Supporting Information (28 pages)

Exhaustive Oxidation of a Nickel Dithiolate Complex: Some Mechanistic Insights *En Route* to Sulfate Formation

Erik R. Hosler,[‡] Robert W. Herbst,[†] Michael J. Maroney,[†] Balwant S. Chohan,[§*]

[‡]Department of Chemistry & Biochemistry, Susquehanna University, Selinsgrove, Pennsylvania, 17870.

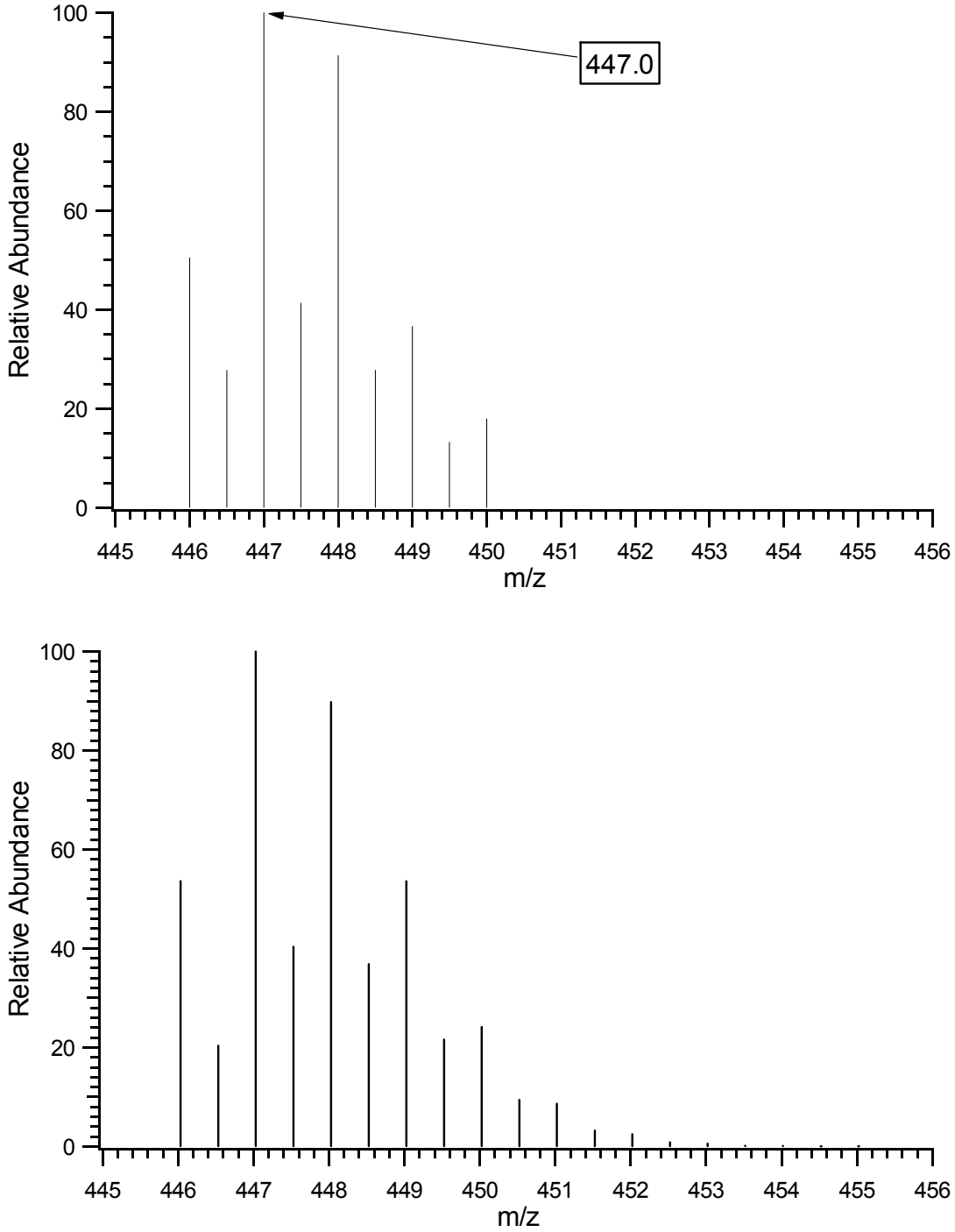
[†]Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, 01003.

[§] School of Science, Engineering, & Technology, Capital College, Penn State University - Harrisburg, Middletown, PA 17057.

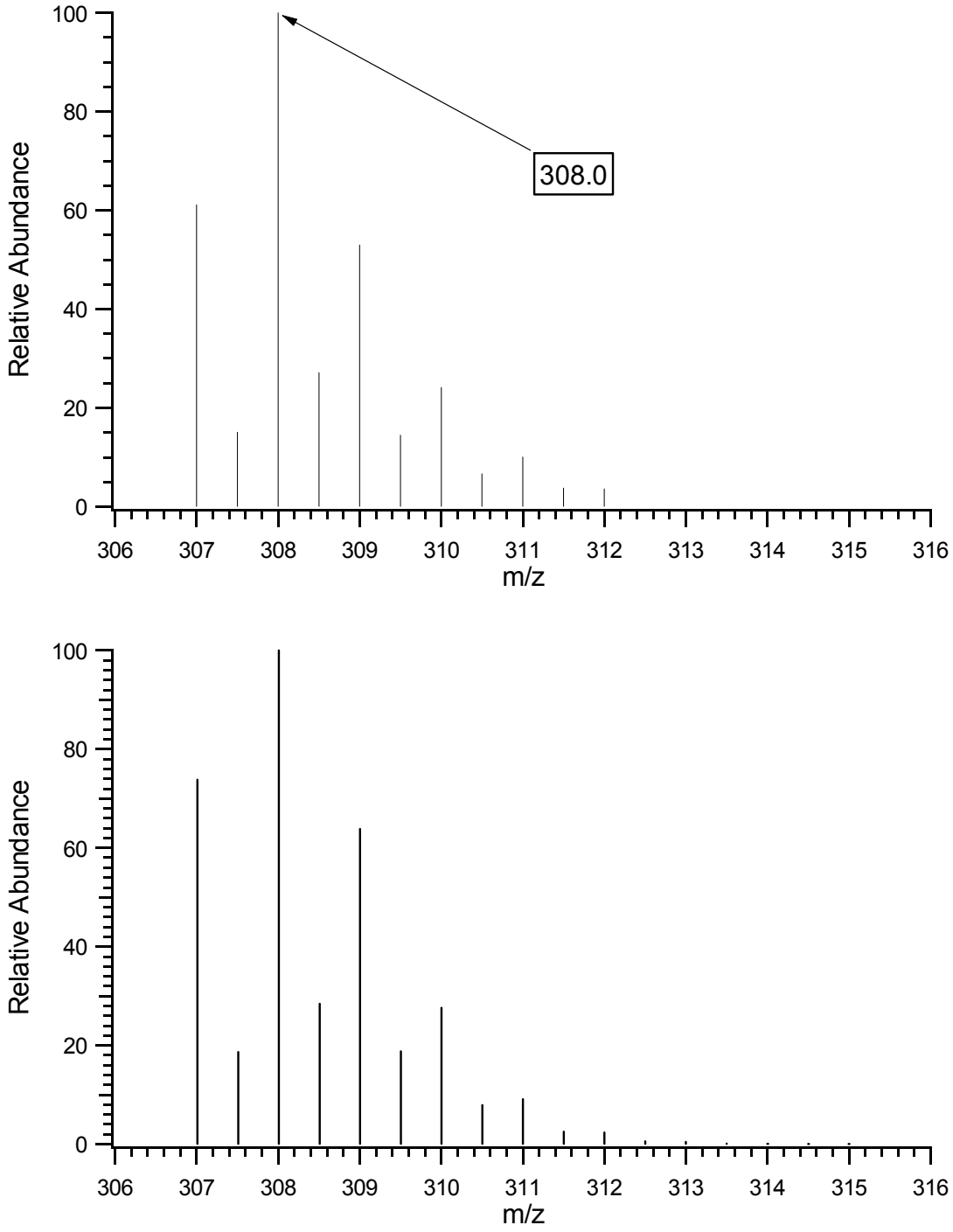
Supporting UV-vis and ESI-MS Data:

Supporting X-Ray Crystallographic Data:

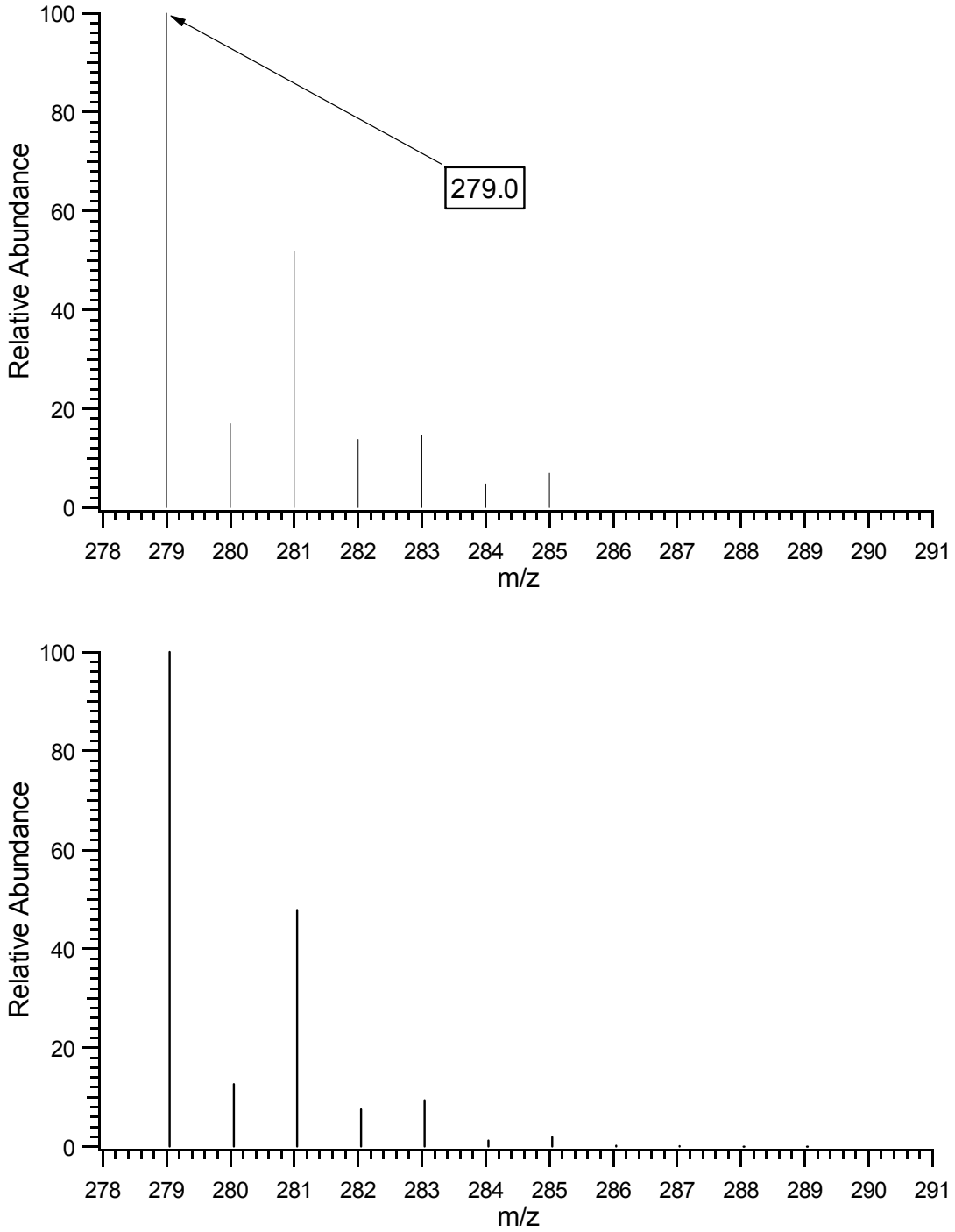
Supporting Information 1.



S1a. Expanded ESI-MS of the m/z = 447.0 isotopic cluster (**top**), and the simulated isotopic spectrum calculated for the tetranuclear cation $(Ni_4C_{27}H_{60}N_6S_6) / 2)^+$ (**bottom**).

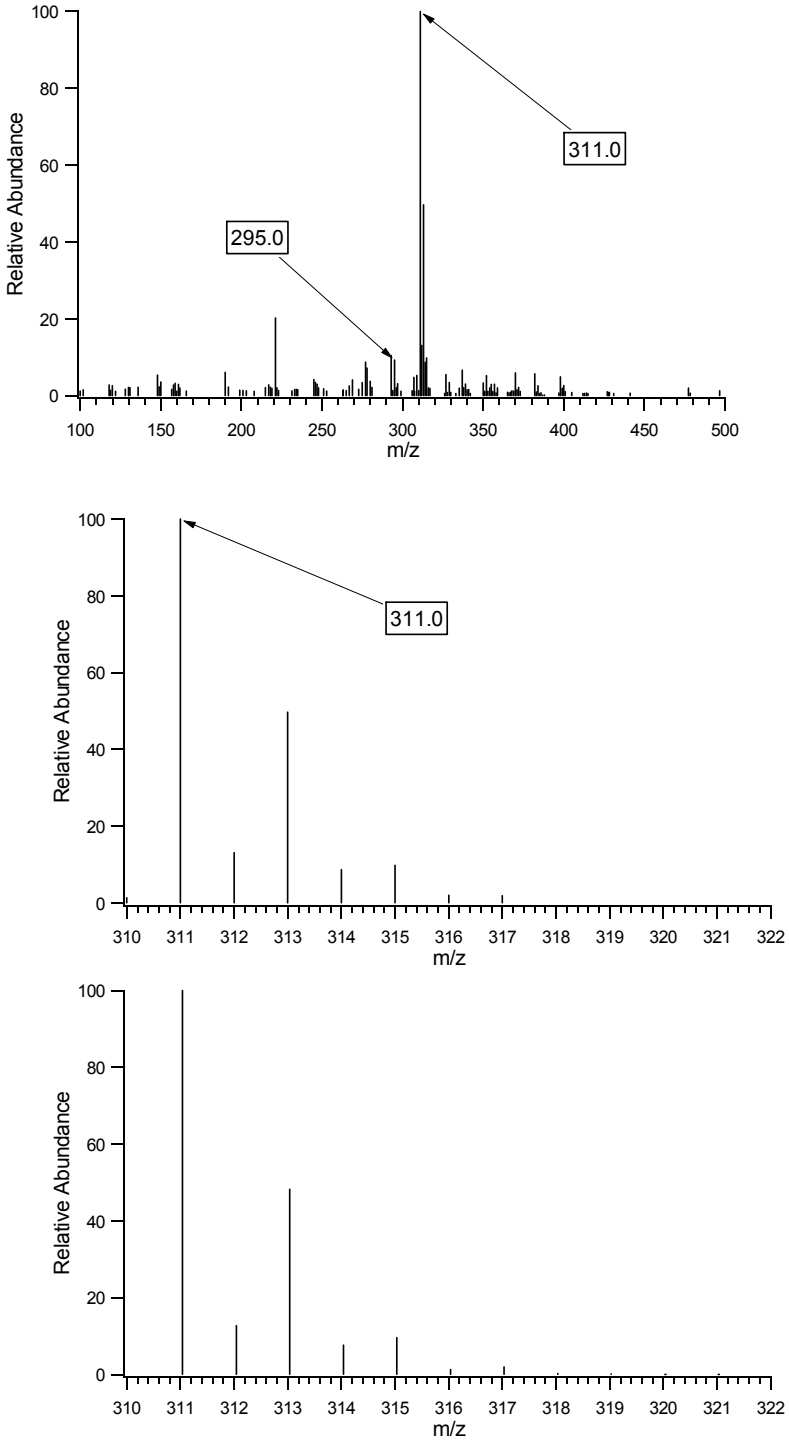


S1b. Expanded ESI-MS of the m/z = 308.0 isotopic cluster (**top**), and the simulated isotopic spectrum calculated for the trinuclear cation $(Ni_3C_{18}H_{40}N_4S_4) / 2)^+$ (**bottom**).



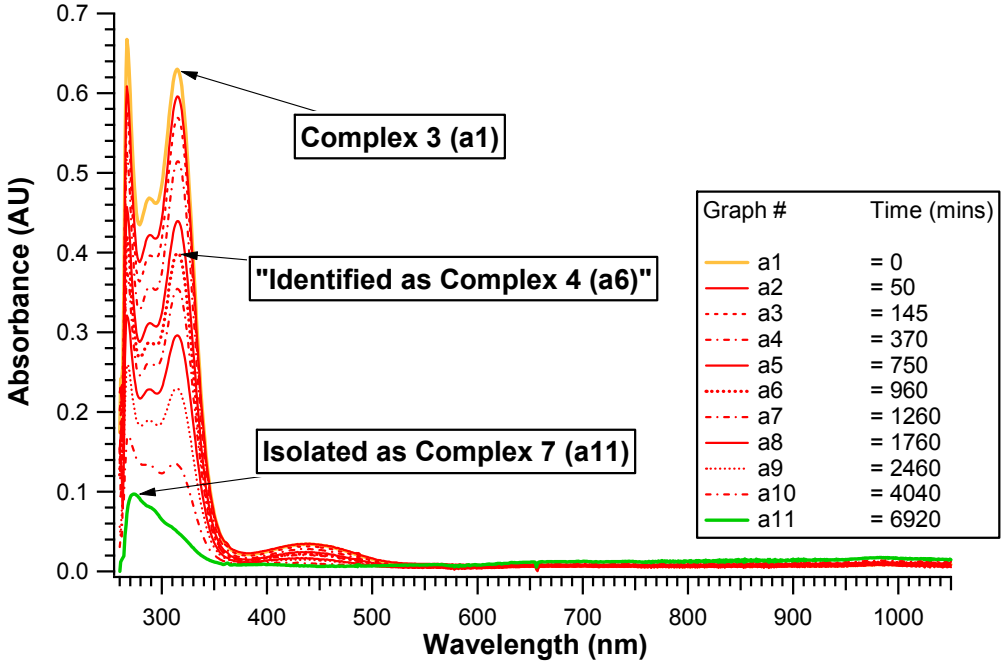
S1c. Expanded ESI-MS of the m/z = 279.0 isotopic cluster (**top**), and the simulated isotopic spectrum calculated for the mononuclear cation $(NiC_9H_{21}N_2S_2)^+$ (**bottom**), **1**.

Supporting Information 2.

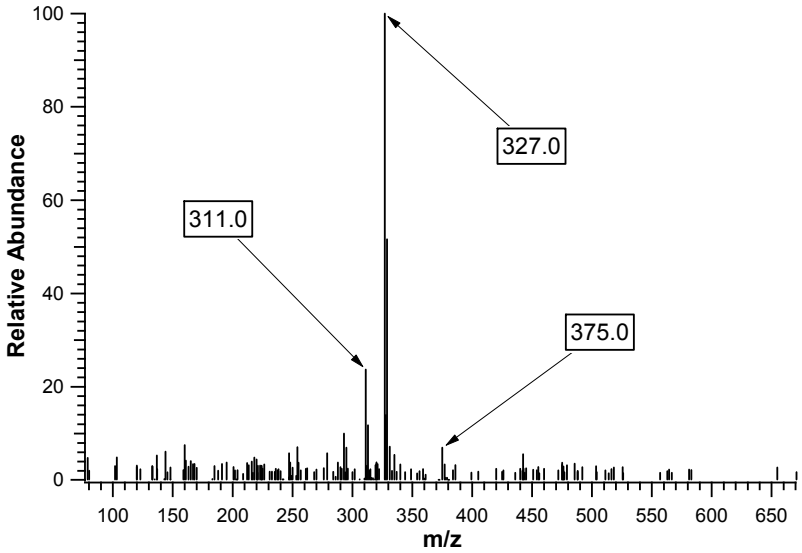


S2. ESI-MS of complex **1** with <u>two</u> equivalents of hydrogen peroxide (**top**). Expanded MS of *m/z* = 311.0 region (middle), and the corresponding simulated isotopic spectrum calculated for the cation $(NiC_9H_{21}N_2S_2O_2)^+$ (**bottom**).

Supporting Information 3.

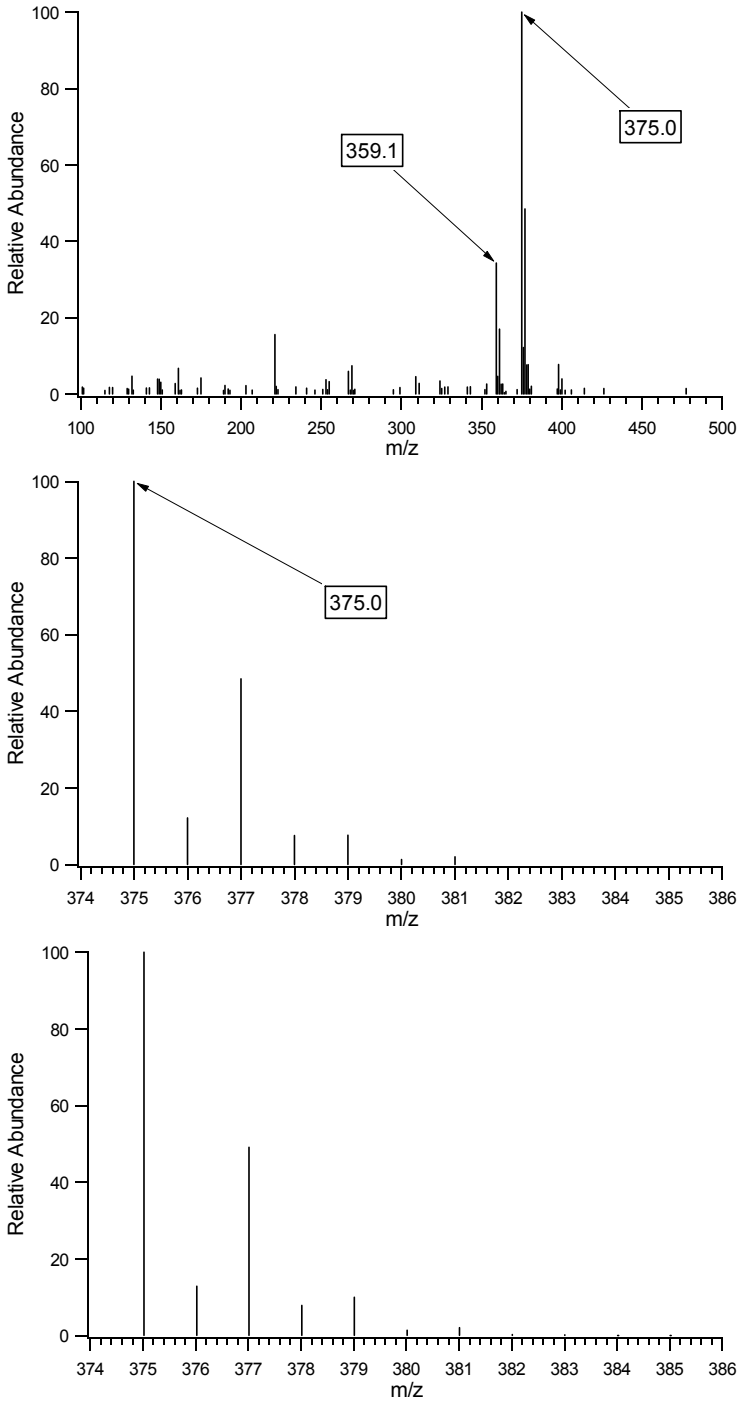


S3a: The UV-vis of a sample taken during the oxygenation (8mg of **3** in 100ml DMF, at 40ºC) of **3** (at t = 11hrs) matches that of **4**, consistent with its intermediacy in the formation of further oxygenation products.



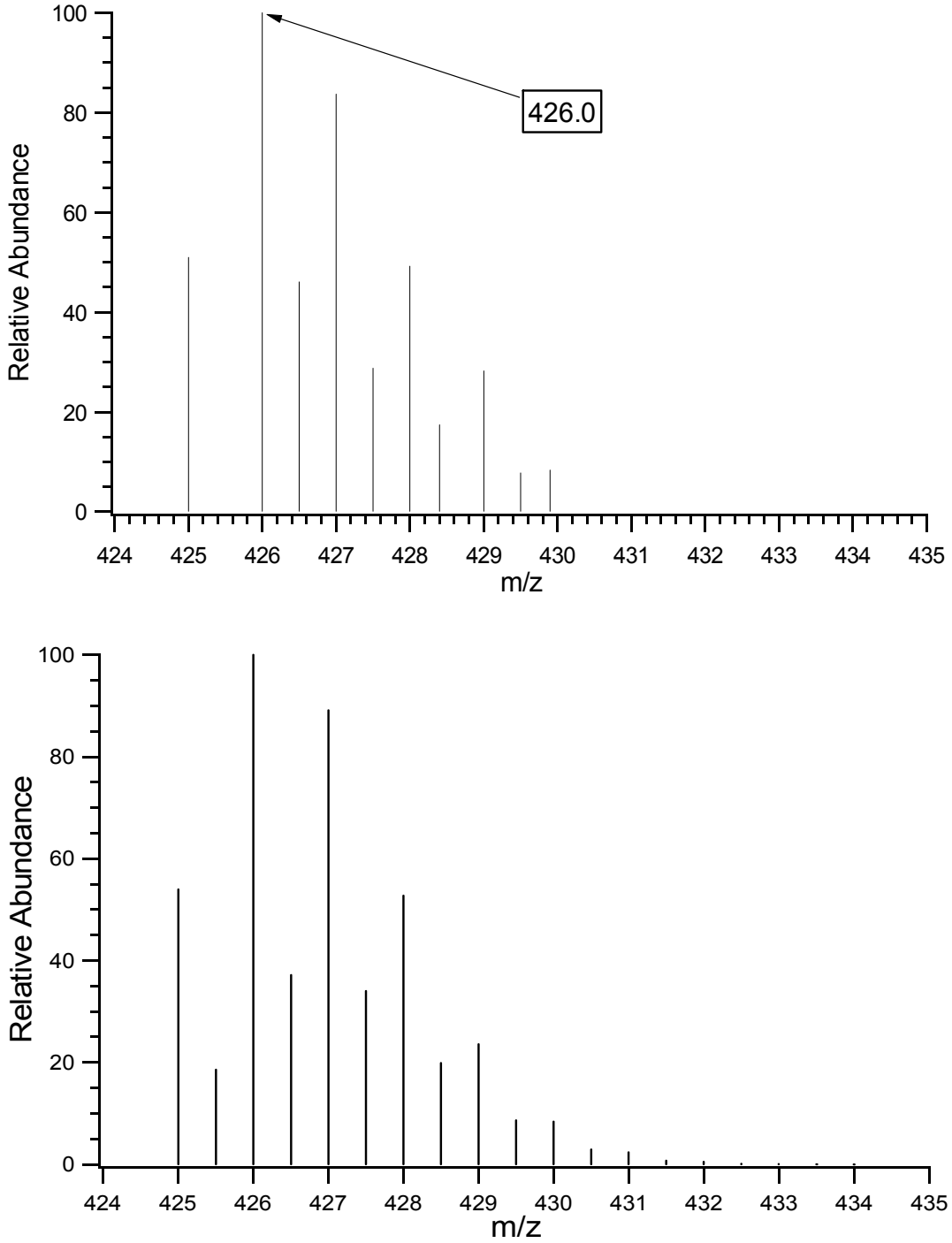
S3b: ESI-MS of a sample taken during the oxygenation (8mg of **3** in 100ml DMF, at 40ºC) of complex **3** (at t = 11hrs). The MS cluster at *m/z* = 375.0(7), corresponds to **7**. The cluster at *m/z* = 327.0(100) is **4**. The cluster at *m/z* = 311.0(24) is unreacted **3**. Simulated isotopic spectrum calculated for the cations of **7**, **4**, **3** are reported in this paper.

Supporting Information 4.

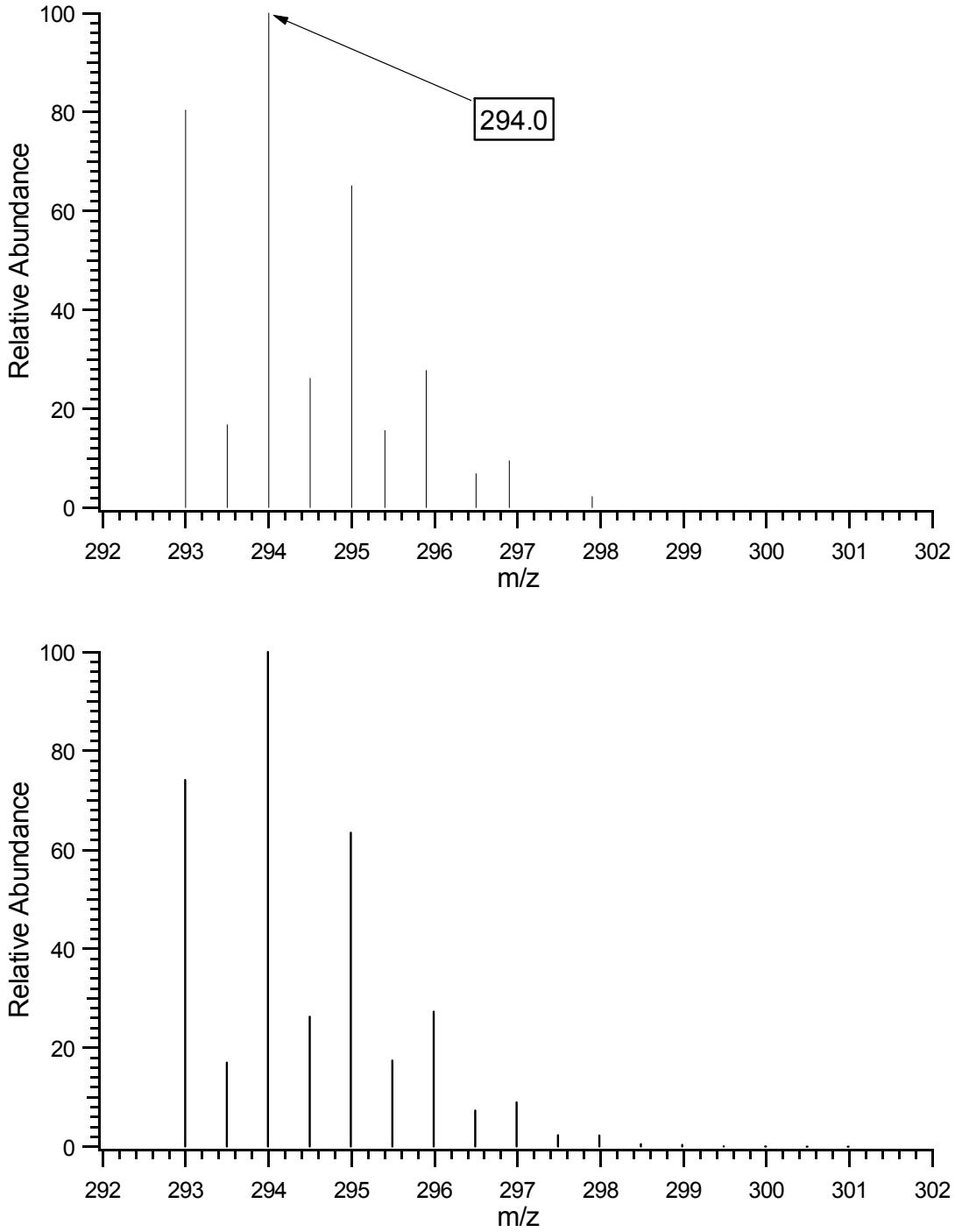


S4. ESI-MS of complex **1** with <u>six</u> equivalents of hydrogen peroxide (**top**). Expanded MS of *m/z* = 375.0 region (**middle**), and the corresponding simulated isotopic spectrum calculated for the cation $(NiC_9H_{21}N_2S_2O_6)^+$ (**bottom**).

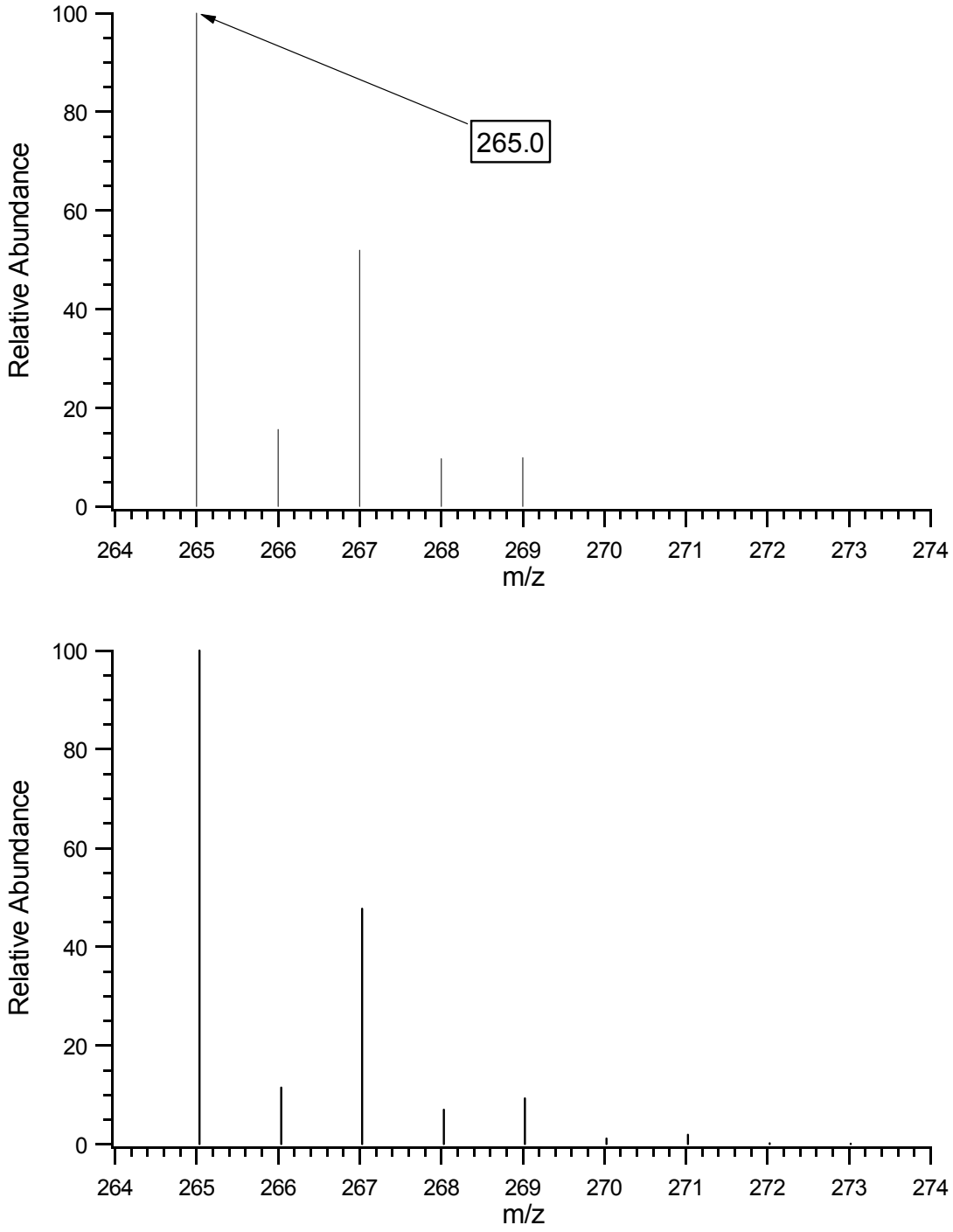
Supporting Information 5.



S5a: Expanded ESI-MS of the m/z = 426.0 isotopic cluster (**top**), and the simulated isotopic spectrum calculated for the tetranuclear cation $(Ni_4C_{24}H_{54}N_6S_6)/2)^+$ (**bottom**).

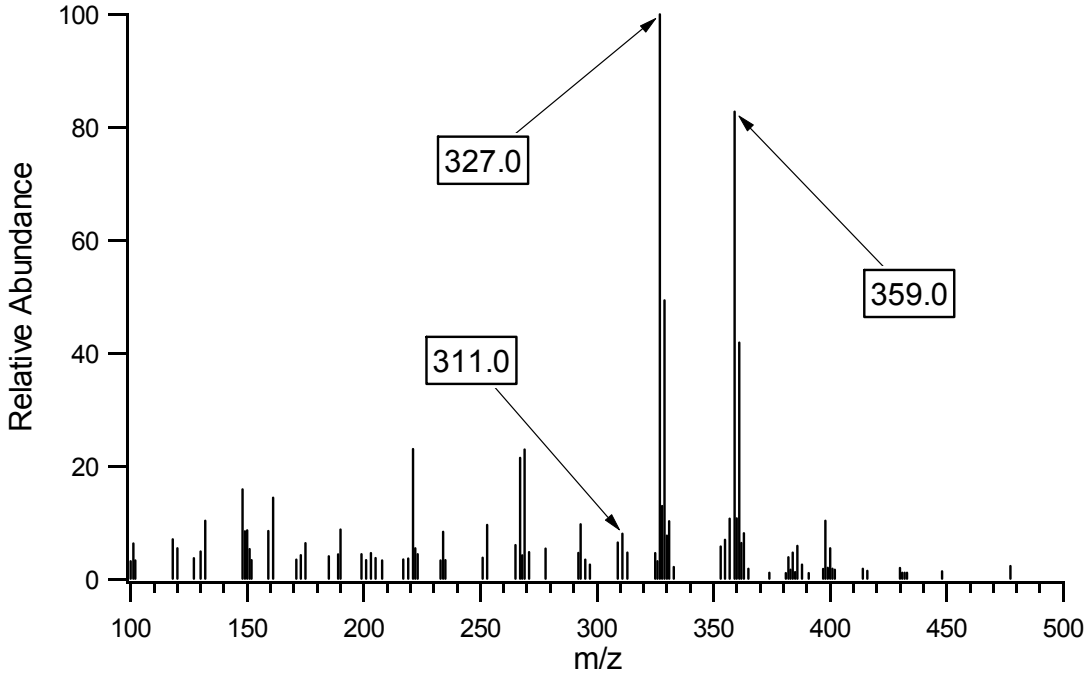


S5b: Expanded ESI-MS of the m/z = 294.0 isotopic cluster (**top**), and the simulated isotopic spectrum calculated for the trinuclear cation $(Ni_3C_{16}H_{36}N_4S_4)/2)^+$ (**bottom**).



S5c: Expanded ESI-MS of the m/z = 265.0 isotopic cluster (**top**), and the simulated isotopic spectrum calculated for the mononuclear cation $(NiC_8H_{19}N_2S_2)^+$ (**bottom**), **8**.

Supporting Information 6.



S6. ESI-MS of **1**, with four equivalents of hydrogen peroxide.

Supplementary Information, Table S7:

Crystallographic data for complex **8**.

Table 1. Crystal data and structure refinement for Complex **8** (BC56).

Identification code	Complex **8** (BC56)
Empirical formula	C8 H18 N2 Ni S2
Formula weight	265.07
Crystal system	monoclinic
Space group	Pc
Temperature	293(2) K
Crystal size	0.25 x 0.20 x 0.03 mm
Unit cell dimensions	a = 8.7150(3)A alpha = 90deg. b = 9.2850(3)A beta = 113.517(2)deg. c = 7.7890(4)A gamma = 90deg.
Volume	577.93(4) A^3
Z	2
Density (calculated)	1.523 Mg/m^3
Absorption coefficient	1.999 mm^-1
Theta range for data collection	4.39 to 25.02 deg.
Index ranges	-10<=h<=10, -11<=k<=10, -9<=l<=9
Reflections collected	4693
Independent reflections	1956 [R(int) = 0.052]
Reflections with I>2sigma(I)	1844
Data / restraints / parameters	1956 / 2 / 119
Goodness-of-fit on F^2	1.446
Final R indices [I>2sigma(I)]	R1 = 0.0269, wR2 = 0.0658
R indices (all data)	R1 = 0.0299, wR2 = 0.0672
Absolute structure parameter	racemic twin refinement
Largest diff. peak and hole	0.203 and -0.323 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for Complex **8**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ni(1)	1720(1)	2473(1)	8491(1)	33(1)
S(1)	4026(2)	2624(1)	8052(2)	55(1)
S(2)	202(2)	1952(1)	5594(2)	51(1)
N(1)	2984(5)	2611(3)	11161(5)	39(1)
N(2)	-310(6)	2665(3)	8935(5)	38(1)
C(1)	5436(6)	3160(5)	10436(7)	65(1)
C(2)	4424(5)	3605(4)	11527(5)	56(1)
C(3)	3621(5)	1147(4)	11916(5)	58(1)
C(4)	1859(5)	3159(4)	12021(4)	50(1)
C(5)	167(5)	2443(3)	10993(5)	44(1)
C(6)	-1002(5)	4143(4)	8424(5)	56(1)
C(7)	-1534(4)	1579(4)	7814(5)	46(1)
C(8)	-1807(5)	1694(5)	5797(5)	57(1)

Table 3. Bond lengths [A] and angles [deg] for Complex **8**.

Ni(1)-N(1)	1.931(4)
Ni(1)-N(2)	1.942(4)
Ni(1)-S(2)	2.166(1)
Ni(1)-S(1)	2.173(1)
S(1)-C(1)	1.840(5)
S(2)-C(8)	1.835(4)
N(1)-C(4)	1.481(5)
N(1)-C(2)	1.491(5)
N(1)-C(3)	1.498(4)
N(2)-C(7)	1.474(5)
N(2)-C(6)	1.488(4)
N(2)-C(5)	1.501(5)
C(1)-C(2)	1.506(5)
C(4)-C(5)	1.521(5)
C(7)-C(8)	1.497(5)
N(1)-Ni(1)-N(2)	88.3(2)
N(1)-Ni(1)-S(2)	170.3(1)
N(2)-Ni(1)-S(2)	89.1(1)
N(1)-Ni(1)-S(1)	89.9(1)
N(2)-Ni(1)-S(1)	170.9(1)
S(2)-Ni(1)-S(1)	94.01(6)
C(1)-S(1)-Ni(1)	98.4(2)
C(8)-S(2)-Ni(1)	98.4(1)
C(4)-N(1)-C(2)	111.1(3)
C(4)-N(1)-C(3)	110.0(3)
C(2)-N(1)-C(3)	109.6(3)
C(4)-N(1)-Ni(1)	108.3(2)
C(2)-N(1)-Ni(1)	108.8(2)
C(3)-N(1)-Ni(1)	109.0(2)
C(7)-N(2)-C(6)	110.6(4)
C(7)-N(2)-C(5)	111.4(3)
C(6)-N(2)-C(5)	108.8(3)
C(7)-N(2)-Ni(1)	109.1(2)
C(6)-N(2)-Ni(1)	109.8(3)
C(5)-N(2)-Ni(1)	107.1(3)
C(2)-C(1)-S(1)	109.7(3)
N(1)-C(2)-C(1)	111.1(3)
N(1)-C(4)-C(5)	106.8(3)
N(2)-C(5)-C(4)	107.4(3)
N(2)-C(7)-C(8)	110.3(3)
C(7)-C(8)-S(2)	110.0(2)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for Complex **8**.
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)	38(1)	32(1)	34(1)	2(1)	20(1)	3(1)
S(1)	55(1)	54(1)	76(1)	-7(1)	45(1)	-7(1)
S(2)	59(1)	65(1)	33(1)	0(1)	22(1)	5(1)
N(1)	33(2)	42(2)	38(2)	2(1)	12(2)	-2(1)
N(2)	44(2)	44(2)	33(2)	10(1)	22(2)	11(1)
C(1)	44(2)	61(2)	92(3)	-6(2)	29(2)	-11(2)
C(2)	48(2)	52(2)	65(2)	-9(2)	20(2)	-13(2)
C(3)	50(2)	52(2)	59(2)	15(2)	8(2)	2(2)
C(4)	55(2)	59(2)	35(2)	-7(2)	19(2)	-4(2)
C(5)	44(2)	59(2)	34(2)	3(1)	20(2)	3(1)
C(6)	68(3)	55(2)	56(2)	11(2)	35(2)	24(2)
C(7)	29(2)	61(2)	50(2)	1(2)	17(2)	1(2)
C(8)	41(2)	79(3)	41(2)	-5(2)	6(2)	9(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for Complex **8**.

	x	y	z	U(eq)
H(1A)	6159(6)	2359(5)	11060(7)	78
H(1B)	6135(6)	3955(5)	10378(7)	78
H(2A)	5134(5)	3602(4)	12855(5)	67
H(2B)	4011(5)	4578(4)	11178(5)	67
H(3A)	4349(5)	800(4)	11351(5)	87
H(3B)	2695(5)	498(4)	11632(5)	87
H(3C)	4229(5)	1203(4)	13248(5)	87
H(4A)	1753(5)	4197(4)	11894(4)	59
H(4B)	2299(5)	2918(4)	13342(4)	59
H(5A)	238(5)	1423(3)	11281(5)	53
H(5B)	-665(5)	2872(3)	11371(5)	53
H(6A)	-189(5)	4835(4)	9166(5)	84
H(6B)	-2000(5)	4235(4)	8656(5)	84
H(6C)	-1263(5)	4312(4)	7122(5)	84
H(7A)	-2587(4)	1726(4)	7939(5)	55
H(7B)	-1128(4)	623(4)	8275(5)	55
H(8A)	-2540(5)	2501(5)	5225(5)	69
H(8B)	-2340(5)	824(5)	5140(5)	69

Supporting Information, Table S8:

Crystallographic data for complex **3**

Table 1. Crystal data and structure refinement for Complex 3 (SU-1).

Identification code	Complex 3
Empirical formula	C9 H20 N2 Ni O2 S2
Crystal_description	prism
Crystal_color	brown-orange
Formula weight	311.10
Temperature	293(2) K
Wavelength	0.71069 A
Crystal system	trigonal
Space group	R-3
Unit cell dimensions	a = 24.571(5)A alpha = 90deg. b = 24.571(5)A beta = 90deg. c = 10.920(5)A gamma = 120deg.
Volume	5710(3) A^3
Z	18
Density (calculated)	1.628 Mg/m^3
Absorption coefficient	1.846 mm^-1
F(000)	2952
Crystal size	0.4 x 0.4 x 0.3 mm
Theta range for data collection	3.85 to 27.47 deg.
Index ranges	-31<=h<=31, -31<=k<=31, -13<=l<=14
Reflections collected	2893
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2893 / 0 / 225
Goodness-of-fit on F^2	0.808
Final R indices [I>2sigma(I)]	R1 = 0.0293, wR2 = 0.0693
R indices (all data)	R1 = 0.0468, wR2 = 0.0798

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for Complex 3. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor. Hydrogen coordinates and isotropic displacement parameters are also given.

	x	y	z	U(eq)
Ni1	0.532658(13)	0.099214(13)	0.63912(2)	0.02399(10)
S1	0.52418(3)	0.17031(3)	0.54234(6)	0.03378(16)
S2	0.43191(3)	0.05385(3)	0.66324(6)	0.03877(17)
O2	0.50299(10)	0.14954(10)	0.41665(19)	0.0536(5)
O1	0.49306(11)	0.19998(10)	0.6037(2)	0.0626(6)
N1	0.62625(9)	0.15115(9)	0.61767(18)	0.0302(4)
N2	0.53214(10)	0.02648(9)	0.72282(18)	0.0312(4)
C2	0.64155(13)	0.19640(14)	0.5127(3)	0.0414(6)
C8	0.46899(14)	-0.03077(12)	0.7033(3)	0.0429(6)
C9	0.41717(14)	-0.01838(13)	0.7373(3)	0.0439(7)
C6	0.57943(15)	0.00993(14)	0.6773(3)	0.0425(6)
C7	0.54150(17)	0.03991(16)	0.8567(2)	0.0435(7)
C5	0.64645(15)	0.06334(16)	0.6770(3)	0.0485(7)
C4	0.65871(13)	0.11517(15)	0.5885(3)	0.0425(6)
C3	0.65418(14)	0.18830(15)	0.7319(3)	0.0442(7)
C1	0.60554(14)	0.23043(13)	0.5244(3)	0.0464(7)
H6A	0.5842(17)	0.0755(16)	0.873(3)	0.058(10)
H12A	0.6274(14)	0.1697(14)	0.438(3)	0.046(8)
H4A	0.4679(15)	-0.0646(16)	0.751(3)	0.056(9)
H4B	0.4663(13)	-0.0424(14)	0.616(3)	0.041(8)
H6C	0.5127(16)	0.0514(15)	0.883(3)	0.052(9)
H6B	0.5328(14)	0.0020(15)	0.899(3)	0.050(9)
H8A	0.6605(14)	0.0807(14)	0.759(3)	0.045(8)
H11A	0.6991(18)	0.2180(18)	0.714(3)	0.071(11)
H9B	0.6451(13)	0.0981(13)	0.509(3)	0.039(7)
H11B	0.6323(16)	0.2066(16)	0.754(3)	0.055(10)
H8B	0.6704(14)	0.0461(14)	0.651(3)	0.044(8)
H12B	0.6860(16)	0.2238(16)	0.509(3)	0.058(9)
H9A	0.7042(16)	0.1466(15)	0.584(3)	0.053(9)
H11C	0.6521(15)	0.1600(16)	0.797(3)	0.055(9)
H3A	0.3791(16)	-0.0517(15)	0.708(3)	0.053(9)
H7A	0.5662(13)	-0.0063(12)	0.594(3)	0.033(7)
H7B	0.5737(15)	-0.0248(15)	0.726(3)	0.051(8)
H13A	0.6065(15)	0.2508(16)	0.448(3)	0.054(9)
H3B	0.4155(15)	-0.0131(15)	0.826(3)	0.053(9)
H13B	0.6155(15)	0.2559(16)	0.598(3)	0.057(9)

Table 3. Bond angles [deg] for Complex 3.

N2 Ni1 N1	96.58(8)
N2 Ni1 S1	174.25(6)
N1 Ni1 S1	88.38(6)
N2 Ni1 S2	89.40(6)
N1 Ni1 S2	173.13(6)
S1 Ni1 S2	85.83(3)
O1 S1 O2	114.89(15)
O1 S1 C1	106.49(15)
O2 S1 C1	103.78(15)
O1 S1 Ni1	118.11(10)
O2 S1 Ni1	109.92(9)
C1 S1 Ni1	101.62(10)
C9 S2 Ni1	100.11(10)
C4 N1 C3	108.8(2)
C4 N1 C2	105.4(2)
C3 N1 C2	108.4(2)
C4 N1 Ni1	115.46(17)
C3 N1 Ni1	108.71(16)
C2 N1 Ni1	109.94(15)
C7 N2 C6	109.3(2)
C7 N2 C8	108.6(2)
C6 N2 C8	106.1(2)
C7 N2 Ni1	108.60(16)
C6 N2 Ni1	115.61(16)
C8 N2 Ni1	108.32(16)
C1 C2 N1	110.4(2)
C1 C2 H12A	109.3(17)
N1 C2 H12A	105.0(18)
C1 C2 H12B	113(2)
N1 C2 H12B	109(2)
H12A C2 H12B	110(3)
C9 C8 N2	111.1(2)
C9 C8 H4A	112.2(19)
N2 C8 H4A	107.4(19)
C9 C8 H4B	110.9(17)
N2 C8 H4B	107.3(17)
H4A C8 H4B	108(2)
C8 C9 S2	108.34(19)
C8 C9 H3A	108(2)
S2 C9 H3A	109(2)
C8 C9 H3B	111.6(19)
S2 C9 H3B	108.1(19)
H3A C9 H3B	111(3)
N2 C6 C5	115.0(2)
N2 C6 H7A	105.9(15)
C5 C6 H7A	110.3(16)
N2 C6 H7B	105.6(19)
C5 C6 H7B	112.8(19)
H7A C6 H7B	107(2)
N2 C7 H6A	110.2(19)
N2 C7 H6C	109(2)
H6A C7 H6C	108(3)
N2 C7 H6B	108.8(18)
H6A C7 H6B	113(3)

H6C C7 H6B	108(3)
C4 C5 C6	114.1(2)
C4 C5 H8A	109.9(18)
C6 C5 H8A	111.8(18)
C4 C5 H8B	106.5(19)
C6 C5 H8B	105.6(19)
H8A C5 H8B	109(3)
N1 C4 C5	115.1(2)
N1 C4 H9B	106.4(17)
C5 C4 H9B	109.7(17)
N1 C4 H9A	106.1(18)
C5 C4 H9A	111.3(18)
H9B C4 H9A	108(2)
N1 C3 H11A	106(2)
N1 C3 H11B	109(2)
H11A C3 H11B	114(3)
N1 C3 H11C	109.1(19)
H11A C3 H11C	108(3)
H11B C3 H11C	109(3)
C2 C1 S1	105.9(2)
C2 C1 H13A	110.3(19)
S1 C1 H13A	104.3(19)
C2 C1 H13B	114(2)
S1 C1 H13B	104.8(19)
H13A C1 H13B	117(3)

Table 4. Bond lengths [A] for Complex 3.

Ni1 N2	2.002(2)
Ni1 N1	2.009(2)
Ni1 S1	2.1392(8)
Ni1 S2	2.1635(8)
S1 O1	1.457(2)
S1 O2	1.466(2)
S1 C1	1.807(3)
S2 C9	1.814(3)
N1 C4	1.491(3)
N1 C3	1.495(3)
N1 C2	1.508(3)
N2 C7	1.491(3)
N2 C6	1.495(3)
N2 C8	1.500(3)
C2 C1	1.496(4)
C2 H12A	0.99(3)
C2 H12B	0.96(3)
C8 C9	1.496(4)
C8 H4A	0.97(3)
C8 H4B	0.99(3)
C9 H3A	0.94(3)
C9 H3B	0.98(3)
C6 C5	1.508(5)
C6 H7A	0.98(3)
C6 H7B	0.96(3)
C7 H6A	0.99(4)
C7 H6C	0.93(3)
C7 H6B	0.96(3)
C5 C4	1.504(4)
C5 H8A	0.98(3)
C5 H8B	0.93(3)
C4 H9B	0.95(3)
C4 H9A	0.99(3)
C3 H11A	0.99(4)
C3 H11B	0.89(3)
C3 H11C	0.98(3)
C1 H13A	0.97(3)
C1 H13B	0.97(3)

Table 5. Anisotropic displacement parameters (A^2 x 10^3) for Complex 3.
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
Ni1	0.02334(16)	0.02332(16)	0.02578(16)	0.00109(11)	0.00121(11)	0.01202(12)
S1	0.0336(3)	0.0294(3)	0.0410(4)	0.0079(3)	0.0045(3)	0.0177(3)
S2	0.0263(3)	0.0373(4)	0.0500(4)	0.0092(3)	0.0060(3)	0.0140(3)
O2	0.0536(12)	0.0552(13)	0.0440(11)	0.0101(9)	-0.0093(9)	0.0213(11)
O1	0.0730(15)	0.0465(12)	0.0859(17)	0.0165(11)	0.0310(13)	0.0431(12)
N1	0.0257(10)	0.0340(11)	0.0296(10)	-0.0022(8)	0.0010(8)	0.0138(9)
N2	0.0374(11)	0.0309(11)	0.0290(10)	-0.0004(8)	0.0011(8)	0.0198(9)
C2	0.0293(14)	0.0416(15)	0.0429(15)	0.0114(13)	0.0094(11)	0.0100(12)
C8	0.0494(17)	0.0257(13)	0.0501(17)	0.0036(12)	0.0029(13)	0.0162(12)
C9	0.0376(15)	0.0309(14)	0.0490(17)	0.0055(12)	0.0067(13)	0.0066(12)
C6	0.0546(17)	0.0440(16)	0.0453(16)	0.0013(13)	0.0019(13)	0.0368(15)
C7	0.0590(19)	0.0497(18)	0.0286(13)	0.0055(12)	0.0018(13)	0.0324(17)
C5	0.0463(17)	0.064(2)	0.0544(18)	-0.0051(15)	-0.0048(14)	0.0417(16)
C4	0.0324(14)	0.0550(18)	0.0462(16)	-0.0030(14)	0.0051(12)	0.0265(14)
C3	0.0348(15)	0.0455(17)	0.0427(16)	-0.0115(13)	-0.0043(12)	0.0129(14)
C1	0.0405(16)	0.0323(14)	0.0577(19)	0.0125(14)	0.0048(14)	0.0116(12)

Supporting Information, Table S9:

Crystallographic data for complex **7**.

Table 1. Crystal data and structure refinement for Complex **7** (BC25).

Identification code	Complex 7
Empirical formula	C12 H29 N3 Ni O8 S2
Formula weight	466.21
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 10.453(3)A alpha = 90deg. b = 14.741(3)A beta = 105.28(2)deg. c = 13.011(4)A gamma = 90deg.
Volume	1934.0(9) A^3
Z	4
Density (calculated)	1.601 Mg/m^3
Absorption coefficient	1.263 mm^-1
F(000)	984
Crystal size	0.30 x 0.25 x 0.10 mm
Theta range for data collection	2.02 to 21.97 deg.
Index ranges	0<=h<=10, 0<=k<=15, -13<=l<=13
Reflections collected	2353
Independent reflections	2353 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2106 / 0 / 235
Goodness-of-fit on F^2	1.115
Final R indices [I>2sigma(I)]	R1 = 0.0482, wR2 = 0.1191
R indices (all data)	R1 = 0.0955, wR2 = 0.1464
Largest diff. peak and hole	0.395 and -0.659 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for Complex 7. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ni	6459(1)	4178(1)	1648(1)	27(1)
S(1)	3630(2)	4597(1)	2176(2)	39(1)
S(2)	8027(2)	6075(1)	1374(2)	38(1)
O(1)	4642(5)	4772(3)	1602(4)	43(1)
O(2)	2383(5)	4994(4)	1620(5)	63(2)
O(3)	4087(7)	4854(4)	3276(5)	74(2)
O(4)	6829(4)	5521(3)	1257(4)	35(1)
O(5)	7815(6)	6786(4)	597(5)	61(2)
O(6)	8573(5)	6374(4)	2451(4)	59(2)
O(7)	7224(5)	4380(4)	3240(4)	40(1)
O(1W)	5661(4)	3977(3)	12(3)	35(1)
N(1)	5771(6)	2871(4)	2047(4)	35(2)
N(2)	8414(5)	3741(4)	1559(5)	34(2)
N(3)	7819(6)	5269(4)	4689(4)	38(2)
C(1)	3460(8)	3414(5)	2125(7)	50(2)
C(2)	4745(8)	2931(5)	2652(7)	48(2)
C(3)	6888(8)	2353(5)	2768(6)	47(2)
C(4)	8090(8)	2218(5)	2364(7)	51(2)
C(5)	8949(7)	3047(5)	2400(6)	46(2)
C(6)	9423(7)	4486(5)	1807(7)	46(2)
C(7)	9174(7)	5308(5)	1075(7)	46(2)
C(8)	5235(8)	2294(5)	1075(6)	52(2)
C(9)	8450(8)	3356(5)	512(6)	48(2)
C(10)	7259(7)	5130(6)	3683(6)	42(2)
C(11)	8382(12)	4524(6)	5392(7)	89(4)
C(12)	7913(10)	6164(6)	5148(7)	65(3)

Table 3. Bond lengths [A] and angles [deg] for Complex 7.

Ni-O(7)	2.036(5)
Ni-O(1)	2.078(5)
Ni-O(1W)	2.093(4)
Ni-O(4)	2.105(5)
Ni-N(1)	2.167(6)
Ni-N(2)	2.175(6)
S(1)-O(3)	1.435(6)
S(1)-O(2)	1.437(6)
S(1)-O(1)	1.470(5)
S(1)-C(1)	1.753(8)
S(2)-O(5)	1.433(6)
S(2)-O(6)	1.435(5)
S(2)-O(4)	1.469(5)
S(2)-C(7)	1.764(8)
O(7)-C(10)	1.242(9)
N(1)-C(2)	1.491(9)
N(1)-C(3)	1.499(9)
N(1)-C(8)	1.505(9)
N(2)-C(9)	1.486(9)
N(2)-C(5)	1.495(9)
N(2)-C(6)	1.498(9)
N(3)-C(10)	1.302(9)
N(3)-C(12)	1.441(10)
N(3)-C(11)	1.451(10)
C(1)-C(2)	1.515(11)
C(3)-C(4)	1.498(11)
C(4)-C(5)	1.510(11)
C(6)-C(7)	1.521(11)
O(7)-Ni-O(1)	94.5(2)
O(7)-Ni-O(1W)	179.6(2)
O(1)-Ni-O(1W)	85.1(2)
O(7)-Ni-O(4)	93.5(2)
O(1)-Ni-O(4)	79.7(2)
O(1W)-Ni-O(4)	86.4(2)
O(7)-Ni-N(1)	87.3(2)
O(1)-Ni-N(1)	91.3(2)
O(1W)-Ni-N(1)	92.9(2)
O(4)-Ni-N(1)	171.1(2)
O(7)-Ni-N(2)	88.5(2)
O(1)-Ni-N(2)	171.1(2)
O(1W)-Ni-N(2)	91.8(2)
O(4)-Ni-N(2)	91.7(2)
N(1)-Ni-N(2)	97.2(2)
O(3)-S(1)-O(2)	114.4(4)
O(3)-S(1)-O(1)	111.4(4)
O(2)-S(1)-O(1)	110.6(3)
O(3)-S(1)-C(1)	107.7(4)
O(2)-S(1)-C(1)	108.5(4)
O(1)-S(1)-C(1)	103.6(4)
O(5)-S(2)-O(6)	114.3(4)
O(5)-S(2)-O(4)	111.3(3)
O(6)-S(2)-O(4)	112.4(3)
O(5)-S(2)-C(7)	107.5(4)

O(6)-S(2)-C(7)	107.1(4)
O(4)-S(2)-C(7)	103.4(3)
S(1)-O(1)-Ni	133.3(3)
S(2)-O(4)-Ni	134.7(3)
C(10)-O(7)-Ni	123.9(5)
C(2)-N(1)-C(3)	104.5(6)
C(2)-N(1)-C(8)	108.4(6)
C(3)-N(1)-C(8)	107.1(6)
C(2)-N(1)-Ni	113.9(4)
C(3)-N(1)-Ni	110.5(4)
C(8)-N(1)-Ni	112.0(4)
C(9)-N(2)-C(5)	108.4(6)
C(9)-N(2)-C(6)	106.9(6)
C(5)-N(2)-C(6)	103.7(5)
C(9)-N(2)-Ni	114.4(4)
C(5)-N(2)-Ni	109.8(5)
C(6)-N(2)-Ni	112.9(4)
C(10)-N(3)-C(12)	121.6(7)
C(10)-N(3)-C(11)	121.0(7)
C(12)-N(3)-C(11)	117.4(6)
C(2)-C(1)-S(1)	112.4(6)
N(1)-C(2)-C(1)	117.6(7)
C(4)-C(3)-N(1)	115.8(6)
C(3)-C(4)-C(5)	115.4(7)
N(2)-C(5)-C(4)	115.2(6)
N(2)-C(6)-C(7)	117.0(6)
C(6)-C(7)-S(2)	112.7(6)
O(7)-C(10)-N(3)	123.9(7)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for Complex 7.
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	22(1)	26(1)	28(1)	1(1)	-1(1)	1(1)
S(1)	35(1)	40(1)	45(1)	0(1)	16(1)	-3(1)
S(2)	29(1)	34(1)	50(1)	-4(1)	7(1)	-8(1)
O(1)	27(3)	38(3)	66(4)	13(3)	16(3)	2(2)
O(2)	27(3)	54(4)	105(5)	0(3)	10(3)	6(3)
O(3)	102(5)	70(4)	53(4)	-15(3)	25(4)	-12(4)
O(4)	21(3)	29(3)	52(3)	8(2)	7(2)	-2(2)
O(5)	66(4)	46(4)	71(4)	12(3)	20(3)	-8(3)
O(6)	52(4)	64(4)	57(4)	-24(3)	9(3)	-15(3)
O(7)	46(3)	36(3)	33(3)	-1(3)	0(2)	6(2)
O(1W)	34(3)	33(3)	30(3)	0(2)	-3(2)	0(2)
N(1)	39(4)	29(3)	32(3)	0(3)	-1(3)	-5(3)
N(2)	26(3)	30(3)	39(4)	-5(3)	-3(3)	4(3)
N(3)	54(4)	34(4)	21(3)	-1(3)	1(3)	2(3)
C(1)	46(5)	42(5)	66(6)	7(4)	21(4)	-13(4)
C(2)	43(5)	39(5)	62(6)	16(4)	13(4)	-5(4)
C(3)	63(6)	28(4)	38(5)	9(4)	-7(4)	1(4)
C(4)	47(5)	39(5)	55(5)	8(4)	-6(4)	15(4)
C(5)	32(4)	47(5)	51(5)	6(4)	-5(4)	16(4)
C(6)	22(4)	45(5)	64(6)	-1(4)	-2(4)	3(4)
C(7)	25(4)	49(5)	63(5)	-15(4)	13(4)	-9(4)
C(8)	55(6)	30(4)	63(6)	0(4)	4(4)	-9(4)
C(9)	41(5)	53(5)	49(5)	-10(4)	12(4)	10(4)
C(10)	35(5)	40(5)	46(6)	8(4)	5(4)	5(4)
C(11)	153(11)	54(6)	40(5)	1(5)	-8(6)	25(7)
C(12)	80(7)	53(6)	52(6)	-17(5)	1(5)	2(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for Complex 7.

	x	y	z	U(eq)
H(1A)	2787(8)	3238(5)	2476(7)	61
H(1B)	3163(8)	3224(5)	1386(7)	61
H(2A)	5140(8)	3234(5)	3323(7)	58
H(2B)	4528(8)	2318(5)	2820(7)	58
H(3A)	7156(8)	2669(5)	3445(6)	56
H(3B)	6557(8)	1762(5)	2902(6)	56
H(4A)	7803(8)	2008(5)	1632(7)	61
H(4B)	8627(8)	1742(5)	2780(7)	61
H(5A)	9079(7)	3332(5)	3092(6)	56
H(5B)	9812(7)	2853(5)	2337(6)	56
H(6A)	10276(7)	4230(5)	1800(7)	55
H(6B)	9493(7)	4694(5)	2527(7)	55
H(7A)	8842(7)	5105(5)	344(7)	55
H(7B)	10007(7)	5620(5)	1133(7)	55
H(8A)	5885(8)	2249(5)	677(6)	77
H(8B)	4442(8)	2566(5)	639(6)	77
H(8C)	5035(8)	1699(5)	1290(6)	77
H(9A)	8109(8)	3793(5)	-39(6)	72
H(9B)	7916(8)	2817(5)	374(6)	72
H(9C)	9348(8)	3208(5)	523(6)	72
H(10)	6861(7)	5620(6)	3271(6)	50
H(11A)	8750(12)	4751(6)	6100(7)	133
H(11B)	9068(12)	4238(6)	5141(7)	133
H(11C)	7701(12)	4089(6)	5400(7)	133
H(12A)	8355(10)	6131(6)	5894(7)	97
H(12B)	7038(10)	6408(6)	5057(7)	97
H(12C)	8407(10)	6551(6)	4799(7)	97

H-bonding parameters, complex 7:

O1W O1'	2.749
O1W O4'	2.790
NI-O1W-O1'	128.1
NI-O1W-O4'	128.6

Primed atoms are generated by **1-x,1-y,-z**. (O1W is the oxygen of water and hydrogens on it were not located).