Supporting Information

Nickel(II) Complexes Based on Dithiolate-Polyamine Binary Ligand Systems: Crystal structures, Hirshfeld surface analysis, Theoretical Study, and Catalytic Activity Study in Photocatalytic Hydrogen Generation

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X-ray crystal structure analysis of 1: A pale yellow plate-like specimen of $C_{12}H_{24}N_6NiOS_3$, approximate dimensions 0.020 mm x 0.060 mm x 0.080 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a monoclinic unit cell yielded a total of 8391 reflections to a maximum θ angle of 28.20° (0.75 Å resolution), of which 4553 were independent (average redundancy 1.843, completeness = 98.4%, R_{int} = 3.12%, R_{sig} = 3.59%) and 3985 (87.52%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.3663(2) Å, b = 14.6831(3) Å, c = 15.5009(4) Å, β = 99.3820(10)°, volume = 1878.71(8) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8980 and 0.9730. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{12}H_{24}N_6NiOS_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 257 variables converged at R1 = 3.83%, for the observed data and wR2 = 9.63% for all data. The goodness-of-fit was 1.053. The largest peak in the final difference electron density synthesis was 0.403 $e^-/Å^3$ and the largest hole was -0.729 $e^-/Å^3$ with an RMS deviation of 0.079 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.496 g/cm^3 and F(000), 888 e^-. The hydrogens at N3, N5 and N6 atoms were refined freely. CCDC number: 2054290.

X-ray crystal structure analysis of 2: A dark orange plate-like specimen of $C_{16}H_{26}N_{10}Ni_2S_4$, approximate dimensions 0.020 mm x 0.030 mm x 0.060 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a monoclinic unit cell yielded a total of 5608 reflections to a maximum θ angle of 28.17° (0.75 Å resolution), of which 2999 were independent (average redundancy 1.870, completeness = 99.3%, R_{int} = 5.12%, R_{sig} = 5.68%) and 2344 (78.16%) were greater than $2\sigma(F^2)$. The final cell constants of a = 16.3199(6) Å, b = 9.1021(3) Å, c = 18.1332(7) Å, β = 114.143(3)°, volume = 2457.99(16) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8950 and 0.9630. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *C*2/*c*, with Z = 4 for the formula unit, $C_{16}H_{26}N_{10}Ni_2S_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 167 variables converged at R1 = 4.95%, for the observed data and wR2 = 11.48% for all data. The goodness-of-fit was 1.025. The largest peak in the final difference electron density synthesis was 0.438 $e^-/Å^3$ and the largest hole was -0.430 $e^-/Å^3$ with an RMS deviation of 0.105 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.633 g/cm^3 and F(000), 1248 e^-. The hydrogen atoms at N3, N4 and N5 were refined freely. CCDC number: 2054291.

X-ray crystal structure analysis of 3: A dark orange prism-like specimen of $C_{26}H_{30}N_{10}Ni_2O_2S_4$, approximate dimensions 0.020 mm x 0.060 mm x 0.090 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a monoclinic unit cell yielded a total of 3885 reflections to a maximum θ angle of 28.20° (0.75 Å resolution), of which 2226 were independent (average redundancy 1.745, completeness = 98.8%, R_{int} = 3.38%, R_{sig} = 3.65%) and 1856 (83.38%) were greater than $2\sigma(F^2)$. The final cell constants of a = 18.658(4) Å, b = 7.2167(14) Å, c = 14.534(3) Å, β = 120.13(3)°, volume = 1692.6(7) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8840 and 0.9730. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *C*2/*m*, with Z = 2 for the formula unit, $C_{26}H_{30}N_{10}Ni_2O_2S_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 150 variables converged at R1 = 4.64%, for the observed data and wR2 = 12.61% for all data. The goodness-of-fit was 1.046. The largest peak in the final difference electron density synthesis was 0.626 $e^-/Å^3$ and the largest hole was -0.439 $e^-/Å^3$ with an RMS deviation of 0.077 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.492 g/cm^3 and F(000), 784 e^-. The hydrogen atoms at N3 were refined freely, but with N-H distance restraints (DFIX, SADI). CCDC number: 2054292.

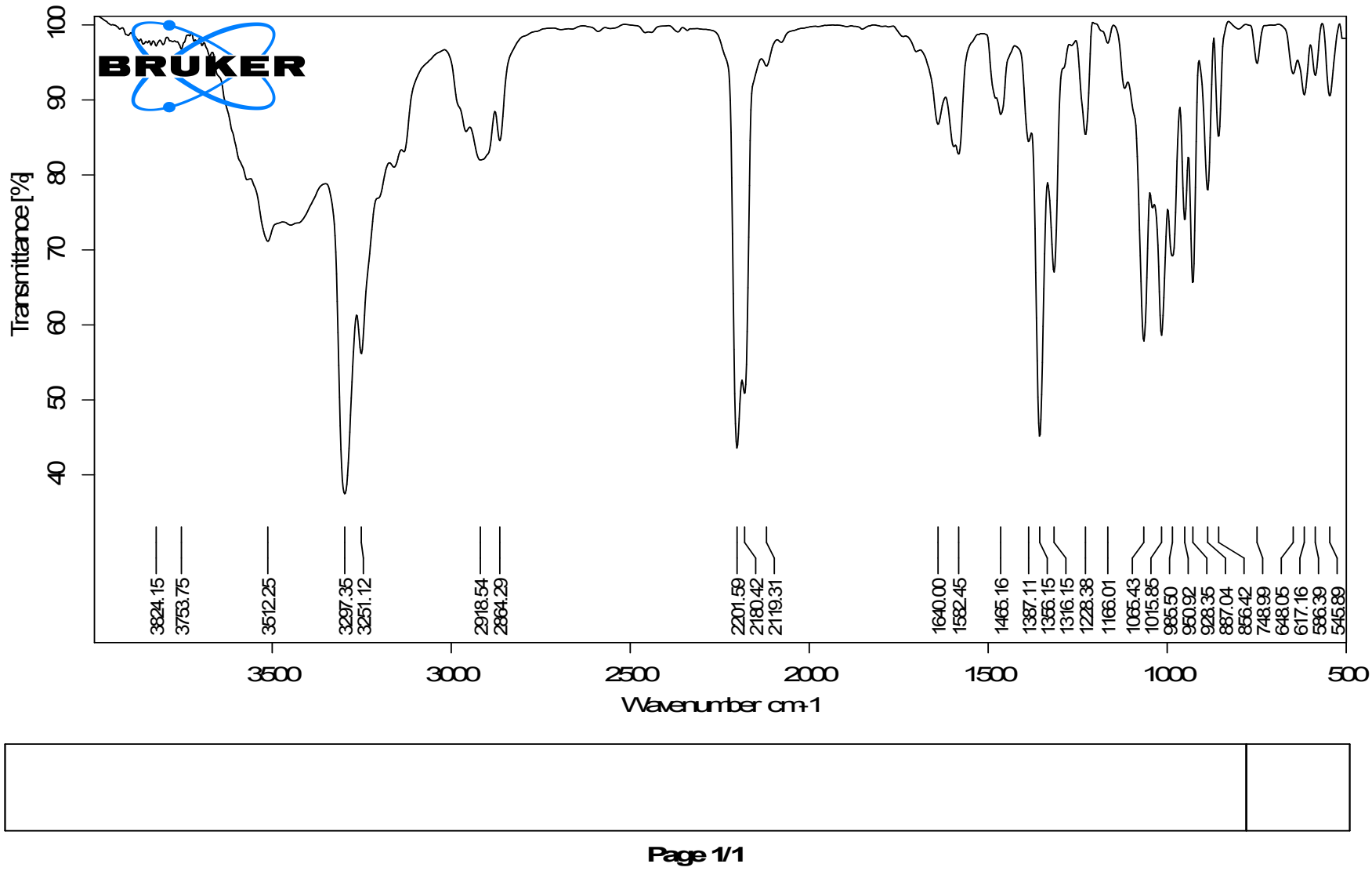

Figure S1. FT-IR spectrum of *[Ni(tetraen)(i-mnt)](DMSO)*

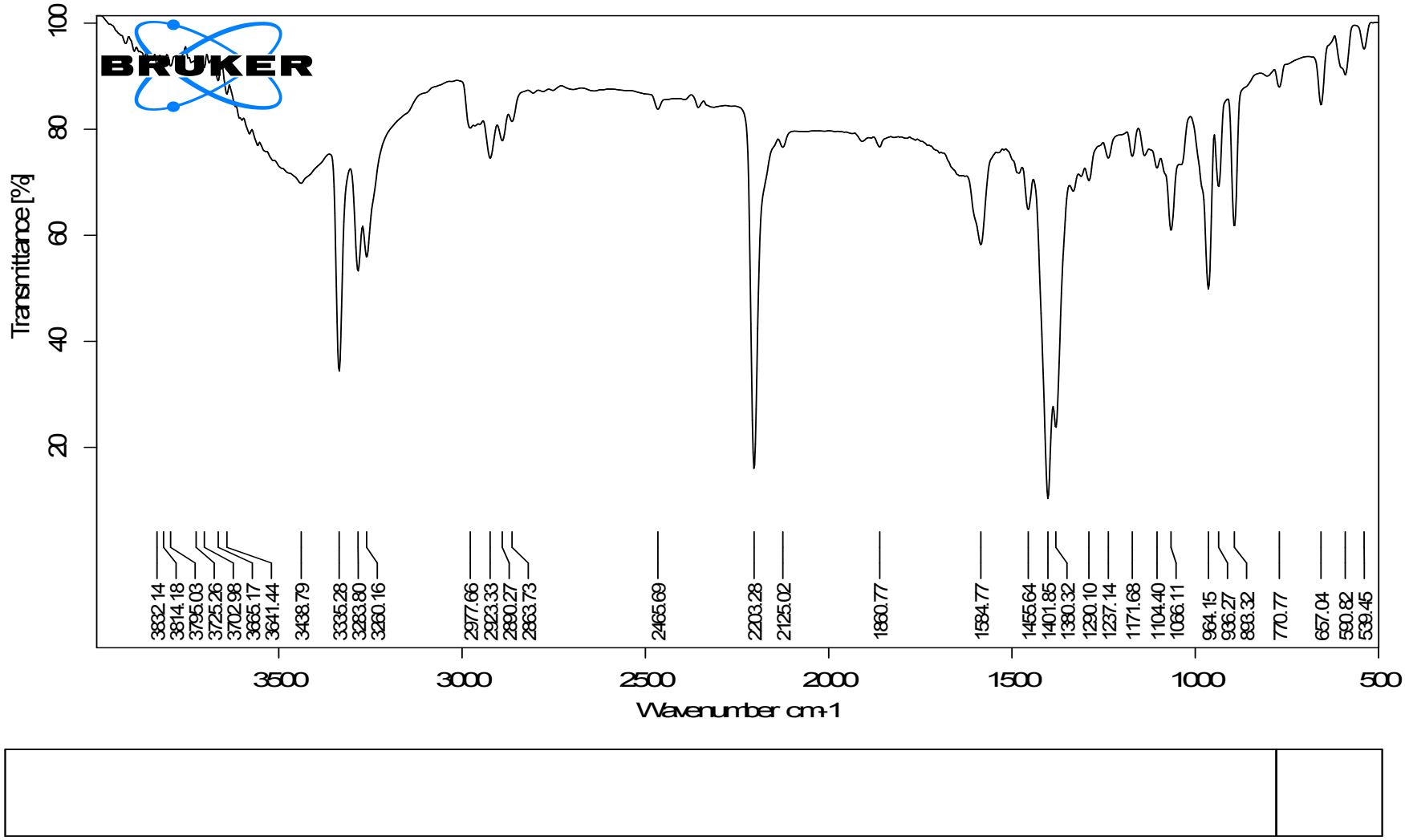

Figure S2. FT-IR spectrum of *[$Ni_2(tren)_2(i\text{-}mnt)_2$]*

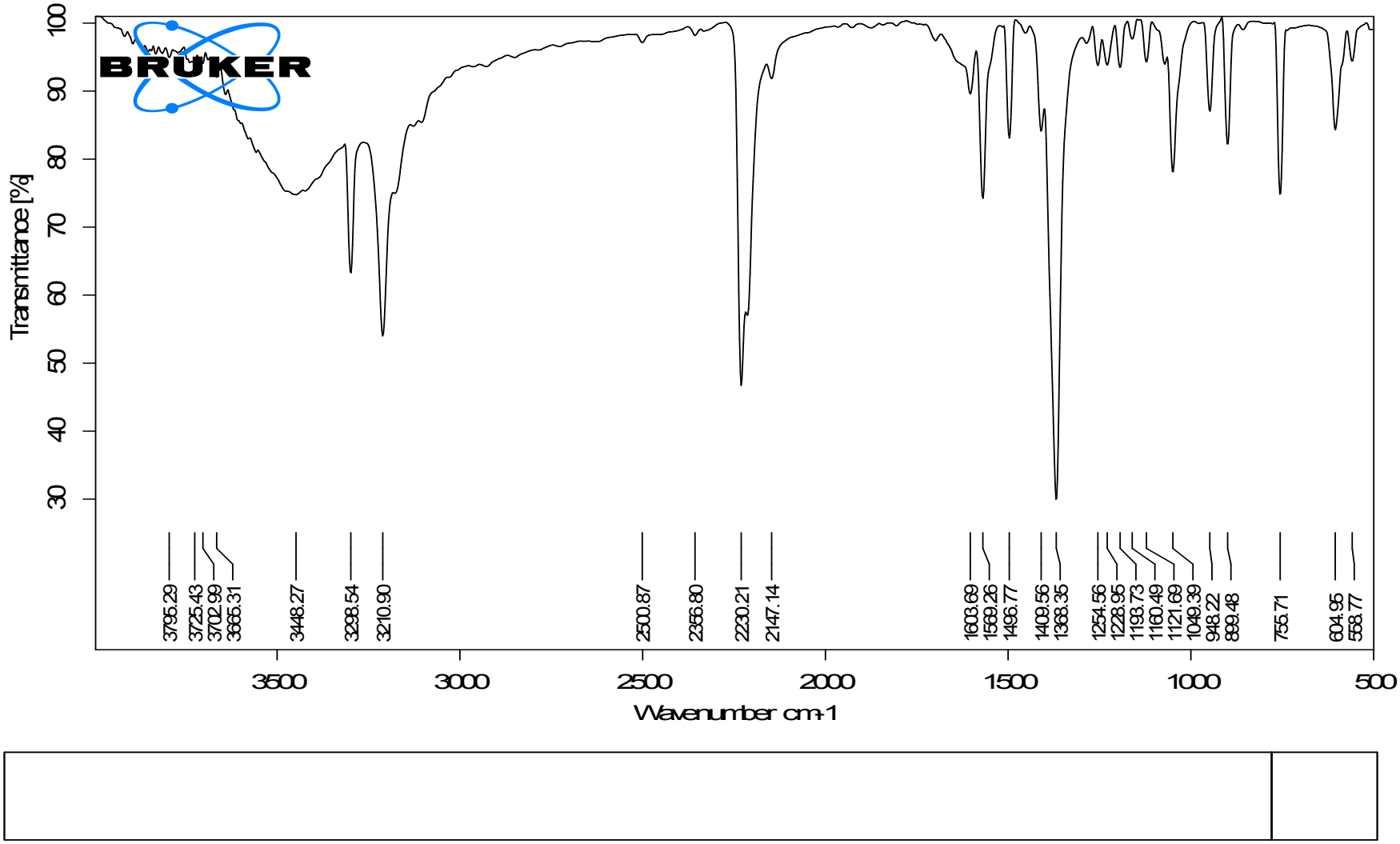

Figure S3. FT-IR spectrum of *[Ni$_2$(i-mnt)$_2$(opda)$_2$]n*

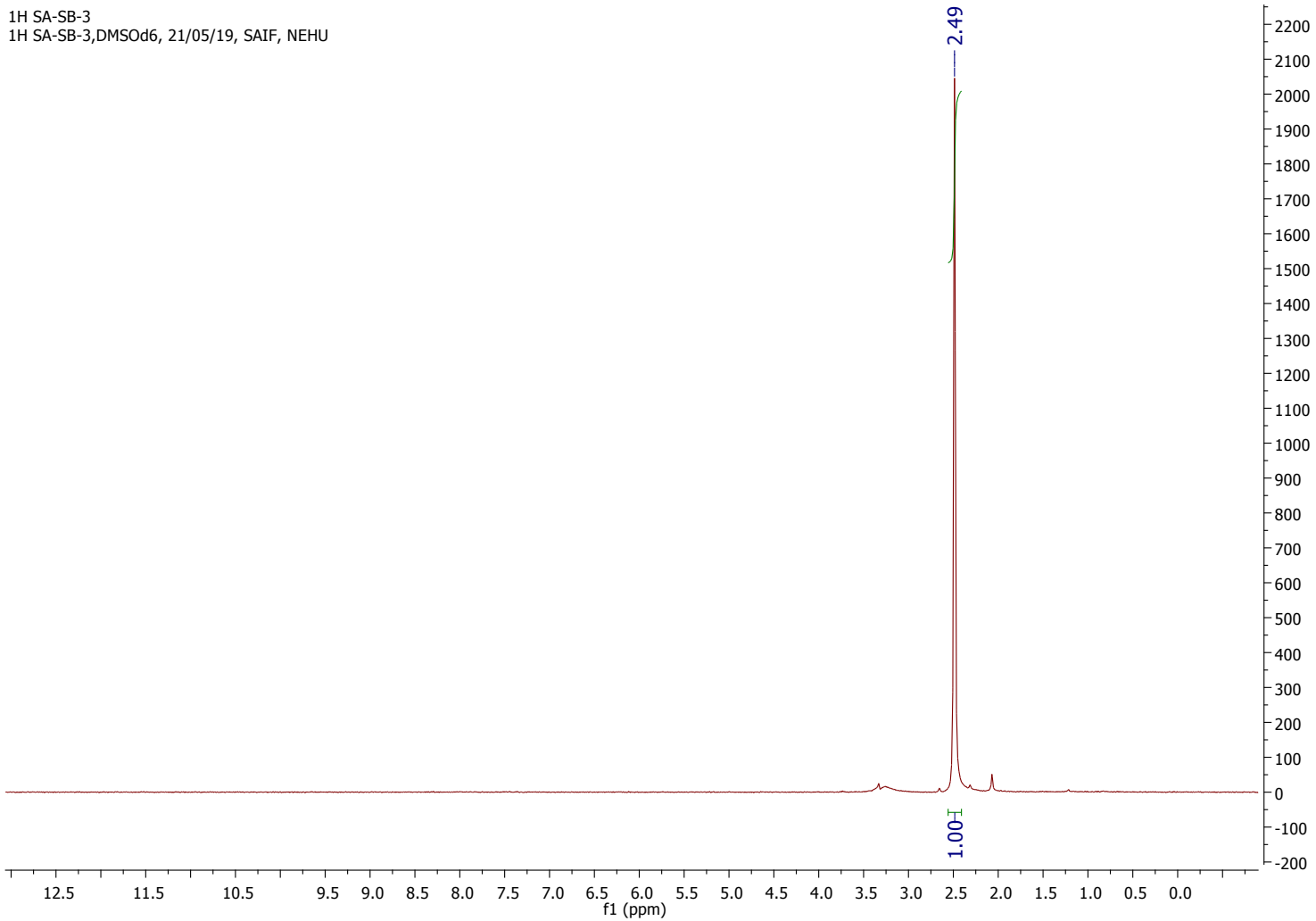

Figure S4. [1]H NMR Spectrum of complex **1** in dmso-d_6

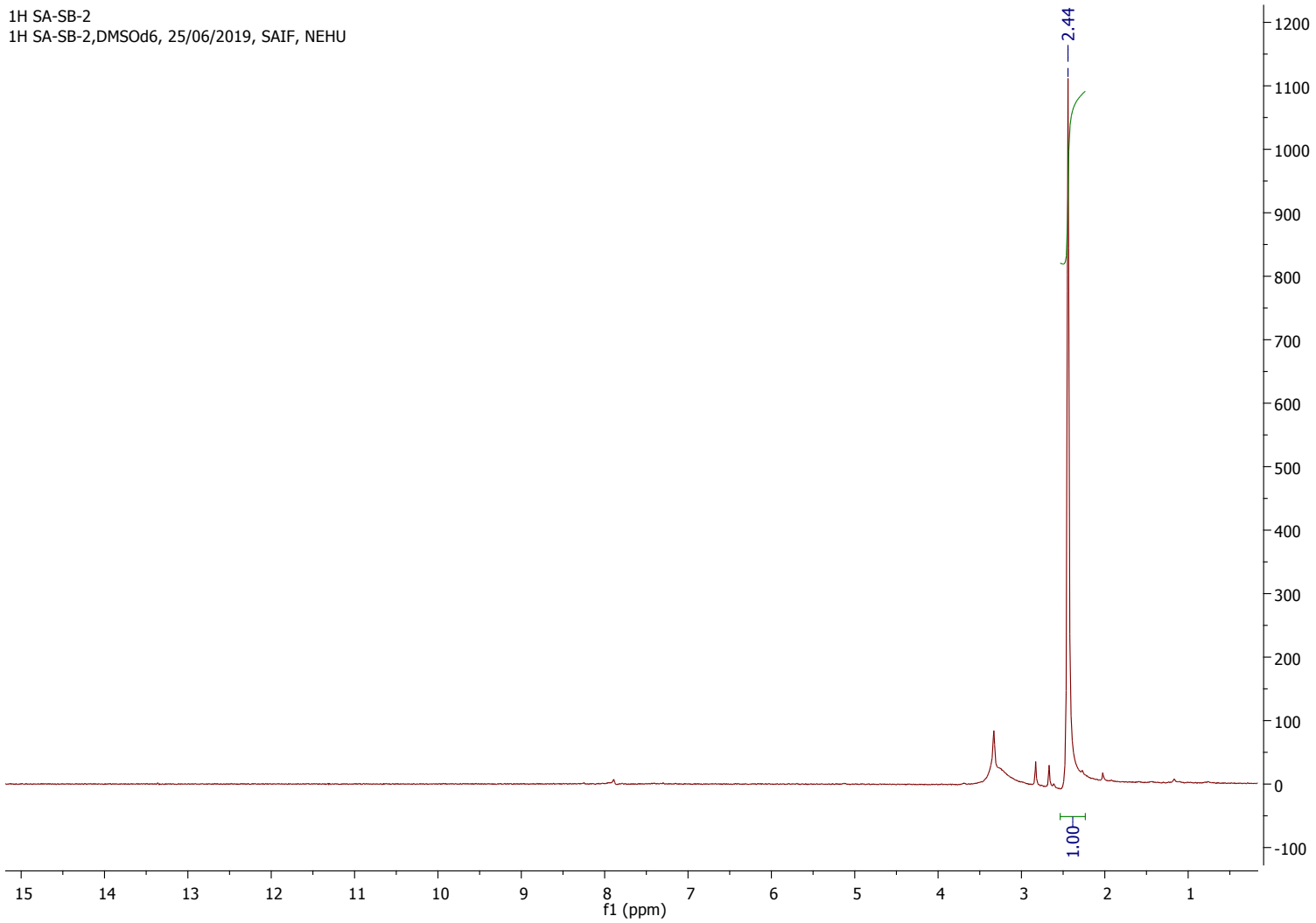

Figure S5. ^{1}H NMR Spectrum of complex **2** in dmso-d_6

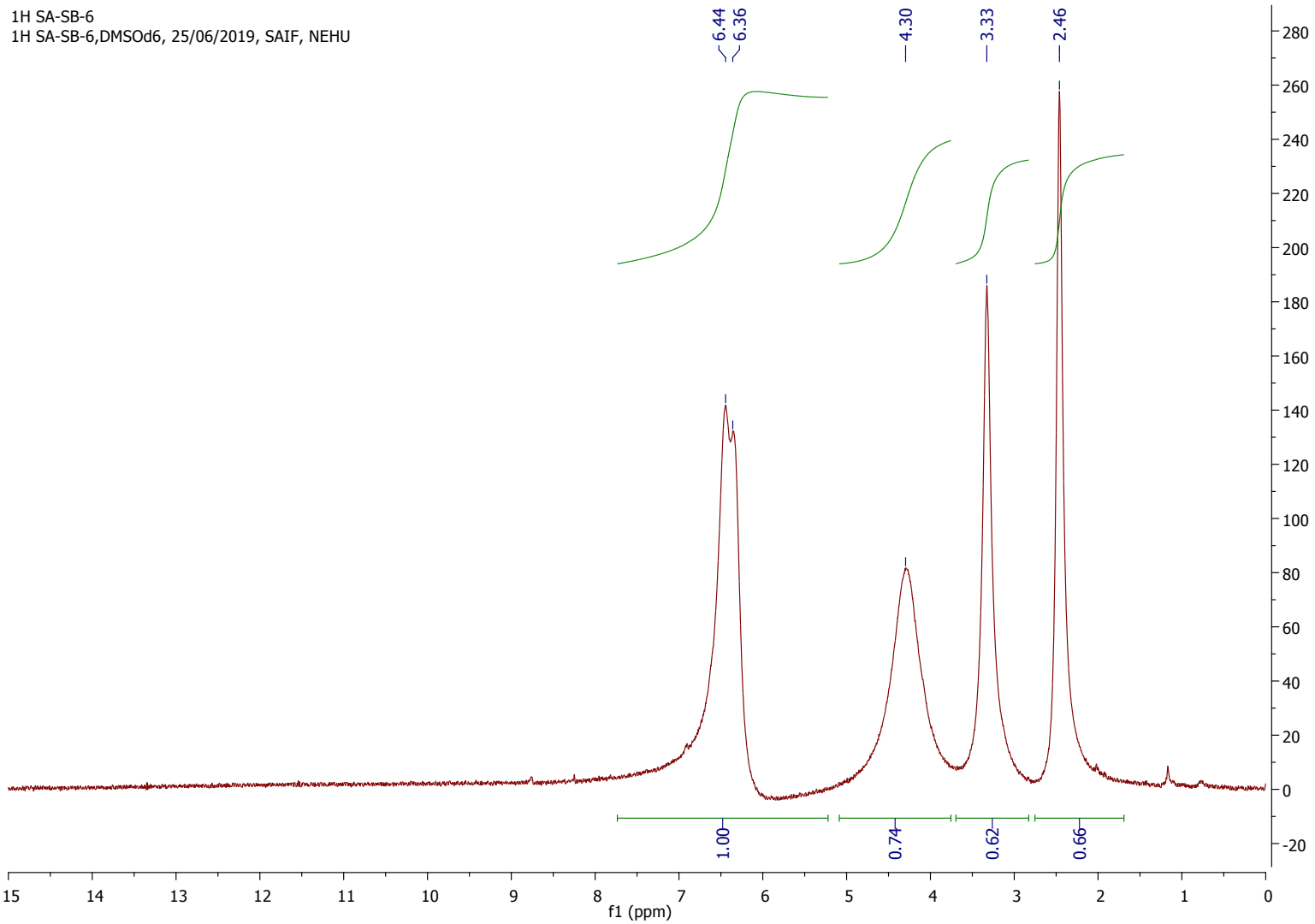

Figure S6. [1]H NMR Spectrum of complex **3** in dmso-d_6

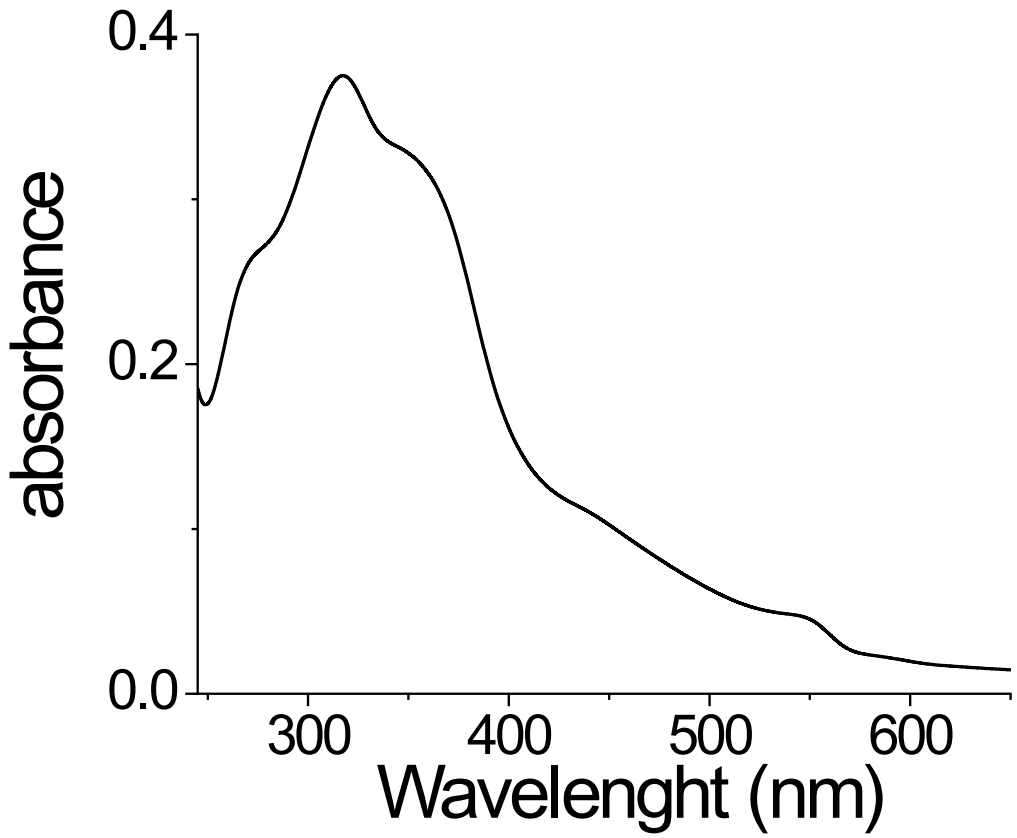

Figure S7. UV-Vis spectra of complex **1** (1 X 10^{-4} M) in 4% DMSO in $CHCl_3$

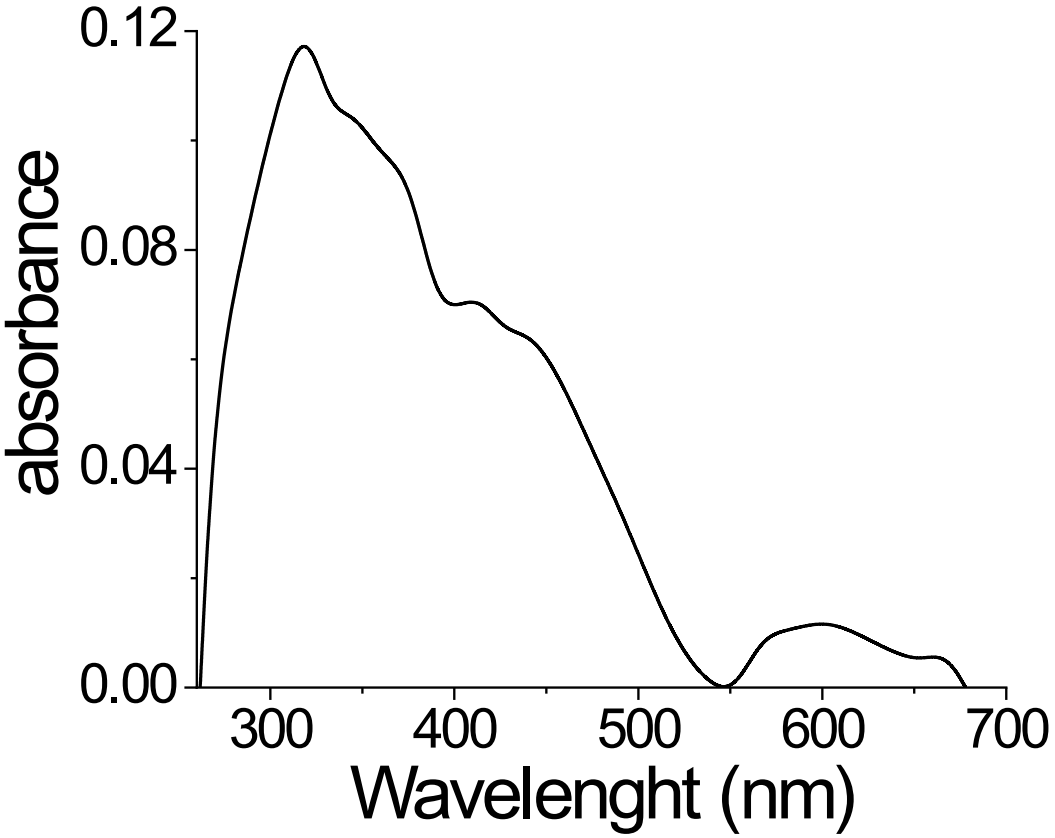

Figure S8. UV-Vis spectra of complex **2** (1 X 10^{-4} M) in 4% DMSO in $CHCl_3$

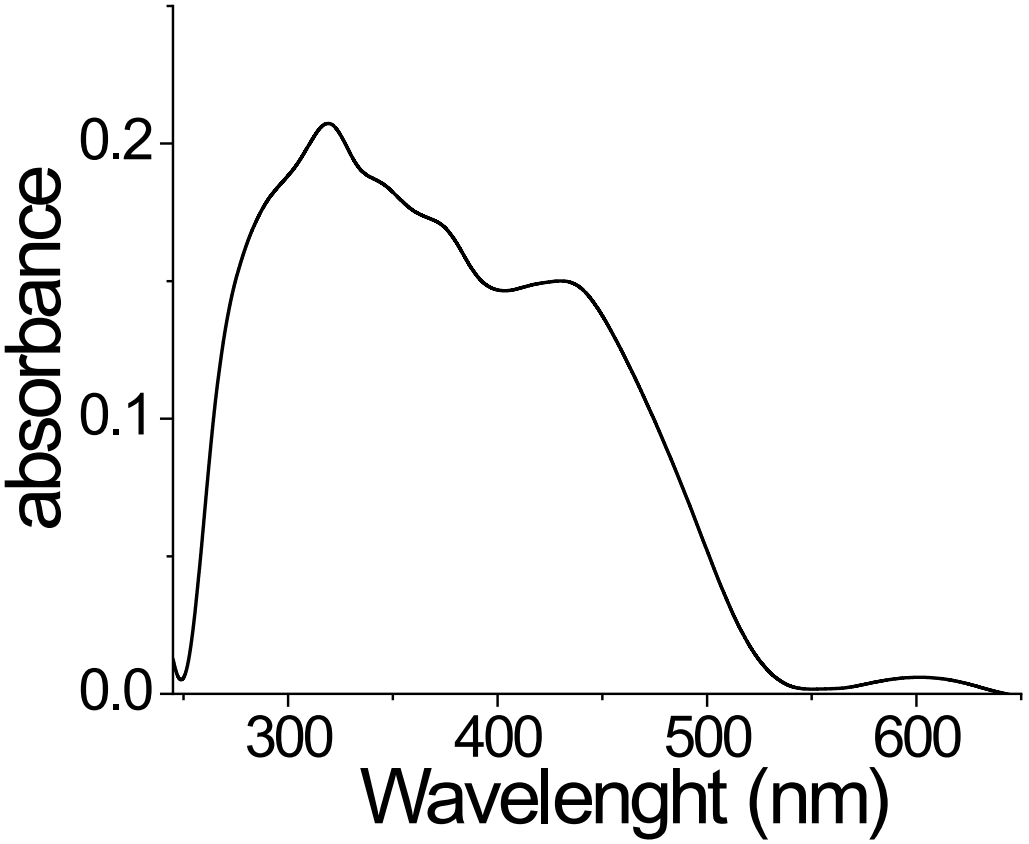

Figure S9. UV-Vis spectra of complex **3** (1 X 10^{-4} M) in 4% DMSO in $CHCl_3$

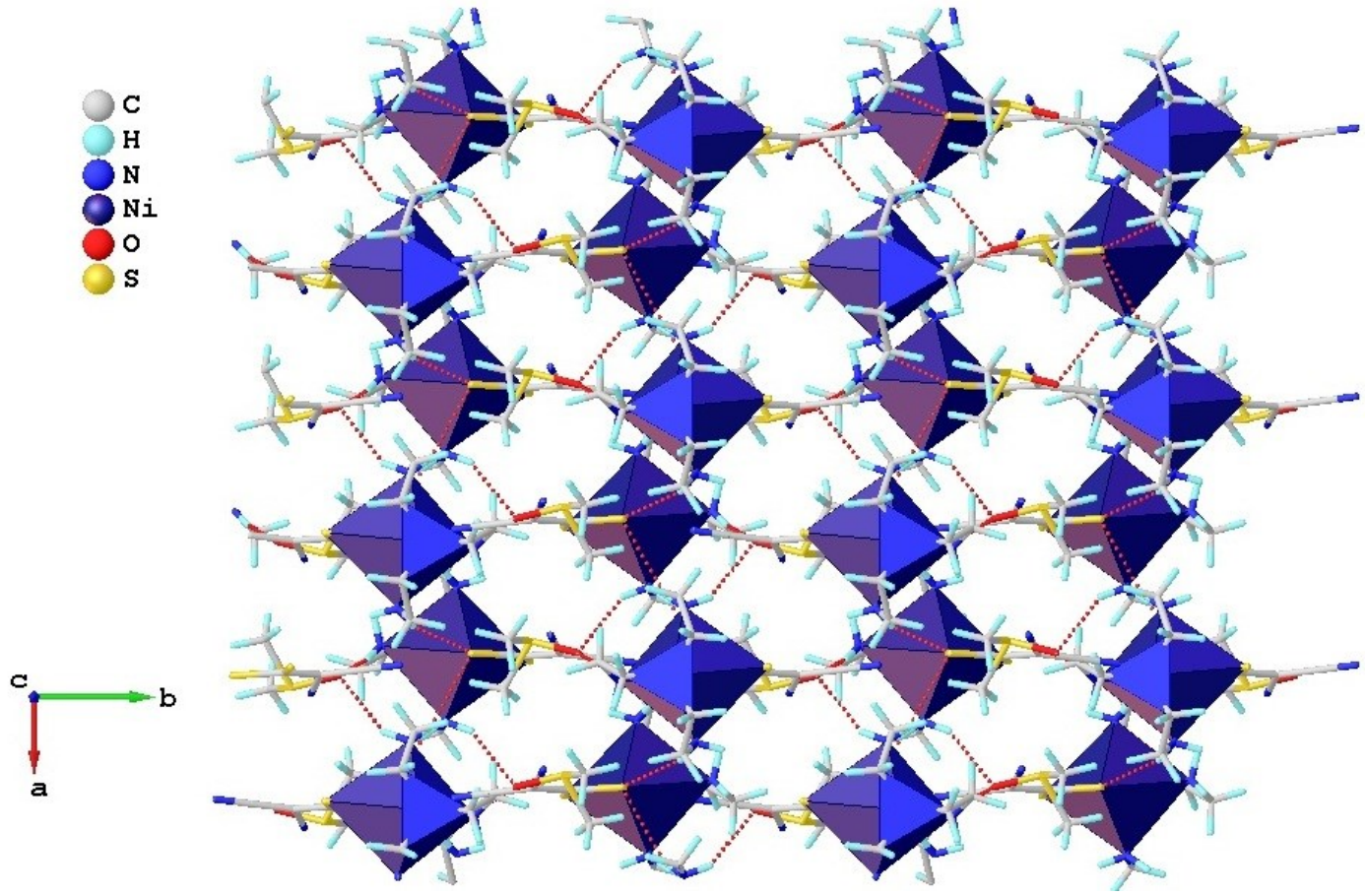

Figure S10. Partial view of 3D supramolecular framework of **1**.

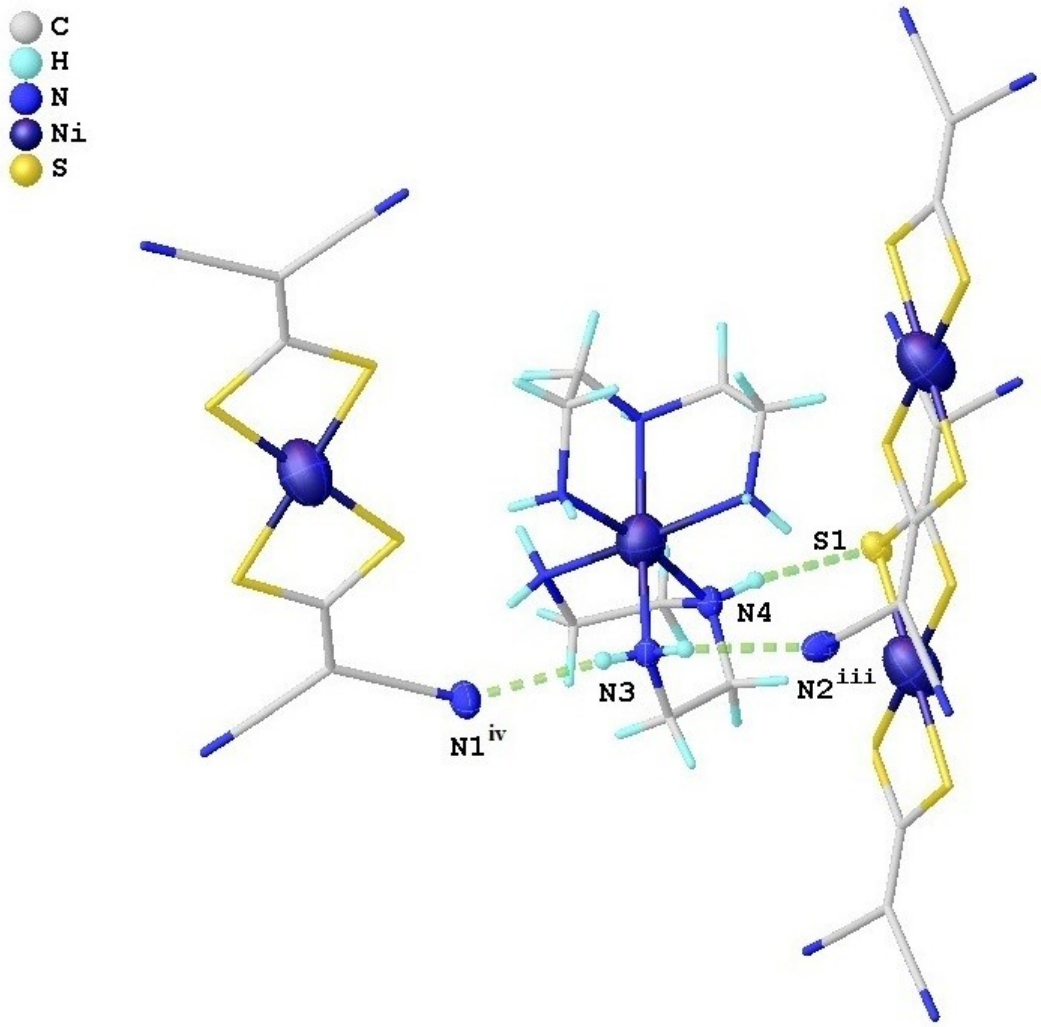

Figure S11. Partial view of hydrogen bonds in **2**.

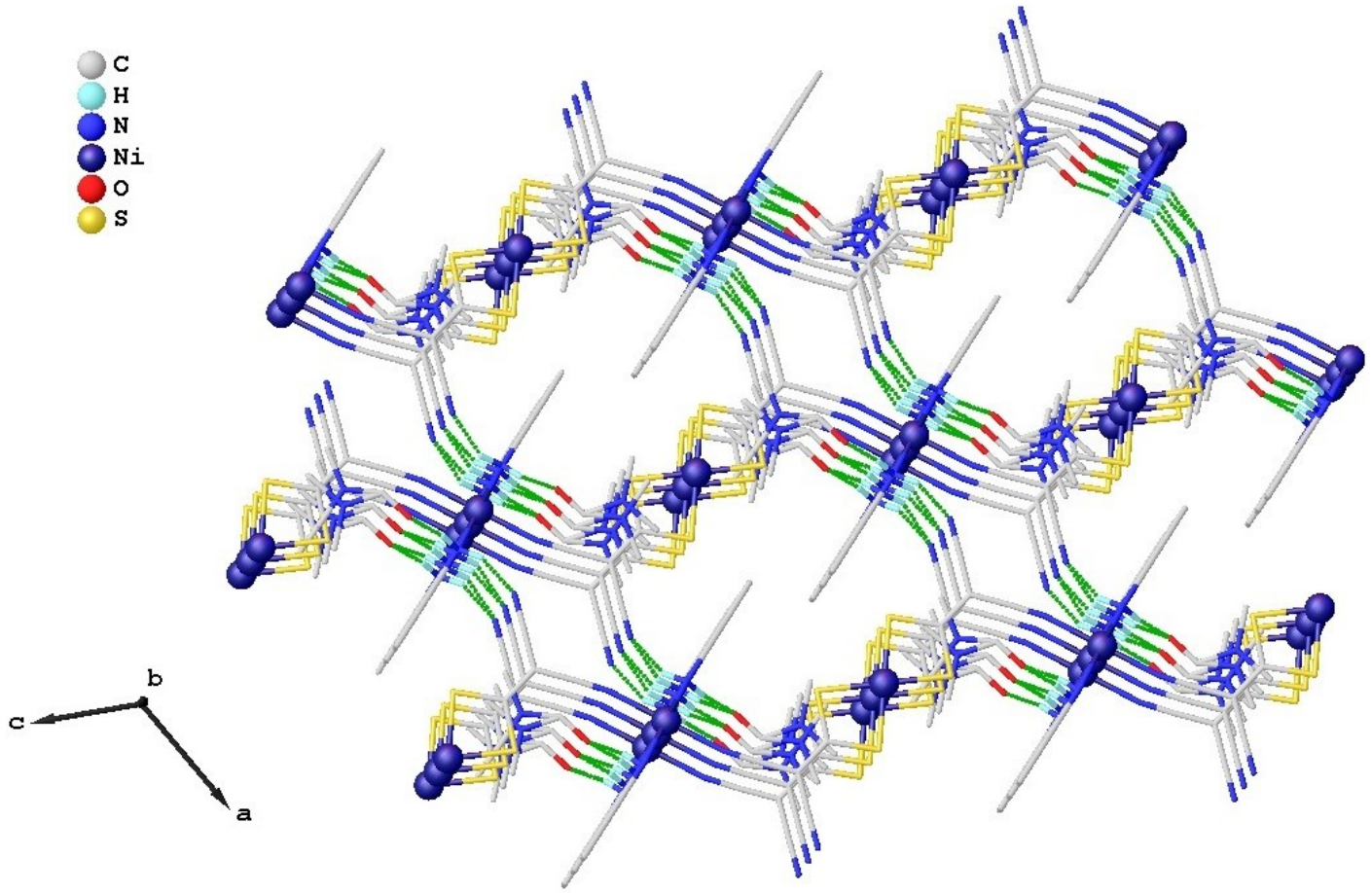

Figure S12. 3D architecture of **3** showing circular ribbon like stacking assembly.

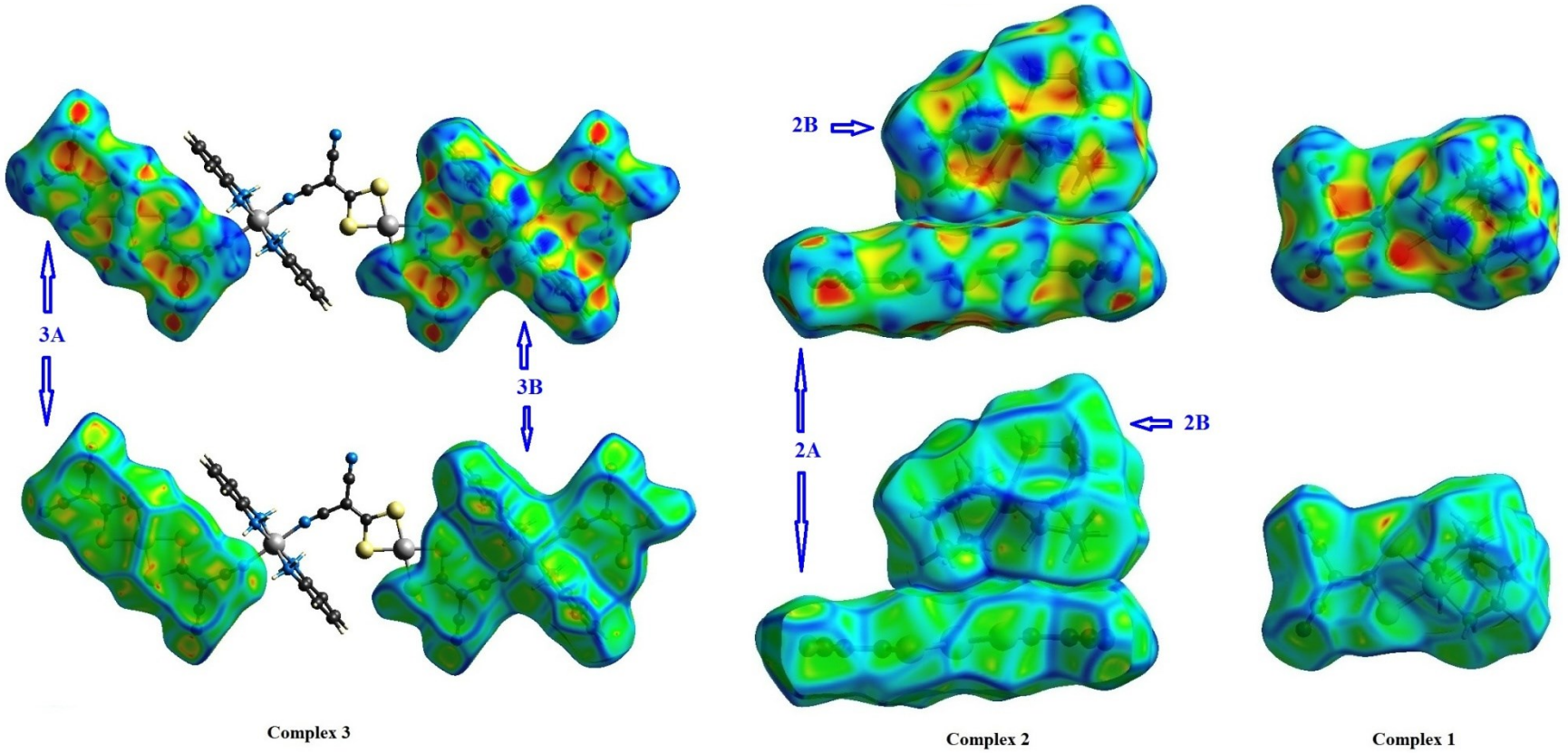

Figure S13. Hirshfeld surfaces mapped with shape index and curvedness for **1-3**

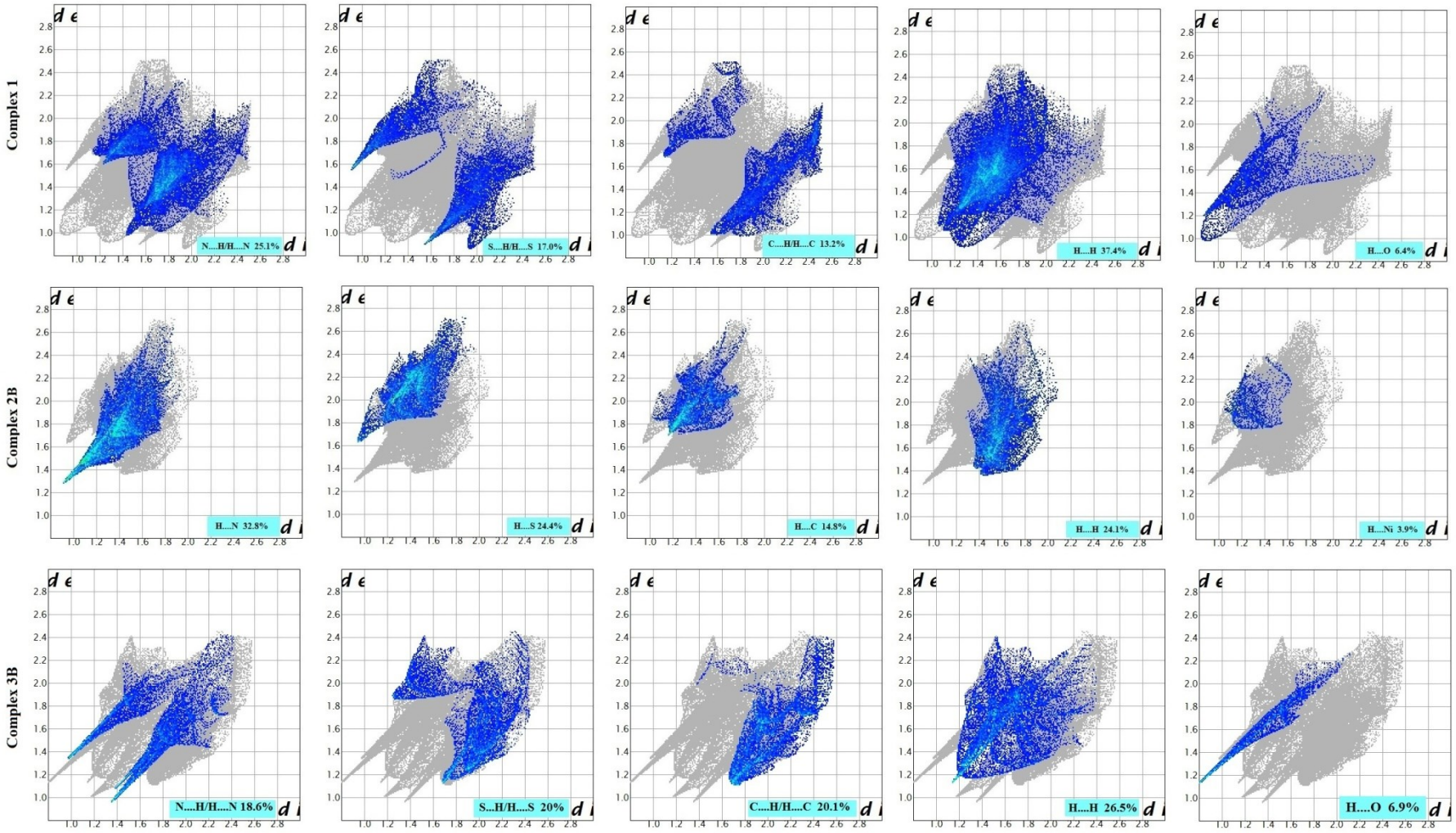

Figure S14. 2D fngerprint plots with di vs de for **1**, **2B** and **3B** showing N…H/H....N, S…H/H....S, C…H/H…C, H…H and H....O interactions (from left to right).

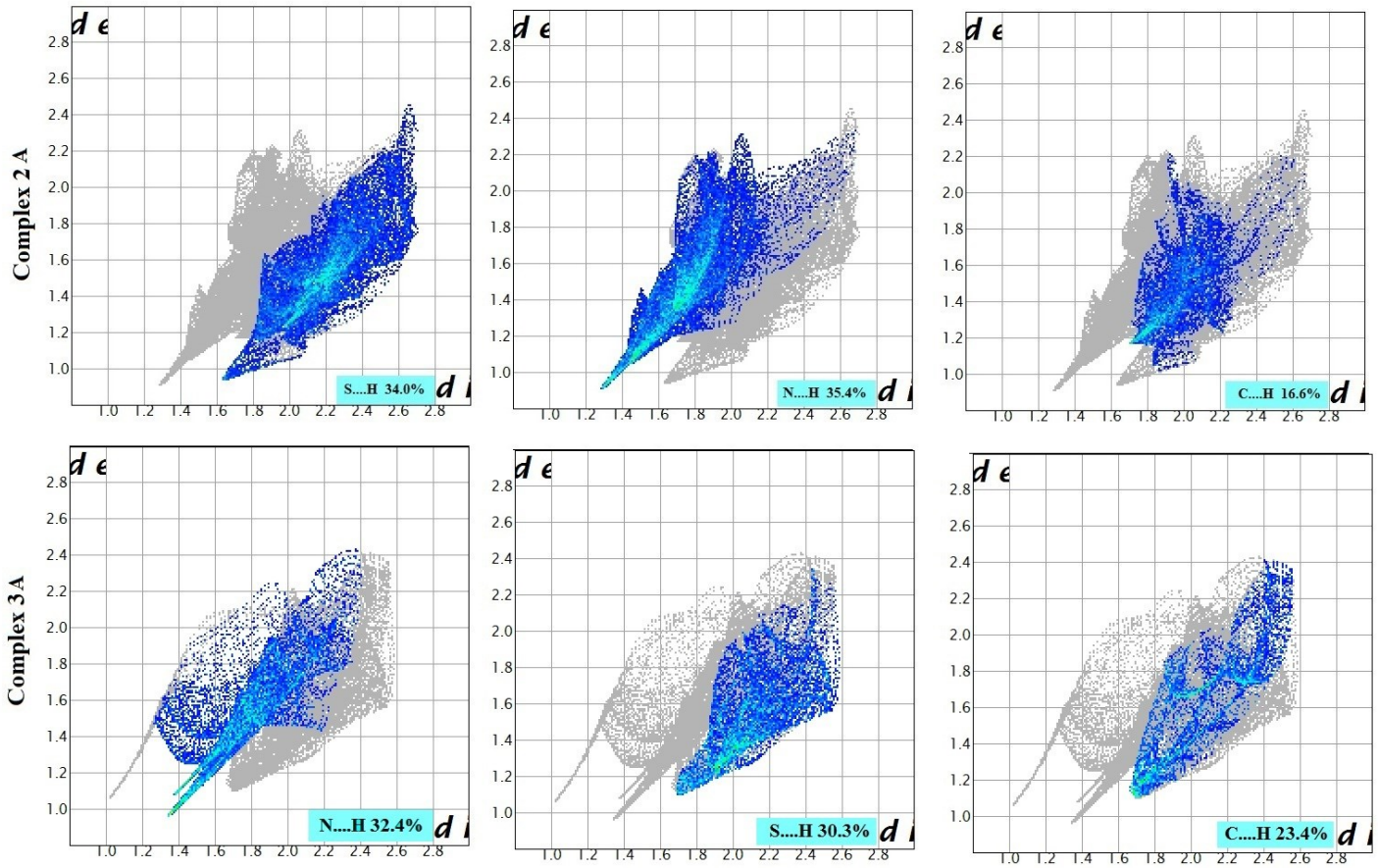

Figure S15. 2D fngerprint plots with di vs de for **2A** and **3A** showing S…H, N....H, and C…H interactions.

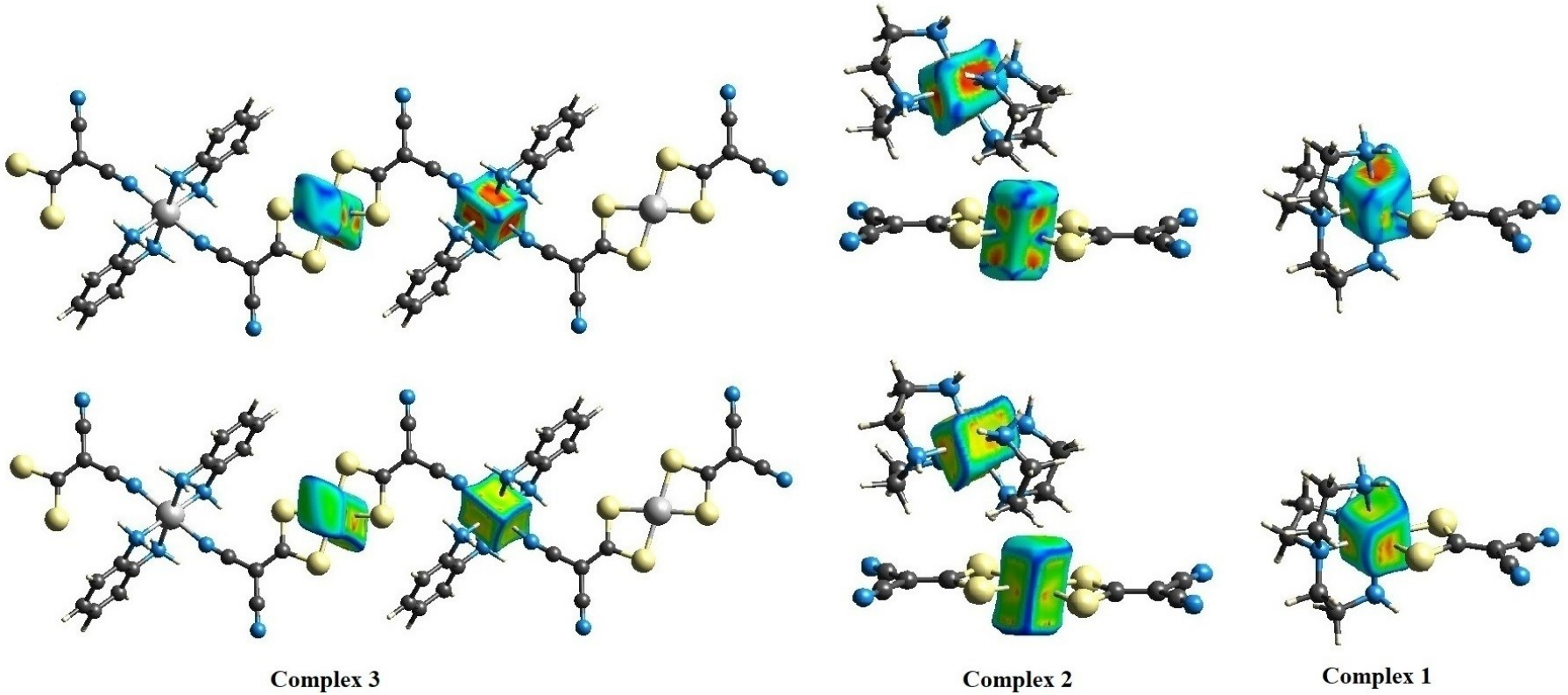

Figure S16. Views of Hirshfeld surfaces for nickel center in **1-3** mapped over shape index (s) in the range -1.0 Å to 1.0 Å and curvedness (c) in the range -4.0 Å to 0.4 Å.

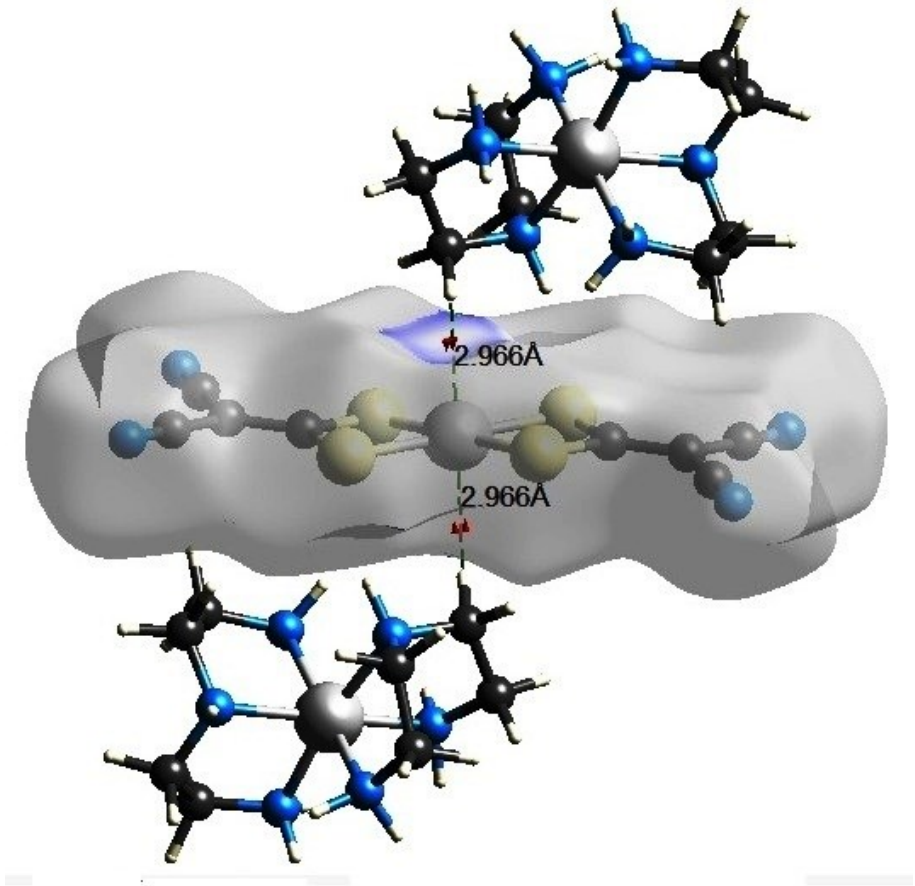

Figure S17. C-H....Ni interaction between $[Ni(i\text{-}mnt)_2]^{2-}$ and $[Ni(tren)_2]^{+2}$.

Table S1: Bond lengths (Å) for **1-3.**

Bond length					
Complex 1					
Ni1—N4	2.0971(19)	C21—H21B	0.98	C13—H13A	0.99
Ni1—N6	2.121(2)	C22—H22A	0.98	C14—H14A	0.99
Ni1—S1	2.4080(6)	C22—H22C	0.98	C15—C16	1.523(3)
S1—C1	1.724(2)	S3A—C22A	1.769(17)	C15—H15B	0.99
N1—C3	1.157(4)	C22A—H22D	0.98	C16—H16B	0.99
N3—C11	1.489(3)	C22A—H22F	0.98	S3—C22	1.778(3)
N3—H3B	0.84(3)	C21A—H21E	0.98	C21—H21A	0.98
N4—C15	1.480(3)	Ni1—N5	2.102(2)	C21—H21C	0.98
N5—C13	1.475(3)	Ni1—N3	2.122(2)	C22—H22B	0.98
N5—H5B	0.90(3)	Ni1—S2	2.5260(6)	S3A—O1A	1.496(18)
N6—H6A	0.82(4)	S2—C1	1.711(2)	S3A—C21A	1.772(18)
C1—C2	1.401(3)	N2—C4	1.146(4)	C22A—H22E	0.98
C2—C4	1.429(4)	N3—H3A	0.88(3)	C21A—H21D	0.98
C11—H11A	0.99	N4—C12	1.477(3)	C21A—H21F	0.98
C12—H12A	0.99	N4—C14	1.496(3)	C12—H12B	0.99
C13—C14	1.529(4)	N5—H5A	0.82(3)	S3—C21	1.783(4)
C13—H13B	0.99	N6—C16	1.478(3)	C11—H11B	0.99
C14—H14B	0.99	N6—H6B	0.92(4)	S3—O1	1.507(2)
C15—H15A	0.99	C2—C3	1.416(4)		
C16—H16A	0.99	C11—C12	1.522(3)		
Complex 2					
Ni2—N3	2.086 (3)	Ni1—S2^{ii}	2.2098 (10)	N1—C3	1.142 (5)

N4—C12	1.483 (5)	C2—C4	1.428 (5)	C12—H12B	0.99
Ni2—N3^{i}	2.086 (3)	Ni1—S2	2.2098 (10)	N2—C4	1.145 (5)
N4—H4	0.86 (4)	C2—C3	1.428 (5)	C13—C14	1.513 (5)
Ni2—N4^{i}	2.135 (3)	Ni1—S1^{ii}	2.2129 (10)	N3—C11	1.464 (5)
N5—C13	1.474 (5)	C11—C12	1.523 (6)	C13—H13A	0.99
Ni2—N4	2.135 (3)	Ni1—S1	2.2130 (10)	N3—H3A	0.87 (5)
N5—H5A	0.87 (5)	C11—H11A	0.99	C13—H13B	0.99
Ni2—N5^{i}	2.154 (3)	S1—C1	1.721 (4)	N3—H3B	0.82 (6)
N5—H5B	0.80 (4)	C11—H11B	0.99	C14—H14A	0.99
Ni2—N5	2.154 (3)	S2—C1	1.729 (4)	N4—C14	1.478 (5)
C1—C2	1.381 (5)	C12—H12A	0.99	C14—H14B	0.99
Complex 3					
Ni1—S2	2.1974 (14)	C2—C4	1.427 (6)	Ni2—N1^{ii}	2.110 (3)
C13—C13^{iii}	1.365 (8)	N4—C22	1.447 (10)	N4A—C23A	1.421 (13)
Ni1—S2^{i}	2.1974 (14)	C3—N1	1.145 (5)	N3—C11	1.456 (4)
C13—H13	0.95	C22—H22A	0.98	C22A—H22D	0.98
Ni1—S1^{i}	2.2125 (10)	C4—N2	1.149 (6)	N3—H3A	0.920 (19)
O1—C21	1.205 (6)	C22—H22B	0.98	C22A—H22E	0.98
Ni1—S1	2.2125 (10)	N1—Ni2	2.110 (3)	N3—H3B	0.916 (18)
C21—N4A	1.285 (11)	C22—H22C	0.98	C22A—H22F	0.98
S1—C1	1.707 (4)	Ni2—N3	2.088 (2)	C11—C11^{iii}	1.381 (6)
C21—N4	1.350 (9)	C23—H23A	0.98	C23A—H23D	0.98
S2—C1	1.719 (4)	Ni2—N3^{ii}	2.088 (2)	C11—C12	1.382 (4)
C21—H21	0.95	C23—H23B	0.98	C23A—H23E	0.98
C1—C2	1.400 (6)	Ni2—N3^{iii}	2.088 (2)	C12—C13	1.394 (5)

C21—H21A	0.95	C23—H23C	0.98	C23A—H23F	0.98
C2—C3	1.409 (5)	Ni2—N3^{iv}	2.088 (2)	C12—H12	0.95
N4—C23	1.441 (9)	N4A—C22A	1.421 (13)		

Symmetry codes: For **2** (i) -x+1, y, -z+½; (ii) -x+1, -y+1, - z; for **3** (i) -x+2, -y-2, -z+1; (ii) -x+2, -y-2, -z; (iii) x, -y-2, z; (iv) -x+2, y, -z

Table S2: Bond angles (^{0}) of **1-3**.

Bond angle					
Complex 1					
N4—Ni1—N5	83.60(8)	H15A—C15—H15B	108.2	C2—C1—S2	122.48(19)
N5—Ni1—N6	92.12(9)	N6—C16—H16A	109.8	S2—C1—S1	116.67(14)
N5—Ni1—N3	94.27(9)	N6—C16—H16B	109.8	C1—C2—C4	121.8(2)
N4—Ni1—S1	174.89(6)	H16A—C16—H16B	108.2	N1—C3—C2	177.7(4)
N6—Ni1—S1	95.26(6)	O1—S3—C21	106.44(18)	N3—C11—C12	109.96(19)
N4—Ni1—S2	102.42(6)	S3—C21—H21A	109.5	C12—C11—H11A	109.7
N6—Ni1—S2	88.33(7)	H21A—C21—H21B	109.5	C12—C11—H11B	109.7
S1—Ni1—S2	72.64(2)	H21A—C21—H21C	109.5	N4—C12—C11	110.09(19)
C1—S2—Ni1	83.52(8)	S3—C22—H22A	109.5	C11—C12—H12A	109.6
C11—N3—H3A	105.8(18)	H22A—C22—H22B	109.5	C11—C12—H12B	109.6
C11—N3—H3B	104.(2)	H22A—C22—H22C	109.5	N5—C13—C14	110.2(2)
H3A—N3—H3B	115.(3)	O1A—S3A—C22A	107.(2)	C14—C13—H13A	109.6
C12—N4—C14	111.98(19)	C22A—S3A—C21A	99.(2)	C14—C13—H13B	109.6
C12—N4—Ni1	105.38(14)	S3A—C22A—H22E	109.5	N4—C14—C13	112.6(2)
C14—N4—Ni1	109.54(15)	S3A—C22A—H22F	109.5	C13—C14—H14A	109.1
C13—N5—H5A	111.(2)	H22E—C22A—H22F	109.5	C13—C14—H14B	109.1

C13—N5—H5B	106.2(19)	S3A—C21A—H21E	109.5	N4—C15—C16	109.84(19)
H5A—N5—H5B	107.(3)	S3A—C21A—H21F	109.5	C16—C15—H15A	109.7
C16—N6—H6A	109.(2)	H21E—C21A—H21F	109.5	C16—C15—H15B	109.7
C16—N6—H6B	109.(2)	N4—Ni1—N6	83.19(8)	N6—C16—C15	109.5(2)
H6A—N6—H6B	104.(3)	N4—Ni1—N3	81.75(8)	C15—C16—H16A	109.8
C2—C1—S1	120.84(18)	N6—Ni1—N3	162.87(8)	C15—C16—H16B	109.8
C1—C2—C3	121.3(2)	N5—Ni1—S1	101.34(6)	O1—S3—C22	105.13(15)
C3—C2—C4	116.8(2)	N3—Ni1—S1	99.03(6)	C22—S3—C21	98.1(2)
N2—C4—C2	178.9(3)	N5—Ni1—S2	173.98(6)	S3—C21—H21B	109.5
N3—C11—H11A	109.7	N3—Ni1—S2	86.98(6)	S3—C21—H21C	109.5
N3—C11—H11B	109.7	C1—S1—Ni1	86.96(8)	H21B—C21—H21C	109.5
H11A—C11—H11B	108.2	C11—N3—Ni1	110.87(15)	S3—C22—H22B	109.5
N4—C12—H12A	109.6	Ni1—N3—H3A	103.8(18)	S3—C22—H22C	109.5
N4—C12—H12B	109.6	Ni1—N3—H3B	118.(2)	H22B—C22—H22C	109.5
H12A—C12—H12B	108.2	C12—N4—C15	112.28(19)	O1A—S3A—C21A	108.(3)
N5—C13—H13A	109.6	C15—N4—C14	111.0(2)	S3A—C22A—H22D	109.5
N5—C13—H13B	109.6	C15—N4—Ni1	106.35(14)	H22D—C22A—H22E	109.5
H13A—C13—H13B	108.1	C13—N5—Ni1	106.28(15)	H22D—C22A—H22F	109.5
N4—C14—H14A	109.1	Ni1—N5—H5A	108.(2)	S3A—C21A—H21D	109.5
N4—C14—H14B	109.1	Ni1—N5—H5B	117.8(19)	H21D—C21A—H21E	109.5
H14A—C14—H14B	107.8	C16—N6—Ni1	109.04(15)	H21D—C21A—H21F	109.5
N4—C15—H15A	109.7	Ni1—N6—H6A	111.(2)		
N4—C15—H15B	109.7	Ni1—N6—H6B	114.(2)		
Complex 2					
N3—Ni2—N3^{i}	92.57 (19)	N3—C11—C12	108.9 (3)	Ni2—N3—H3A	107 (3)

Ni2—N5—H5A	104 (3)	N4—Ni2—N5	80.46 (12)	N5—C13—H13A	109.8
N3—Ni2—N4^{i}	171.53 (13)	N3—C11—H11A	109.9	C11—N3—H3B	112 (4)
C13—N5—H5B	105 (3)	N5^{i}—Ni2—N5	168.5 (2)	C14—C13—H13A	109.8
N3^{i}—Ni2—N4^{i}	82.70 (13)	C12—C11—H11A	109.9	Ni2—N3—H3B	108 (4)
Ni2—N5—H5B	113 (3)	S2^{ii}—Ni1—S2	180.0	N5—C13—H13B	109.8
N3—Ni2—N4	82.70 (13)	N3—C11—H11B	109.9	H3A—N3—H3B	111 (5)
H5A—N5—H5B	107 (4)	S2^{ii}—Ni1—S1^{ii}	79.07 (4)	C14—C13—H13B	109.8
N3^{i}—Ni2—N4	171.53 (13)	C12—C11—H11B	109.9	C14—N4—C12	115.1 (3)
C2—C1—S1	126.2 (3)	S2—Ni1—S1^{ii}	100.93 (4)	H13A—C13—H13B	108.2
N4^{i}—Ni2—N4	102.83 (18)	H11A—C11—H11B	108.3	C14—N4—Ni2	108.0 (2)
C2—C1—S2	124.5 (3)	S2^{ii}—Ni1—S1	100.93 (4)	N4—C14—C13	111.3 (3)
N3—Ni2—N5^{i}	93.00 (13)	N4—C12—C11	112.7 (3)	C12—N4—Ni2	108.1 (2)
S1—C1—S2	109.4 (2)	S2—Ni1—S1	79.07 (4)	N4—C14—H14A	109.4
N3^{i}—Ni2—N5^{i}	94.91 (14)	N4—C12—H12A	109.1	C14—N4—H4	107 (3)
C1—C2—C4	120.1 (3)	S1^{ii}—Ni1—S1	180.0	C13—C14—H14A	109.4
N4^{i}—Ni2—N5^{i}	80.46 (12)	C11—C12—H12A	109.1	C12—N4—H4	104 (3)
C1—C2—C3	121.3 (3)	C1—S1—Ni1	85.53 (13)	N4—C14—H14B	109.4
N4—Ni2—N5^{i}	92.36 (14)	N4—C12—H12B	109.1	Ni2—N4—H4	115 (3)
C4—C2—C3	118.6 (3)	C1—S2—Ni1	85.44 (13)	C13—C14—H14B	109.4
N3—Ni2—N5	94.91 (14)	C11—C12—H12B	109.1	C13—N5—Ni2	112.1 (2)
N1—C3—C2	179.3 (5)	C11—N3—Ni2	110.5 (2)	H14A—C14—H14B	108.0
N3^{i}—Ni2—N5	93.00 (13)	H12A—C12—H12B	107.8	C13—N5—H5A	117 (3)
N2—C4—C2	179.0 (4)	C11—N3—H3A	109 (3)		
N4^{i}—Ni2—N5	92.36 (14)	N5—C13—C14	109.6 (3)		

Complex 3

S2—Ni1—S2^{i}	180.0	N1—C3—C2	177.2 (4)	N3^{ii}—Ni2—N1^{ii}	89.79 (9)
C11—C12—H12	120.1	N4—C22—H22A	109.5	C22A—N4A—C23A	123.6 (15)
S2—Ni1—S1^{i}	100.72 (4)	N2—C4—C2	179.0 (4)	N3^{iii}—Ni2—N1^{ii}	90.21 (9)
C13—C12—H12	120.1	N4—C22—H22B	109.5	N4A—C22A—H22D	109.5
S2^{i}—Ni1—S1^{i}	79.28 (4)	C3—N1—Ni2	170.1 (3)	N3^{iv}—Ni2—N1^{ii}	89.79 (9)
C13^{iii}—C13—C12	120.1 (2)	H22A—C22—H22B	109.5	N4A—C22A—H22E	109.5
S2—Ni1—S1	79.28 (4)	N3—Ni2—N3^{ii}	180.0	N1—Ni2—N1^{ii}	180.0
C13^{iii}—C13—H13	119.9	N4—C22—H22C	109.5	H22D—C22A—H22E	109.5
S2^{i}—Ni1—S1	100.72 (4)	N3—Ni2—N3^{iii}	83.21 (13)	C11—N3—Ni2	109.70 (18)
C12—C13—H13	119.9	H22A—C22—H22C	109.5	N4A—C22A—H22F	109.5
S1^{i}—Ni1—S1	180.0	N3^{ii}—Ni2—N3^{iii}	96.79 (13)	C11—N3—H3A	112 (2)
O1—C21—N4A	142.6 (9)	H22B—C22—H22C	109.5	H22D—C22A—H22F	109.5
C1—S1—Ni1	85.07 (14)	N3—Ni2—N3^{iv}	96.79 (13)	Ni2—N3—H3A	112 (2)
O1—C21—N4	119.4 (7)	N4—C23—H23A	109.5	H22E—C22A—H22F	109.5
C1—S2—Ni1	85.25 (14)	N3^{ii}—Ni2—N3^{iv}	83.21 (13)	C11—N3—H3B	112 (2)
O1—C21—H21	120.3	N4—C23—H23B	109.5	N4A—C23A—H23D	109.5
C2—C1—S1	124.9 (3)	N3^{iii}—Ni2—N3^{iv}	180.00 (10)	Ni2—N3—H3B	105 (2)
N4—C21—H21	120.3	H23A—C23—H23B	109.5	N4A—C23A—H23E	109.5
C2—C1—S2	124.7 (3)	N3—Ni2—N1	89.79 (9)	H3A—N3—H3B	105 (3)
O1—C21—H21A	108.7	N4—C23—H23C	109.5	H23D—C23A—H23E	109.5
S1—C1—S2	110.4 (2)	N3^{ii}—Ni2—N1	90.21 (9)	C11^{iii}—C11—C12	120.06 (19)
N4A—C21—H21A	108.7	H23A—C23—H23C	109.5	N4A—C23A—H23F	109.5
C1—C2—C3	119.0 (3)	N3^{iii}—Ni2—N1	89.79 (9)	C11^{iii}—C11—N3	118.56 (15)
C21—N4—C23	121.2 (7)	H23B—C23—H23C	109.5	H23D—C23A—H23F	109.5
C1—C2—C4	121.8 (3)	N3^{iv}—Ni2—N1	90.21 (9)	C12—C11—N3	121.4 (3)
C21—N4—C22	120.1 (7)	C21—N4A—C22A	119.5 (13)	H23E—C23A—H23F	109.5
C3—C2—C4	119.2 (4)	N3—Ni2—N1^{ii}	90.21 (9)	C11—C12—C13	119.8 (3)
C23—N4—C22	118.7 (8)	C21—N4A—C23A	117.0 (13)		

Symmetry codes: For **2** (i) -x+1, y, -z+½; (ii) -x+1, -y+1, -z; for **3** (i) -x+2, -y-2, -z+1; (ii) -x+2, -y-2, -z; (iii) x, -y-2, z; (iv) -x+2, y, -z

Table S3: Torsion angles (^{0}) of **1-3**.

Torsion angle			
Complex 1			
Ni1—S2—C1—C2	-175.0(2)	Ni1—S2—C1—S1	4.24(11)
Ni1—S1—C1—C2	174.8(2)	Ni1—S1—C1—S2	-4.43(12)
S2—C1—C2—C3	172.6(2)	S1—C1—C2—C3	-6.6(4)
S2—C1—C2—C4	-4.6(4)	S1—C1—C2—C4	176.2(2)
Ni1—N3—C11—C12	17.9(3)	C15—N4—C12—C11	165.6(2)
C14—N4—C12—C11	-68.7(3)	Ni1—N4—C12—C11	50.3(2)
N3—C11—C12—N4	-46.0(3)	Ni1—N5—C13—C14	-44.7(2)
C12—N4—C14—C13	98.9(2)	C15—N4—C14—C13	-134.7(2)
Ni1—N4—C14—C13	-17.6(3)	N5—C13—C14—N4	42.5(3)
C12—N4—C15—C16	-159.9(2)	C14—N4—C15—C16	74.0(3)
Ni1—N4—C15—C16	-45.1(2)	Ni1—N6—C16—C15	-31.5(3)
N4—C15—C16—N6	52.2(3)		
Complex 2			
Ni1—S1—C1—C2	172.8 (3)	S1—C1—C2—C4	−176.3 (3)
Ni2—N3—C11—C12	38.7 (4)	Ni2—N5—C13—C14	−26.1 (4)
Ni1—S1—C1—S2	−6.76 (16)	S2—C1—C2—C4	3.2 (5)
C14—N4—C12—C11	−90.8 (4)	C12—N4—C14—C13	77.0 (4)
Ni1—S2—C1—C2	−172.8 (3)	S1—C1—C2—C3	0.9 (6)
Ni2—N4—C12—C11	30.0 (4)	Ni2—N4—C14—C13	−43.9 (4)
Ni1—S2—C1—S1	6.77 (16)	S2—C1—C2—C3	−179.6 (3)

N3—C11—C12—N4	−46.3 (4)	N5—C13—C14—N4	46.9 (5)
Complex 3			
Ni1—S1—C1—C2	180.0 (10)	O1—C21—N4—C23	180.0 (2)
Ni2—N3—C11—C12	−176.3 (2)	S2—C1—C2—C3	180.0 (10)
Ni1—S1—C1—S2	0	O1—C21—N4—C22	0.0 (10)
C11^{iii}—C11—C12—C13	0.2 (3)	S1—C1—C2—C4	180.0 (10)
Ni1—S2—C1—C2	180.0 (10)	O1—C21—N4A—C22A	0.0 (2)
N3—C11—C12—C13	−179.7 (3)	S2—C1—C2—C4	0.0 (10)
Ni1—S2—C1—S1	0	O1—C21—N4A—C23A	180.0 (3)
C11—C12—C13—C13^{iii}	−0.2 (3)	Ni2—N3—C11—C11^{iii}	3.76 (17)
S1—C1—C2—C3	0.0 (10)		

Symmetry codes: For **3** (iii) x, -y-2, z

Table S4: Summary of hydrogen bond parameters in **1-3**.

Crystal	D H···A	d(D H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(D H···A) (^{0})	Symmetry operation
1	N3 H3A···O1^{i}	0.88(3)	2.21(3)	2.979(3)	146(2)	x-1/2, -y+3/2, z+1/2
	N3 H3B···S1^{ii}	0.84(3)	2.67(3)	3.419(2)	150(3)	-x+1, -y+1, -z
	N5 H5A···S1^{iii}	0.82(3)	2.93(3)	3.629(2)	145(3)	-x+2, -y+1, -z
	N5 H5B···O1^{iv}	0.90(3)	2.18(3)	3.068(3)	168(3)	-x+3/2, y-1/2, -z-1/2

	N6	H6A···O1^{v}	0.82(4)	2.60(3)	3.195(3)	130(3)	X+1/2, -y+3/2, z+1/2
	N6	H6B···S1^{iii}	0.92(4)	2.56(4)	3.445(2)	161(3)	-x+2, -y+1, -z
2	N3	H3A···N2^{iii}	0.87(5)	2.39(5)	3.198(5)	156(4)	-x+1/2, -y+3/2, -z
	N3	H3B···N1^{iv}	0.82(6)	2.38(6)	3.111(5)	150(5)	-x+1, y+1, -z+1/2
	N4	H4···S1	0.86(4)	2.72(4)	3.500(3)	151(3)	
3	N3	H3A···O1	0.92(2)	2.03(2)	2.939(3)	169(3)	
	N3	H3B···N2^{v}	0.92(2)	2.41(2)	3.242(4)	151(3)	x+1/2, y+1/2, z