4)
N1-C7-C8-C9	73.5(5)	C7-C8-C9-N2	-71.0(6)
N2-C11-C12-C13	-179.4(4)	N2-C11-C12-S2	53.2(5)
S2-C14-C15-O1	-12.3(6)	S2-C14-C15-N3	169.4(4)
C4-C5-N1-C6	-68.7(5)	C4-C5-N1-C7	175.5(4)
C4-C5-N1-Ni1	55.7(4)	C8-C7-N1-C6	69.2(5)
C8-C7-N1-C5	-174.5(4)	C8-C7-N1-Ni1	-57.9(5)
C12-C11-N2-C10	71.2(5)	C12-C11-N2-C9	-171.0(4)
C12-C11-N2-Ni1	-48.8(4)	C8-C9-N2-C11	173.7(4)
C8-C9-N2-C10	-69.1(5)	C8-C9-N2-Ni1	54.1(5)
C6-N1-Ni1-O1	-176.5(3)	C5-N1-Ni1-O1	63.0(3)
C7-N1-Ni1-O1	-53.0(3)	C6-N1-Ni1-O2	12.2(3)
C5-N1-Ni1-O2	-108.3(3)	C7-N1-Ni1-O2	135.7(3)
C6-N1-Ni1-N2	-86.1(3)	C5-N1-Ni1-N2	153.3(3)
C7-N1-Ni1-N2	37.4(3)	C6-N1-Ni1-S2	152.8(10)
C5-N1-Ni1-S2	32.2(13)	C7-N1-Ni1-S2	-83.7(12)
C6-N1-Ni1-S1	94.0(3)	C5-N1-Ni1-S1	-26.6(2)
C7-N1-Ni1-S1	-142.5(3)	C11-N2-Ni1-O1	-61.4(3)
C10-N2-Ni1-O1	179.2(3)	C9-N2-Ni1-O1	56.0(3)
C11-N2-Ni1-O2	111.7(3)	C10-N2-Ni1-O2	-7.7(3)
C9-N2-Ni1-O2	-130.9(3)	C11-N2-Ni1-N1	-153.3(3)
C10-N2-Ni1-N1	87.3(3)	C9-N2-Ni1-N1	-35.9(3)
C11-N2-Ni1-S2	22.4(3)	C10-N2-Ni1-S2	-97.0(3)
C9-N2-Ni1-S2	139.8(3)	C11-N2-Ni1-S1	26(3)
C10-N2-Ni1-S1	-94(2)	C9-N2-Ni1-S1	143(2)
N3-C15-O1-Ni1	177.0(4)	C14-C15-O1-Ni1	-1.2(6)
O2-Ni1-O1-C15	-43.3(9)	N1-Ni1-O1-C15	-167.7(4)
N2-Ni1-O1-C15	96.0(4)	S2-Ni1-O1-C15	9.7(3)
S1-Ni1-O1-C15	-81.6(3)	N4-C2-O2-Ni1	-175.6(4)
C1-C2-O2-Ni1	7.3(6)	O1-Ni1-O2-C2	-34.6(9)
N1-Ni1-O2-C2	89.7(3)	N2-Ni1-O2-C2	-173.4(3)
S2-Ni1-O2-C2	-87.1(3)	S1-Ni1-O2-C2	4.2(3)
C2-C1-S1-C4	-81.1(4)	C2-C1-S1-Ni1	17.5(4)
C5-C4-S1-C1	126.1(3)	C3-C4-S1-C1	-112.7(4)
C5-C4-S1-Ni1	27.4(3)	C3-C4-S1-Ni1	148.6(4)
O1-Ni1-S1-C1	162.4(2)	O2-Ni1-S1-C1	-11.1(2)
N1-Ni1-S1-C1	-105.8(2)	N2-Ni1-S1-C1	75(2)
S2-Ni1-S1-C1	78.53(18)	O1-Ni1-S1-C4	-92.42(18)
O2-Ni1-S1-C4	94.16(18)	N1-Ni1-S1-C4	-0.56(18)
N2-Ni1-S1-C4	-180(100)	S2-Ni1-S1-C4	-176.25(16)
C15-C14-S2-C12	-82.4(4)	C15-C14-S2-Ni1	15.6(4)
C11-C12-S2-C14	69.4(4)	C13-C12-S2-C14	-56.9(4)
C11-C12-S2-Ni1	-27.7(3)	C13-C12-S2-Ni1	-154.0(4)
O1-Ni1-S2-C14	-12.30(19)	O2-Ni1-S2-C14	159.29(19)
N1-Ni1-S2-C14	18.6(12)	N2-Ni1-S2-C14	-102.9(2)
S1-Ni1-S2-C14	77.24(17)	O1-Ni1-S2-C12	93.36(18)
O2-Ni1-S2-C12	-95.05(17)	N1-Ni1-S2-C12	124.3(12)
N2-Ni1-S2-C12	2.77(18)	S1-Ni1-S2-C12	-177.10(16)

Symmetry transformations used to generate equivalent atoms (if any):

Table 6. Anisotropic atomic displacement parameters ($Å^2$) for btw5.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2} U_{11} + ... + 2hka^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.060(3)	0.060(3)	0.047(2)	0.004(2)	-0.019(2)	-0.029(2)
C2	0.043(2)	0.046(2)	0.0350(19)	0.0009(16)	-0.0101(16)	-0.0109(17)
C3	0.051(3)	0.078(4)	0.086(4)	0.000(3)	0.003(3)	-0.024(3)
C4	0.044(2)	0.044(2)	0.055(3)	0.0046(19)	-0.0108(19)	-0.0053(18)
C5	0.046(2)	0.044(2)	0.044(2)	-0.0013(17)	-0.0061(18)	-0.0059(18)
C6	0.063(3)	0.034(2)	0.056(3)	0.0083(18)	-0.016(2)	-0.0033(19)
C7	0.064(3)	0.047(2)	0.043(2)	-0.0099(19)	-0.011(2)	-0.013(2)
C8	0.064(3)	0.050(2)	0.056(3)	-0.011(2)	-0.015(2)	-0.023(2)
C9	0.058(3)	0.057(3)	0.051(3)	-0.005(2)	-0.018(2)	-0.023(2)
C10	0.065(3)	0.061(3)	0.052(3)	0.014(2)	-0.016(2)	-0.031(2)
C11	0.042(2)	0.060(3)	0.047(2)	-0.001(2)	-0.0119(18)	-0.015(2)
C12	0.045(2)	0.057(3)	0.041(2)	-0.0005(19)	-0.0034(18)	-0.011(2)
C13	0.054(3)	0.070(3)	0.071(4)	-0.003(3)	-0.001(3)	-0.003(3)
C14	0.062(3)	0.040(2)	0.043(2)	0.0025(17)	-0.011(2)	-0.009(2)
C15	0.042(2)	0.044(2)	0.037(2)	0.0057(16)	-0.0084(16)	-0.0075(17)
C16	0.52(4)	0.110(10)	0.192(17)	0.027(11)	-0.07(2)	-0.155(18)
O3	0.140(5)	0.092(4)	0.075(3)	-0.008(3)	0.008(3)	-0.035(4)
O4	0.108(4)	0.214(8)	0.068(3)	0.021(4)	-0.027(3)	-0.070(5)
C17	0.249(15)	0.313(18)	0.088(6)	0.052(9)	-0.070(8)	-0.234(15)
I1	0.0684(2)	0.0667(2)	0.0634(2)	0.00471(16)	-0.02080(17)	-0.03390(18)
I3	0.0789(3)	0.0604(2)	0.0652(2)	0.00360(17)	-0.01951(19)	0.00588(18)
N1	0.0492(19)	0.0367(16)	0.0373(17)	0.0020(13)	-0.0123(15)	-0.0090(14)
N2	0.0480(19)	0.0471(18)	0.0367(17)	0.0017(14)	-0.0123(14)	-0.0180(16)
N3	0.076(3)	0.048(2)	0.041(2)	0.0094(17)	-0.0100(19)	0.006(2)
N4	0.060(3)	0.082(3)	0.055(2)	0.020(2)	-0.030(2)	-0.032(2)
Ni1	0.0408(3)	0.0347(2)	0.0312(2)	0.00251(18)	-0.01086(19)	-0.0100(2)
O1	0.0543(17)	0.0395(14)	0.0347(14)	0.0014(11)	-0.0120(12)	-0.0060(13)
O2	0.0475(16)	0.0529(17)	0.0386(15)	0.0085(12)	-0.0150(12)	-0.0202(14)
S1	0.0477(6)	0.0399(5)	0.0442(5)	0.0055(4)	-0.0100(4)	-0.0145(4)
S2	0.0506(6)	0.0433(5)	0.0352(5)	-0.0026(4)	-0.0110(4)	-0.0106(4)

Table 7. Hydrogen atom coordinates and isotropic atomic displacement parameters ($Å^2$) for btw5.

	x/a	y/b	z/c	U
H1A	1.0766	0.2906	0.3870	0.063
H1B	0.9433	0.4069	0.4213	0.063
H3C	1.2746	0.1772	0.0942	0.110
H3D	1.2415	0.2992	0.1619	0.110
H3E	1.1655	0.3063	0.0744	0.110
H4	1.1300	0.1494	0.2399	0.059
H5A	0.9832	0.2067	0.0846	0.056
H5B	1.0873	0.0720	0.0988	0.056
H6A	1.0229	-0.0740	0.2143	0.080
H6B	0.8892	-0.0275	0.2967	0.080
H6C	1.0138	0.0246	0.2964	0.080
H7A	0.9101	-0.0195	0.0879	0.062
H7B	0.8190	0.1209	0.0730	0.062
H8A	0.7299	-0.0322	0.2240	0.066
H8B	0.6943	-0.0315	0.1197	0.066
H9A	0.5756	0.1937	0.1445	0.064
H9B	0.5049	0.1054	0.2129	0.064
H10A	0.5670	0.1807	0.4337	0.084
H10B	0.6508	0.0552	0.3702	0.084
H10C	0.4896	0.1062	0.3843	0.084
H11A	0.3792	0.2952	0.3148	0.059
H11B	0.4587	0.3643	0.2338	0.059
H12	0.4447	0.3824	0.4370	0.059
H13A	0.3177	0.5746	0.3157	0.105
H13B	0.3182	0.6000	0.4259	0.105
H13C	0.2411	0.5070	0.4000	0.105
H14A	0.5093	0.6146	0.2413	0.060
H14B	0.6580	0.6202	0.2406	0.060
H16A	0.9306	0.3621	0.9054	0.394
H16B	0.9210	0.4265	0.8030	0.394
H16C	0.9229	0.2827	0.8163	0.394
H3	0.7024	0.3487	0.8853	0.160
H4O	0.7359	0.0948	0.7156	0.187
H17A	0.5663	0.1026	0.6709	0.267
H17B	0.6611	-0.0111	0.5986	0.267
H17C	0.6380	0.1319	0.5656	0.267
H3A	0.6670	0.5007	0.0093	0.074
H3B	0.5919	0.6229	0.0671	0.074
H4A	0.9013	0.1363	0.5542	0.073
H4B	1.0073	0.2047	0.5400	0.073

Supplementary Information 4

Table 1. Crystal data and structure refinement for Complex BC39 (**Complex 6**).

Identification code	Complex BC39
Empirical formula	C13 H28 I2 N4 Ni O2 S2
Formula weight	649.02
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Crystal size	0.15 x 0.15 x 0.05 mm
Unit cell dimensions	a = 11.2811(9)A alpha = 90deg. b = 12.8465(8)A beta = 83.251(4)deg. c = 15.4674(13)A gamma = 90deg.
Volume	2226.0(3) A^3
Z, Calculated density	4, 1.937 Mg/m^3
Absorption coefficient	3.846 mm^-1
F(000)	1264
Theta range for data collection	2.07 to 23.36 deg.
Limiting indices	0<=h<=12, -13<=k<=13, -16<=l<=17
Reflections collected / unique	5962 / 3113 [R(int) = 0.1168]
Completeness to theta = 23.36	96.0 %
Reflections with I>2sigma(I)	2038
Max. and min. transmission	0.8309 and 0.5962
Data / restraints / parameters	3113 / 0 / 217
Goodness-of-fit on F^2	1.089
Final R indices [I>2sigma(I)]	R1 = 0.0641, wR2 = 0.1383
R indices (all data)	R1 = 0.1071, wR2 = 0.1548
Largest diff. peak and hole	0.925 and -0.806 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for Complex BC39. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ni	7554(1)	2998(1)	1017(1)	39(1)
S(1)	8950(3)	2128(2)	1834(2)	51(1)
S(2)	7018(3)	4372(2)	2087(2)	50(1)
O(1)	9096(7)	3938(6)	668(6)	50(2)
O(2)	6728(8)	3940(6)	215(5)	45(2)
N(1)	8047(10)	1938(7)	6(7)	52(3)
N(2)	5913(9)	2284(7)	1491(7)	49(3)
N(3)	10705(11)	4712(9)	1071(8)	73(4)
N(4)	6487(10)	5561(8)	-197(7)	57(3)
C(1)	9891(12)	3968(10)	1172(9)	54(3)
C(2)	9916(12)	3219(10)	1897(9)	61(4)
C(3)	9673(13)	1426(12)	899(9)	69(4)
C(4)	8750(16)	1104(11)	322(11)	86(5)
C(5)	8770(15)	2477(12)	-722(10)	83(5)
C(6)	6996(17)	1514(12)	-402(11)	86(5)
C(7)	5979(14)	1034(12)	202(10)	72(4)
C(8)	5316(12)	1849(11)	772(10)	65(4)
C(9)	6051(13)	1442(11)	2129(10)	72(4)
C(10)	5091(11)	3101(10)	1898(9)	58(4)
C(11)	5663(12)	3771(11)	2541(8)	56(4)
C(12)	6516(14)	5282(8)	1309(8)	62(4)
C(13)	6568(11)	4870(9)	407(7)	41(3)
I(1)	12873(1)	5544(1)	2437(1)	68(1)
I(2)	7275(1)	8090(1)	733(1)	66(1)

Table 3. Bond lengths [A] and angles [deg] for Complex BC39.

Ni-O(2)	2.035(8)
Ni-N(1)	2.098(10)
Ni-N(2)	2.118(10)
Ni-O(1)	2.134(8)
Ni-S(1)	2.407(4)
Ni-S(2)	2.446(3)
S(1)-C(2)	1.785(13)
S(1)-C(3)	1.815(14)
S(2)-C(11)	1.781(14)
S(2)-C(12)	1.815(12)
O(1)-C(1)	1.256(15)
O(2)-C(13)	1.238(13)
N(1)-C(4)	1.451(17)
N(1)-C(5)	1.482(17)
N(1)-C(6)	1.509(19)
N(2)-C(8)	1.476(16)
N(2)-C(9)	1.485(15)
N(2)-C(10)	1.491(15)
N(3)-C(1)	1.321(16)
N(4)-C(13)	1.300(14)
C(1)-C(2)	1.482(18)
C(3)-C(4)	1.51(2)
C(6)-C(7)	1.52(2)
C(7)-C(8)	1.508(19)
C(10)-C(11)	1.516(18)
C(12)-C(13)	1.487(17)
O(2)-Ni-N(1)	91.9(4)
O(2)-Ni-N(2)	91.4(4)
N(1)-Ni-N(2)	97.0(4)
O(2)-Ni-O(1)	85.8(3)
N(1)-Ni-O(1)	92.4(4)
N(2)-Ni-O(1)	170.3(4)
O(2)-Ni-S(1)	166.1(3)
N(1)-Ni-S(1)	87.6(3)
N(2)-Ni-S(1)	102.5(3)
O(1)-Ni-S(1)	80.3(3)
O(2)-Ni-S(2)	83.6(2)
N(1)-Ni-S(2)	174.3(3)
N(2)-Ni-S(2)	86.7(3)
O(1)-Ni-S(2)	83.8(2)
S(1)-Ni-S(2)	96.00(12)
C(2)-S(1)-C(3)	102.3(7)
C(2)-S(1)-Ni	96.0(4)
C(3)-S(1)-Ni	94.2(5)
C(11)-S(2)-C(12)	102.7(7)
C(11)-S(2)-Ni	95.0(5)
C(12)-S(2)-Ni	95.0(4)
C(1)-O(1)-Ni	118.8(8)
C(13)-O(2)-Ni	119.5(8)
C(4)-N(1)-C(5)	109.1(12)
C(4)-N(1)-C(6)	111.2(11)
C(5)-N(1)-C(6)	103.9(12)
C(4)-N(1)-Ni	109.6(9)
C(5)-N(1)-Ni	109.7(8)
C(6)-N(1)-Ni	113.2(9)
C(8)-N(2)-C(9)	108.5(11)

C(8)-N(2)-C(10)	105.6(10)
C(9)-N(2)-C(10)	109.9(10)
C(8)-N(2)-Ni	111.2(8)
C(9)-N(2)-Ni	113.0(8)
C(10)-N(2)-Ni	108.5(7)
O(1)-C(1)-N(3)	119.1(13)
O(1)-C(1)-C(2)	121.8(12)
N(3)-C(1)-C(2)	119.0(13)
C(1)-C(2)-S(1)	113.8(10)
C(4)-C(3)-S(1)	109.3(10)
N(1)-C(4)-C(3)	116.1(12)
N(1)-C(6)-C(7)	117.5(13)
C(8)-C(7)-C(6)	111.3(12)
N(2)-C(8)-C(7)	117.7(11)
N(2)-C(10)-C(11)	112.7(11)
C(10)-C(11)-S(2)	113.5(9)
C(13)-C(12)-S(2)	114.3(8)
O(2)-C(13)-N(4)	120.5(11)
O(2)-C(13)-C(12)	123.8(11)
N(4)-C(13)-C(12)	115.6(10)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for Complex BC39. The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Ni	39(1)	32(1)	45(1)	1(1)	-2(1)	-1(1)
S(1)	50(2)	50(2)	53(2)	10(2)	-1(2)	5(2)
S(2)	59(2)	47(2)	43(2)	-2(2)	-5(2)	2(2)
O(1)	43(6)	49(5)	58(6)	6(4)	-1(5)	-14(4)
O(2)	59(6)	32(5)	44(5)	5(4)	-10(4)	1(4)
N(1)	60(7)	42(6)	55(7)	-8(5)	-8(6)	8(5)
N(2)	49(7)	45(6)	54(7)	14(5)	-7(5)	-3(5)
N(3)	79(9)	70(8)	72(9)	10(7)	-22(7)	-29(7)
N(4)	86(9)	44(6)	41(6)	1(5)	-3(6)	11(6)
C(1)	43(9)	54(8)	66(10)	-7(7)	-6(7)	-2(7)
C(2)	43(8)	76(9)	64(9)	5(8)	-11(7)	-6(7)
C(3)	56(10)	76(10)	73(11)	1(8)	-3(8)	33(8)
C(4)	98(14)	66(10)	92(13)	-21(9)	-7(10)	48(10)
C(5)	107(14)	76(10)	61(10)	4(8)	16(9)	8(10)
C(6)	118(15)	63(9)	78(12)	-22(9)	-18(11)	7(10)
C(7)	74(11)	65(9)	78(11)	-20(8)	-15(9)	-23(9)
C(8)	44(9)	69(9)	83(11)	9(8)	-19(8)	-26(7)
C(9)	65(10)	68(9)	81(11)	32(8)	-1(8)	-2(8)
C(10)	36(8)	71(9)	65(9)	26(8)	7(6)	-6(7)
C(11)	59(9)	74(9)	35(7)	9(7)	-5(6)	4(7)
C(12)	102(12)	24(6)	56(9)	0(6)	2(8)	16(7)
C(13)	52(8)	36(7)	33(7)	1(6)	0(6)	-1(6)
I(1)	62(1)	82(1)	60(1)	-6(1)	-12(1)	11(1)
I(2)	79(1)	50(1)	71(1)	6(1)	-19(1)	-11(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for Complex BC39.

	x	y	z	U(iso)
H(3A)	10686	5167	665	87
H(3B)	11255	4741	1412	87
H(4A)	6543	5374	-734	68
H(4B)	6376	6205	-59	68
H(2A)	9689	3579	2443	73
H(2B)	10726	2969	1902	73
H(3C)	10268	1866	577	82
H(3D)	10073	814	1093	82
H(4C)	9152	737	-177	103
H(4D)	8208	615	642	103
H(5A)	8312	3033	-930	125
H(5B)	8988	1991	-1185	125
H(5C)	9479	2755	-521	125
H(6A)	7292	990	-825	103
H(6B)	6669	2076	-720	103
H(7A)	5429	691	-142	86
H(7B)	6297	513	566	86
H(8A)	5131	2421	401	78
H(8B)	4563	1549	1021	78
H(9A)	6441	1713	2600	108
H(9B)	6522	889	1847	108
H(9C)	5278	1179	2351	108
H(10A)	4385	2769	2196	70
H(10B)	4838	3542	1444	70
H(11A)	5823	3343	3030	67
H(11B)	5103	4309	2760	67
H(12A)	5700	5481	1506	74
H(12B)	7004	5905	1300	74

Supplementary Information 5

Table 1. Crystal data and structure refinement for btw17o (**Complex 8**).

Identification code	btw17o
Empirical formula	C10 H19 N2 Ni O12
Formula weight	417.96
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pna2(1)
Unit cell dimensions	a = 14.669(5) A alpha = 90 deg. b = 16.306(5) A beta = 90 deg. c = 7.034(2) A gamma = 90 deg.
Volume	1682.5(9) A^3
Z, Calculated density	4, 1.626 Mg/m^3
Absorption coefficient	1.218 mm^-1
F(000)	844
Crystal size	0.30 x 0.02 x 0.02 mm
Theta range for data collection	1.87 to 28.36 deg.
Limiting indices	-19<=h<=18, -21<=k<=19, -9<=l<=7
Reflections collected / unique	11122 / 3752 [R(int) = 0.0289]
Completeness to theta = 28.36	99.6 %
Absorption correction	Empirical
Max. and min. transmission	0.9761 and 0.7114
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3752 / 1 / 227
Goodness-of-fit on F^2	1.064
Final R indices [I>2sigma(I)]	R1 = 0.0368, wR2 = 0.0941
R indices (all data)	R1 = 0.0409, wR2 = 0.0959
Absolute structure parameter	0.047(16)
Largest diff. peak and hole	0.497 and -0.294 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for btw17o. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	1530(2)	7893(2)	2035(5)	27(1)
C(2)	622(2)	8012(2)	3062(5)	23(1)
C(3)	225(2)	6188(2)	7393(5)	23(1)
C(4)	315(2)	5846(2)	5376(4)	24(1)
C(5)	2742(2)	5714(2)	6377(5)	26(1)
C(6)	1890(2)	5351(2)	5496(6)	27(1)
C(7)	2212(2)	6513(2)	2117(5)	24(1)
C(8)	1352(2)	6038(2)	2599(5)	25(1)
C(9)	3088(2)	7720(2)	3160(5)	25(1)
C(10)	3512(2)	7971(2)	1289(5)	22(1)
N(1)	1262(2)	5964(1)	4700(4)	20(1)
N(2)	2187(2)	7341(2)	3014(4)	20(1)
Ni(1)	1636(1)	7098(1)	5767(1)	19(1)
O(1)	537(2)	7720(1)	4721(4)	27(1)
O(2)	30(2)	8405(1)	2186(4)	33(1)
O(3)	784(2)	6704(1)	7971(3)	28(1)
O(4)	-447(2)	5926(1)	8313(4)	34(1)
O(5)	3365(2)	5225(2)	6828(5)	42(1)
O(6)	2771(1)	6478(1)	6647(4)	28(1)
O(7)	4157(2)	8512(1)	1472(4)	31(1)
O(8)	3271(2)	7689(2)	-242(4)	34(1)
O(9)	2029(2)	8138(1)	7145(4)	35(1)
O(10)	9678(2)	8442(2)	8130(5)	52(1)
O(11)	9443(2)	9932(2)	3448(5)	54(1)
O(12)	1821(2)	9626(2)	5606(7)	63(1)

Table 3. Bond lengths [A] and angles [deg] for btw17o.

C(1)-N(2)	1.487(4)
C(1)-C(2)	1.527(4)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(2)-O(2)	1.243(4)
C(2)-O(1)	1.267(4)
C(3)-O(3)	1.244(4)
C(3)-O(4)	1.254(4)
C(3)-C(4)	1.530(4)
C(4)-N(1)	1.481(4)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-O(5)	1.253(4)
C(5)-O(6)	1.259(4)
C(5)-C(6)	1.516(4)
C(6)-N(1)	1.471(4)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-N(2)	1.491(4)
C(7)-C(8)	1.518(4)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-N(1)	1.489(4)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-N(2)	1.463(4)
C(9)-C(10)	1.512(5)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-O(8)	1.223(4)
C(10)-O(7)	1.301(4)
N(1)-Ni(1)	2.069(2)
N(2)-Ni(1)	2.135(3)
Ni(1)-O(9)	2.036(2)
Ni(1)-O(1)	2.041(2)
Ni(1)-O(6)	2.044(2)
Ni(1)-O(3)	2.093(2)
O(7)-H(7)	0.8200

N(2)-C(1)-C(2)	115.0(3)
N(2)-C(1)-H(1A)	108.5
C(2)-C(1)-H(1A)	108.5
N(2)-C(1)-H(1B)	108.5
C(2)-C(1)-H(1B)	108.5
H(1A)-C(1)-H(1B)	107.5
O(2)-C(2)-O(1)	125.6(3)
O(2)-C(2)-C(1)	116.1(3)
O(1)-C(2)-C(1)	118.3(3)
O(3)-C(3)-O(4)	125.5(3)
O(3)-C(3)-C(4)	119.5(3)
O(4)-C(3)-C(4)	115.0(3)
N(1)-C(4)-C(3)	109.4(2)
N(1)-C(4)-H(4A)	109.8
C(3)-C(4)-H(4A)	109.8

N(1)-C(4)-H(4B)	109.8
C(3)-C(4)-H(4B)	109.8
H(4A)-C(4)-H(4B)	108.2
O(5)-C(5)-O(6)	124.5(3)
O(5)-C(5)-C(6)	117.1(3)
O(6)-C(5)-C(6)	118.4(3)
N(1)-C(6)-C(5)	114.0(2)
N(1)-C(6)-H(6A)	108.8
C(5)-C(6)-H(6A)	108.8
N(1)-C(6)-H(6B)	108.8
C(5)-C(6)-H(6B)	108.8
H(6A)-C(6)-H(6B)	107.7
N(2)-C(7)-C(8)	110.3(2)
N(2)-C(7)-H(7A)	109.6
C(8)-C(7)-H(7A)	109.6
N(2)-C(7)-H(7B)	109.6
C(8)-C(7)-H(7B)	109.6
H(7A)-C(7)-H(7B)	108.1
N(1)-C(8)-C(7)	109.7(3)
N(1)-C(8)-H(8A)	109.7
C(7)-C(8)-H(8A)	109.7
N(1)-C(8)-H(8B)	109.7
C(7)-C(8)-H(8B)	109.7
H(8A)-C(8)-H(8B)	108.2
N(2)-C(9)-C(10)	115.1(3)
N(2)-C(9)-H(9A)	108.5
C(10)-C(9)-H(9A)	108.5
N(2)-C(9)-H(9B)	108.5
C(10)-C(9)-H(9B)	108.5
H(9A)-C(9)-H(9B)	107.5
O(8)-C(10)-O(7)	123.5(3)
O(8)-C(10)-C(9)	123.1(3)
O(7)-C(10)-C(9)	113.4(3)
C(6)-N(1)-C(4)	112.1(2)
C(6)-N(1)-C(8)	112.1(3)
C(4)-N(1)-C(8)	114.4(2)
C(6)-N(1)-Ni(1)	107.65(18)
C(4)-N(1)-Ni(1)	104.42(17)
C(8)-N(1)-Ni(1)	105.33(17)
C(9)-N(2)-C(1)	111.3(2)
C(9)-N(2)-C(7)	112.9(2)
C(1)-N(2)-C(7)	111.6(2)
C(9)-N(2)-Ni(1)	110.9(2)
C(1)-N(2)-Ni(1)	106.69(19)
C(7)-N(2)-Ni(1)	102.99(18)
O(9)-Ni(1)-O(1)	88.96(10)
O(9)-Ni(1)-O(6)	92.16(10)
O(1)-Ni(1)-O(6)	176.41(10)
O(9)-Ni(1)-N(1)	172.54(11)
O(1)-Ni(1)-N(1)	95.93(10)
O(6)-Ni(1)-N(1)	83.31(9)
O(9)-Ni(1)-O(3)	94.12(10)
O(1)-Ni(1)-O(3)	87.03(9)
O(6)-Ni(1)-O(3)	96.29(10)
N(1)-Ni(1)-O(3)	80.54(9)
O(9)-Ni(1)-N(2)	99.81(10)
O(1)-Ni(1)-N(2)	83.08(10)
O(6)-Ni(1)-N(2)	93.37(10)

N(1)-Ni(1)-N(2)	86.41(10)
O(3)-Ni(1)-N(2)	162.72(9)
C(2)-O(1)-Ni(1)	116.2(2)
C(3)-O(3)-Ni(1)	111.1(2)
C(5)-O(6)-Ni(1)	114.6(2)
C(10)-O(7)-H(7)	109.5

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for btw17o.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	25(2)	34(2)	21(2)	5(1)	2(1)	6(1)
C(2)	25(2)	22(1)	23(2)	-3(1)	1(1)	0(1)
C(3)	25(2)	22(1)	22(2)	2(1)	4(1)	3(1)
C(4)	20(1)	26(1)	25(2)	-4(1)	2(1)	-4(1)
C(5)	25(2)	32(2)	23(2)	4(1)	2(1)	1(1)
C(6)	29(1)	19(1)	33(2)	0(1)	-2(2)	2(1)
C(7)	23(2)	26(1)	22(2)	-3(1)	3(1)	0(1)
C(8)	27(2)	29(2)	19(2)	-6(1)	3(1)	-2(1)
C(9)	21(1)	35(2)	18(2)	0(1)	-1(1)	-6(1)
C(10)	19(1)	27(2)	20(2)	3(1)	0(1)	3(1)
N(1)	19(1)	21(1)	21(1)	-1(1)	1(1)	-1(1)
N(2)	18(1)	24(1)	17(1)	-2(1)	0(1)	0(1)
Ni(1)	22(1)	20(1)	16(1)	-1(1)	0(1)	-1(1)
O(1)	26(1)	32(1)	23(1)	1(1)	3(1)	6(1)
O(2)	28(1)	41(1)	31(1)	3(1)	-4(1)	10(1)
O(3)	35(1)	28(1)	21(1)	-2(1)	4(1)	-4(1)
O(4)	36(1)	35(1)	30(1)	-4(1)	14(1)	-8(1)
O(5)	32(1)	44(1)	49(2)	6(1)	-8(1)	14(1)
O(6)	27(1)	27(1)	30(1)	0(1)	-8(1)	0(1)
O(7)	32(1)	37(1)	23(1)	2(1)	2(1)	-12(1)
O(8)	35(1)	46(2)	20(1)	-6(1)	-1(1)	-13(1)
O(9)	51(2)	27(1)	28(1)	-6(1)	-6(1)	-6(1)
O(10)	51(2)	52(2)	52(2)	1(2)	3(2)	2(1)
O(11)	61(2)	43(2)	59(2)	1(1)	14(2)	2(1)
O(12)	85(2)	42(1)	63(2)	12(2)	-4(2)	6(1)

Supplementary Information 6

Crystal Structure Information for bsc1o (Complex 10).

A brown plate shaped crystal of bsc1 (C10 H22 N2 Ni S2) with approximate dimensions 0.01 x 0.12 x 0.22 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 298(2) K, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal.

A total of 1850 frames were collected with a scan width of 0.3º in ω and an exposure time of 10 seconds/frame. The total data collection time was about 8 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Orthorhombic unit cell yielded a total of 6619 reflections to a maximum θ angle of 28.23° (0.90 Å resolution), of which 1650 were independent, completeness = 98.3%, R_{int} = 0.0863, R_{sig} = 0.0777 and 1146 were greater than 2σ(I). The final cell constants: a = 9.487(6)Å, b = 7.862(5)Å, c = 18.145(13)Å, α = 90°, β = 90°, γ = 90°, volume = 1353.4(16)$Å^3$, are based upon the refinement of the XYZ-centroids of 915 reflections above 20σ(I) with 2.248° <θ <24.842°. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.3458.

The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group Pbcn, with Z = 4 for the formula unit, C10 H22 N2 Ni S2. The final anisotropic full-matrix least-squares refinement on F^2 with 71 variables converged at R1 = 6.32%, for the observed data and wR2 = 16.41% for all data. The goodness-of-fit was 0.966. The largest peak on the final difference map was 0.802 $e^-/Å^3$ and the largest hole was -0.663 $e^-/Å^3$. Based on the final model, the calculated density of the crystal is 1.439 g/cm^3 and F(000) amounts to 624 electrons.

Table 1. Sample and crystal data for bsc1.

Identification code	bsc1	
Empirical formula	C10 H22 N2 Ni S2	
Formula weight	293.13	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal size	0.22 x 0.12 x 0.01 mm	
Crystal habit	red-brown plate	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 9.487(6) Å	α= 90°
	b = 7.862(5) Å	β= 90°
	c = 18.145(13) Å	γ = 90°
Volume	1353.4(16) $Å^3$	
Z	4	
Density (calculated)	1.439 g/cm^3	
Absorption coefficient	1.715 mm^{-1}	
F(000)	624	
Diffractometer	CCD area detector	
Radiation source	fine-focus sealed tube, MoKα	
Generator power	1600 watts (50 kV, 32mA)	
Detector distance	5.8 cm	
Data collection method	phi and omega scans	
Theta range for data collection	2.24 to 28.23°	
Index ranges	$-12 \leq h \leq 12$, $-9 \leq k \leq 10$, $-13 \leq l \leq 24$	

Table 2. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for bsc1.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C1	0.4353(5)	0.0965(6)	0.3899(3)	0.0399(12)
C2	0.4636(5)	0.2754(6)	0.4163(3)	0.0407(12)
C3	0.3566(7)	0.3271(7)	0.4744(3)	0.0610(16)
C4	0.6738(5)	0.0462(6)	0.3420(3)	0.0447(13)
C5	0.4748(5)	-0.1078(6)	0.2895(3)	0.0451(13)
N1	0.5200(4)	0.0548(5)	0.3232(2)	0.0340(9)
Ni1	0.5000	0.23289(9)	0.2500	0.0262(3)
S1	0.54055(13)	0.41707(15)	0.16365(7)	0.0365(3)

Table 3. Bond lengths (Å) for bsc1.

C1-N1	1.488(6)	C1-C2	1.510(6)
C1-H1A	0.9700	C1-H1B	0.9700
C2-C3	1.519(7)	C2-S1#1	1.829(5)
C2-H2	0.9800	C3-H3A	0.9600
C3-H3B	0.9600	C3-H3C	0.9600
C4-N1	1.500(6)	C4-H4A	0.9600
C4-H4B	0.9600	C4-H4C	0.9600
C5-N1	1.481(6)	C5-C5#1	1.511(10)
C5-H5A	0.9700	C5-H5B	0.9700
N1-Ni1	1.939(4)	Ni1-N1#1	1.939(4)
Ni1-S1	2.1679(16)	Ni1-S1#1	2.1679(16)
S1-C2#1	1.829(5)		

Symmetry transformations used to generate equivalent atoms (if any):
#1 -x+1,y,-z+1/2

Table 4. Bond angles (°) for bsc1.

N1-C1-C2	111.5(4)	N1-C1-H1A	109.3 C2-C1-
H1A	109.3	N1-C1-H1B	109.3 C2-C1-
H1B	109.3	H1A-C1-H1B	108.0 C3-C2-C1
110.5(4)	C3-C2-S1#1	111.9(4)	C1-C2-S1#1
108.2(4)	C3-C2-H2	108.7	C1-C2-H2
108.7	S1#1-C2-H2	108.7	C2-C3-H3A
109.5	C2-C3-H3B	109.5	H3A-C3-H3B
109.5	C2-C3-H3C	109.5	H3A-C3-H3C
109.5	H3B-C3-H3C	109.5	N1-C4-H4A
109.5	N1-C4-H4B	109.5	H4A-C4-H4B
109.5	N1-C4-H4C	109.5	H4A-C4-H4C
109.5	H4B-C4-H4C	109.5	N1-C5-C5#1
107.5(3)	N1-C5-H5A	110.2	C5#1-C5-H5A
110.2	N1-C5-H5B	110.2	C5#1-C5-H5B
110.2	H5A-C5-H5B	108.5	C1-N1-C5
111.7(4)	C1-N1-C4	110.5(4)	C5-N1-C4
109.7(4)	C1-N1-Ni1	110.2(3)	C5-N1-Ni1
108.2(3)	C4-N1-Ni1	106.5(3)	N1#1-Ni1-N1
87.6(2)	N1#1-Ni1-S1	90.24(13)	N1-Ni1-S1
163.74(11)	N1#1-Ni1-S1#1	163.74(11)	N1-Ni1-S1#1
90.24(13)	S1-Ni1-S1#1	96.18(9)	C2#1-S1-Ni1
99.36(18)			

Symmetry transformations used to generate equivalent atoms (if any):
#1 -x+1,y,-z+1/2

Table 5. Torsion angles (°) for bsc1.

N1-C1-C2-C3	168.9(4)	N1-C1-C2-S1#1	46.0(5)
C2-C1-N1-C5	-170.0(4)	C2-C1-N1-C4	67.7(5)
C2-C1-N1-Ni1	-49.7(4)	C5#1-C5-N1-C1	159.6(4)
C5#1-C5-N1-C4	-77.5(5)	C5#1-C5-N1-Ni1	38.2(5)
C1-N1-Ni1-N1#1	-136.3(3)	C5-N1-Ni1-N1#1	-13.9(2)
C4-N1-Ni1-N1#1	103.9(3)	C1-N1-Ni1-S1	141.2(4)
C5-N1-Ni1-S1	-96.5(5)	C4-N1-Ni1-S1	21.3(6)
C1-N1-Ni1-S1#1	27.6(3)	C5-N1-Ni1-S1#1	150.0(3)
C4-N1-Ni1-S1#1	-92.2(3)	N1#1-Ni1-S1-C2#1	-2.7(2)
N1-Ni1-S1-C2#1	79.5(5)	S1#1-Ni1-S1-C2#1	-167.72(18)

Symmetry transformations used to generate equivalent atoms (if any):
#1 -x+1,y,-z+1/2

Table 6. Anisotropic atomic displacement parameters (Å^2) for bsc1.

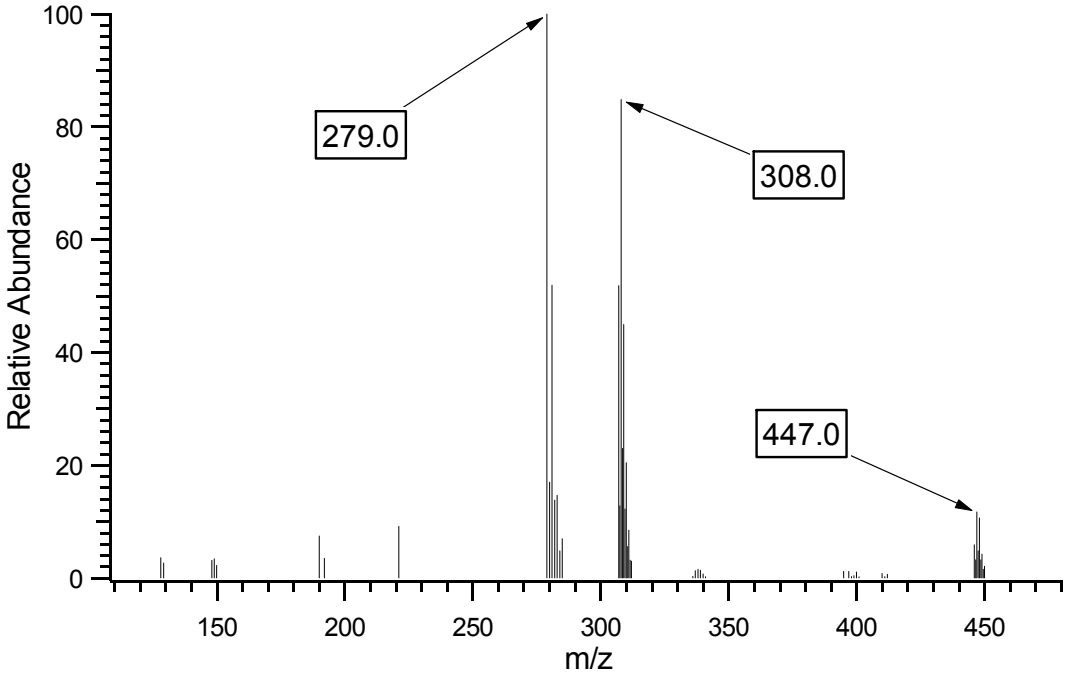
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2} U_{11} + ... + 2hka^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}
	U_{12}				
C1	0.035(3)	0.037(3)	0.047(3)	0.009(2)	0.001(2)
	0.001(2)				
C2	0.036(3)	0.047(3)	0.039(3)	0.001(2)	0.002(2)
	0.007(2)				
C3	0.077(4)	0.062(4)	0.044(3)	0.009(3)	0.018(3)
	0.015(3)				
C4	0.036(3)	0.044(3)	0.054(3)	0.007(2)	-0.002(2)
	0.006(2)				
C5	0.044(3)	0.022(2)	0.069(4)	0.005(2)	-0.001(3)
	0.001(2)				
N1	0.0228(19)	0.032(2)	0.047(2)	-0.0001(19)	-0.0040(16)
	0.0016(15)				
Ni1	0.0238(4)	0.0174(4)	0.0375(5)	0.000	0.0006(3)
	0.000				
S1	0.0402(7)	0.0260(6)	0.0432(7)	0.0031(5)	0.0079(5)
	0.0007(5)				

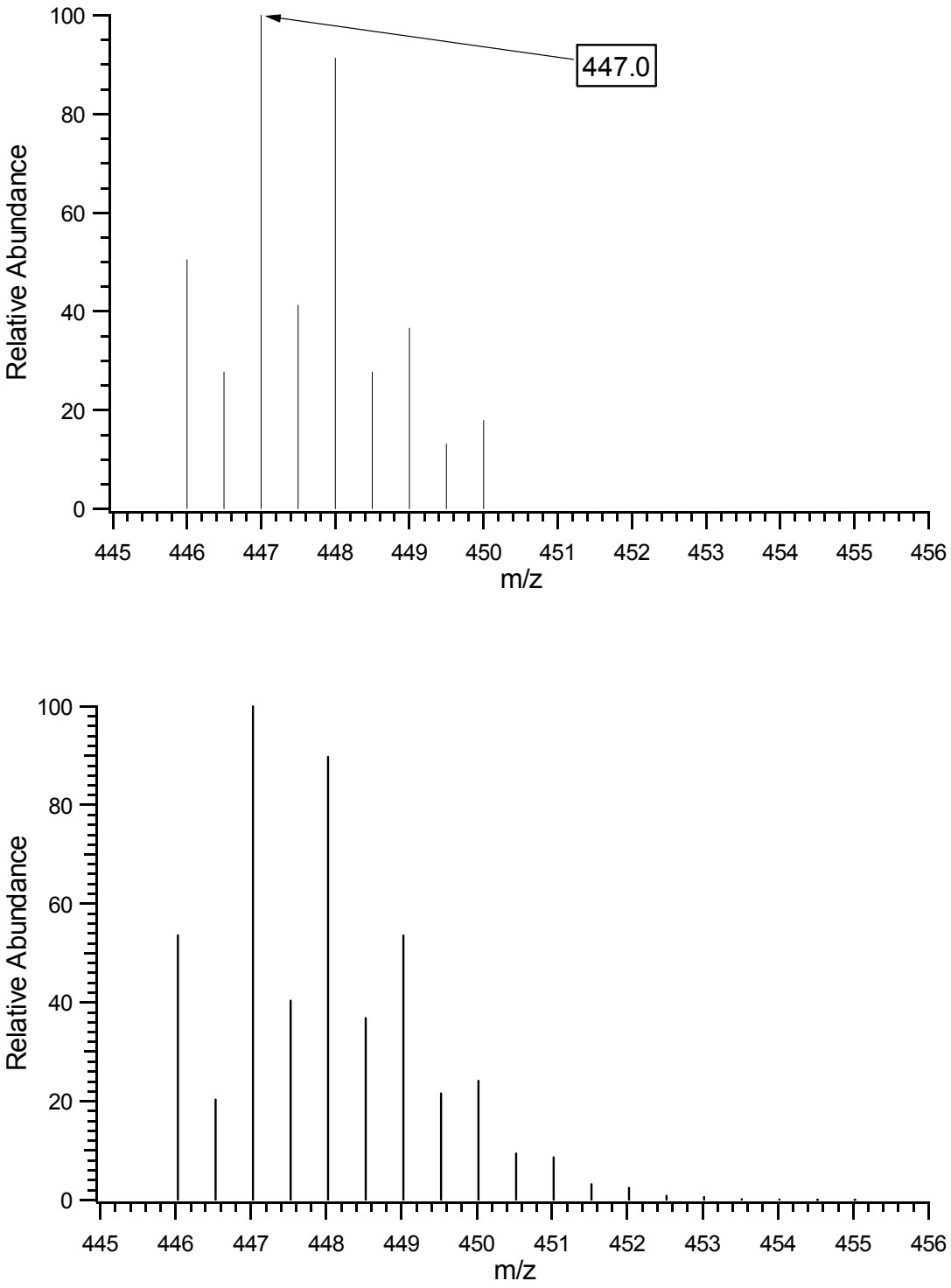
Table 7. Hydrogen atom coordinates and isotropic atomic displacement parameters ($Å^2$) for bsc1.

	x/a	y/b	z/c	U
H1A	0.4581	0.0167	0.4289	0.048
H1B	0.3359	0.0844	0.3786	0.048
H2	0.5580	0.2794	0.4382	0.049
H3A	0.2631	0.3084	0.4558	0.091
H3B	0.3684	0.4453	0.4860	0.091
H3C	0.3706	0.2602	0.5180	0.091
H4A	0.7043	0.1544	0.3608	0.067
H4B	0.7268	0.0186	0.2986	0.067
H4C	0.6887	-0.0397	0.3788	0.067
H5A	0.3729	-0.1178	0.2912	0.054
H5B	0.5154	-0.2030	0.3161	0.054

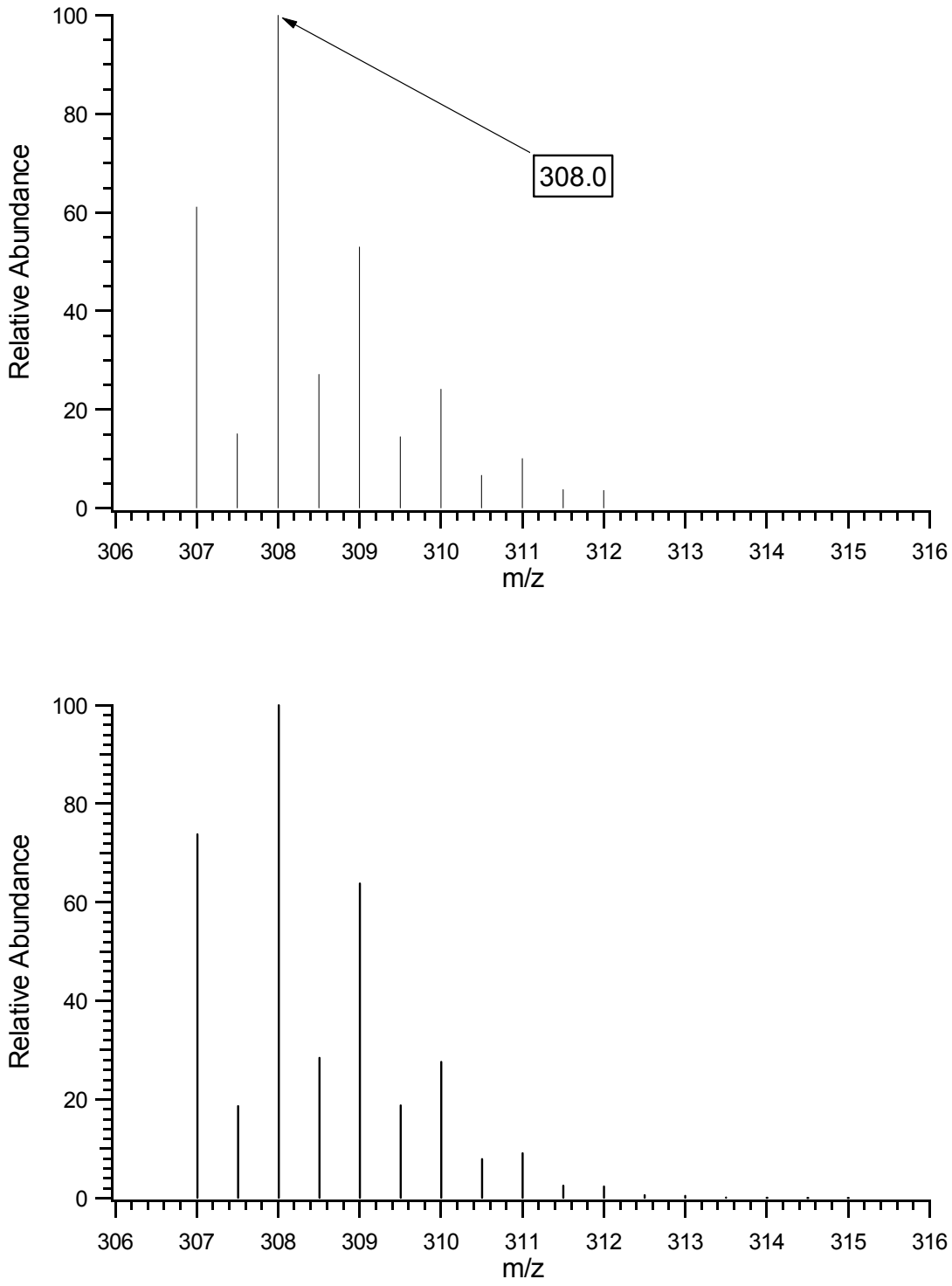
Supplementary Information 7



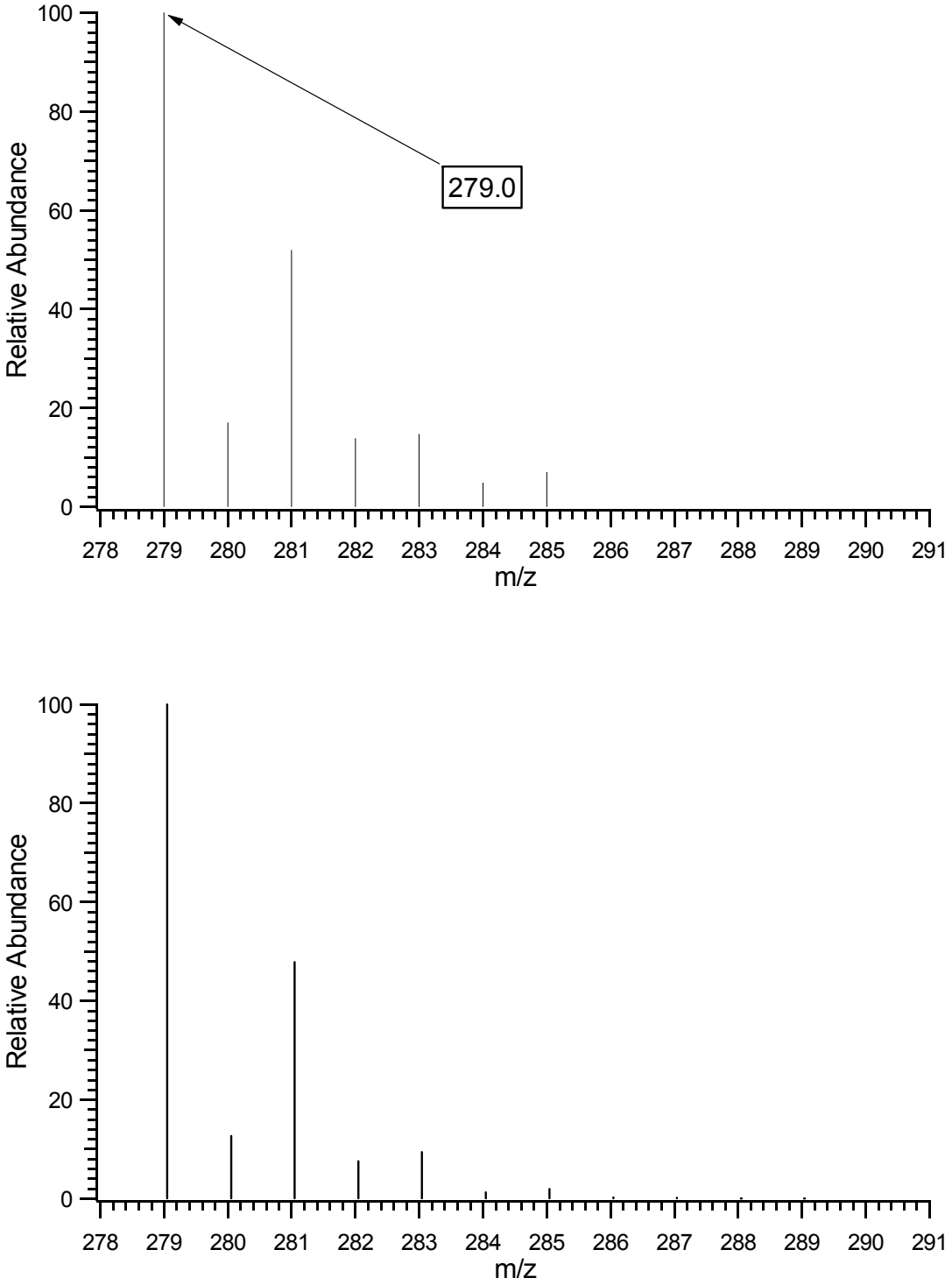
Supplementary Information 7a: ESI-MS of complex **1**.



Supplementary Information 7b: Expanded ESI-MS of the m/z = 447.0 isotopic cluster region (top), and the simulated isotopic fit for the cation $(Ni_4C_{27}H_{60}N_6S_6) / 2)^+$ (bottom).

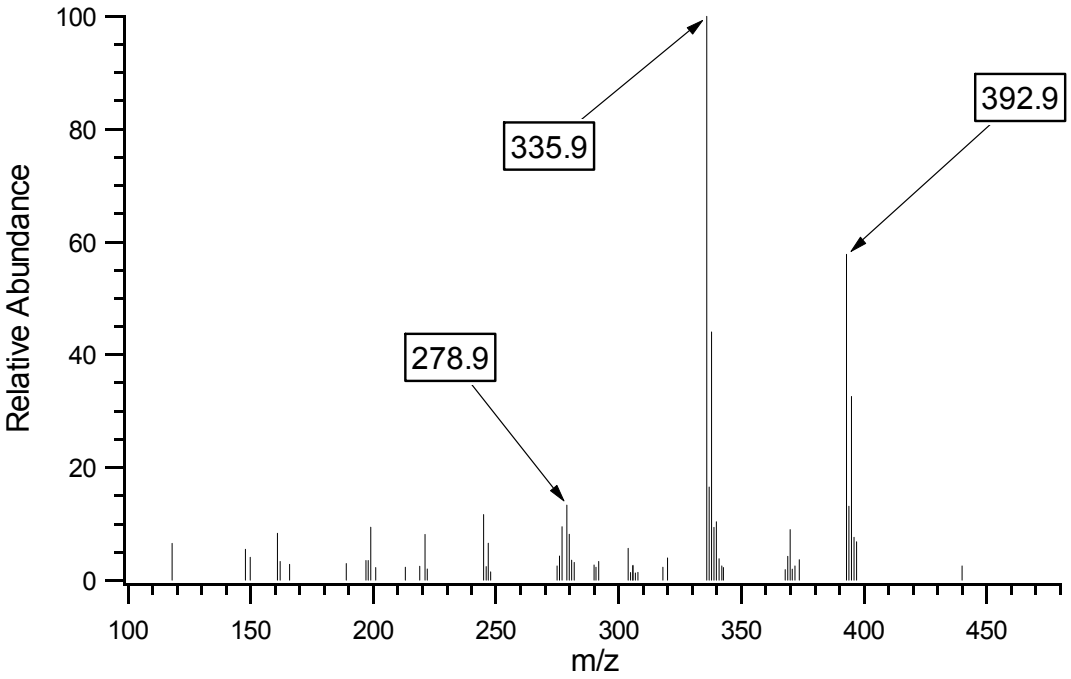


Supplementary Information 7c: Expanded ESI-MS of the m/z = 308.0 isotopic cluster region (top), and the simulated isotopic fit for the cation $(Ni_3C_{18}H_{40}N_4S_4) / 2)^+$ (bottom).

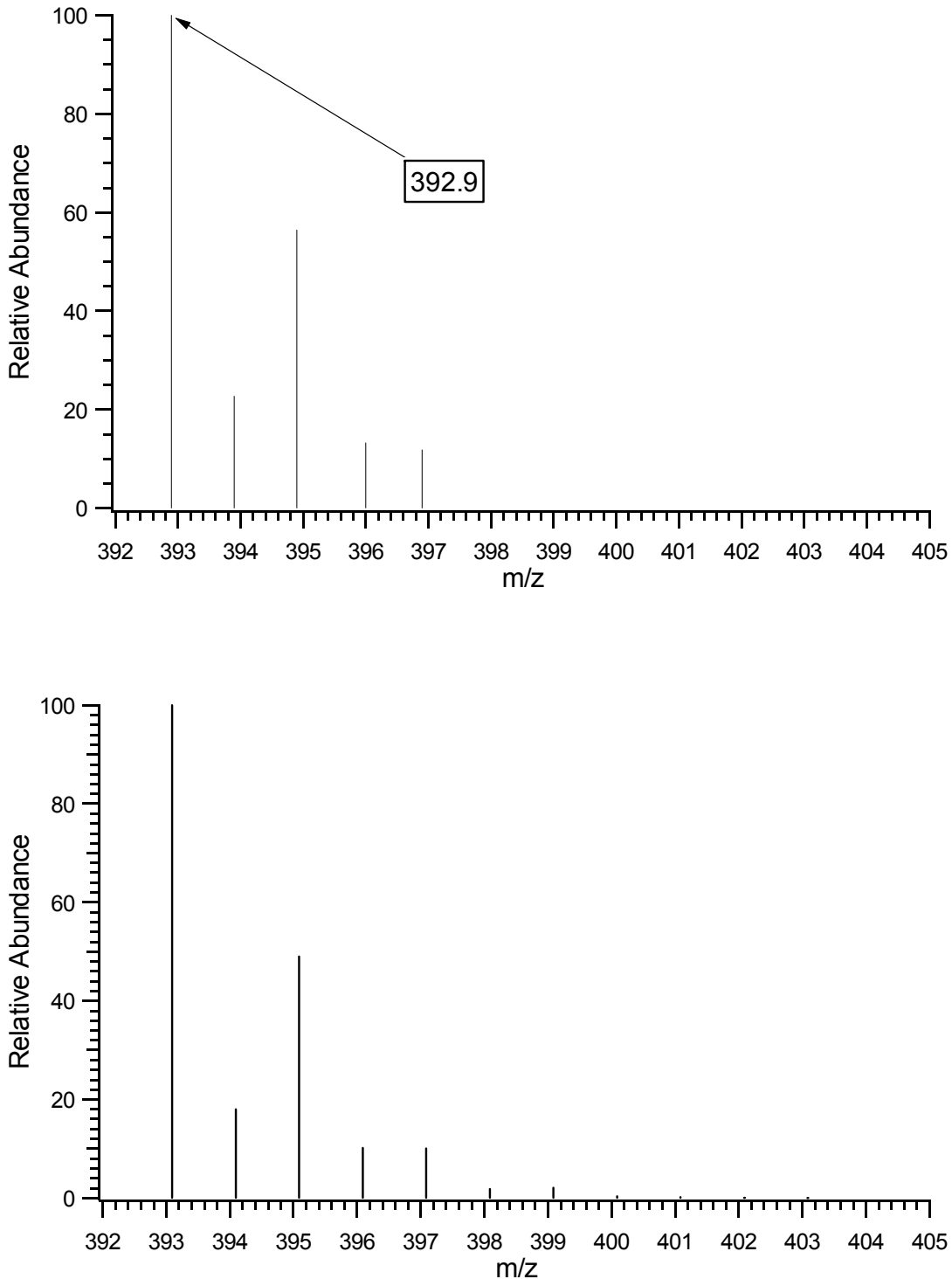


Supplementary Information 7d: Expanded ESI-MS of the m/z = 279.0 isotopic cluster region (top), and the simulated isotopic fit for the cation $(NiC_9H_{21}N_2S_2)^+$ (bottom).

Supplementary Information 8



Supplementary Information 8a: ESI-MS of complex **6**.



Supplementary Information 8b: Expanded ESI-MS of the m/z = 392.9 isotopic cluster region (top), and the simulated isotopic fit for the cation $(NiC_{13}H_{27}N_4O_2S_2)^+$ (bottom).