Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

The role of bridging group in exchange coupling in dinuclear homo- and heterometallic Ni(II) and Co(II) complexes with oxalate, oxamidate and dithiooxamidate bridges

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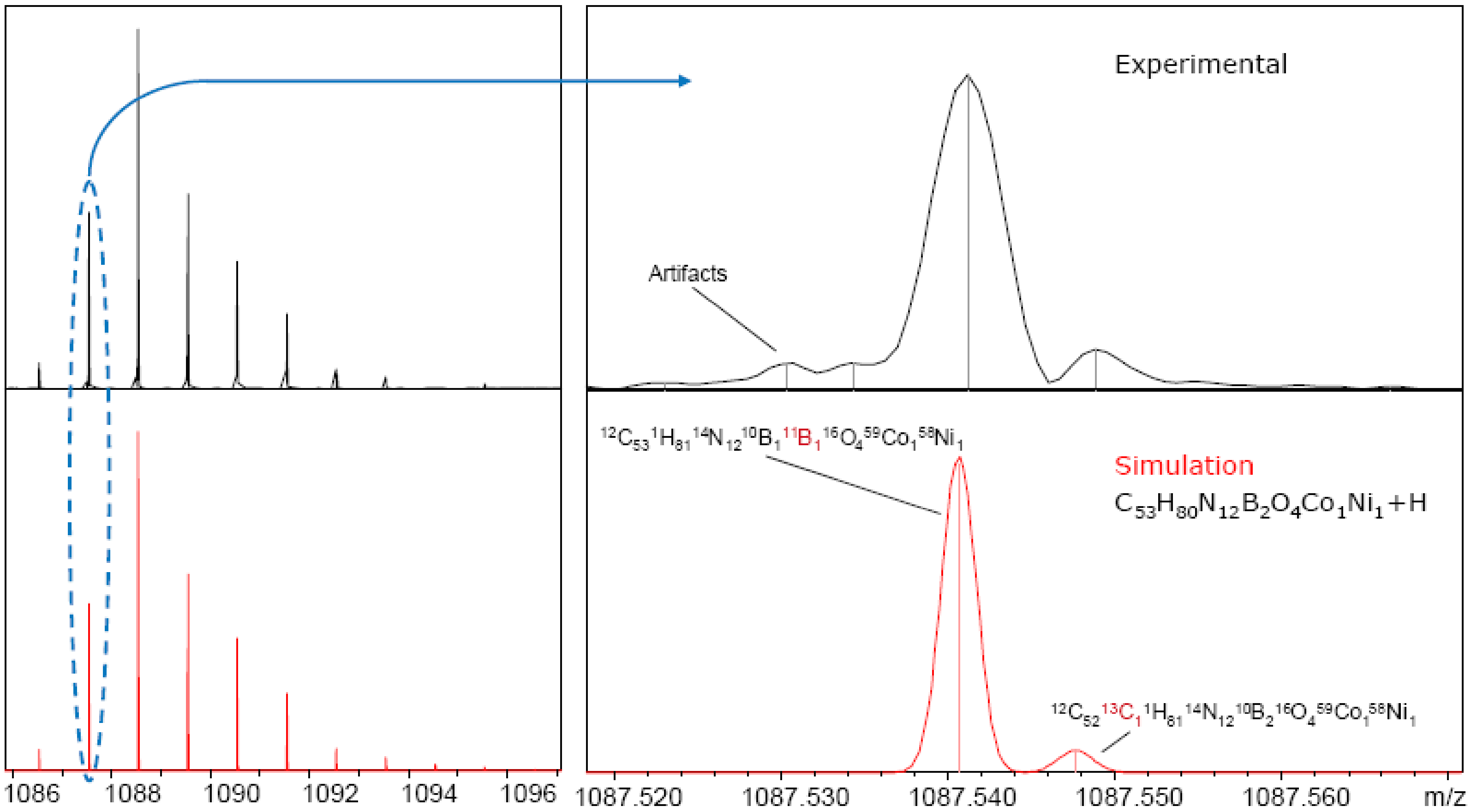

Fig S1. Experimental and calculated fine structure of the peak with m/z 1087.5 for compound **2**.

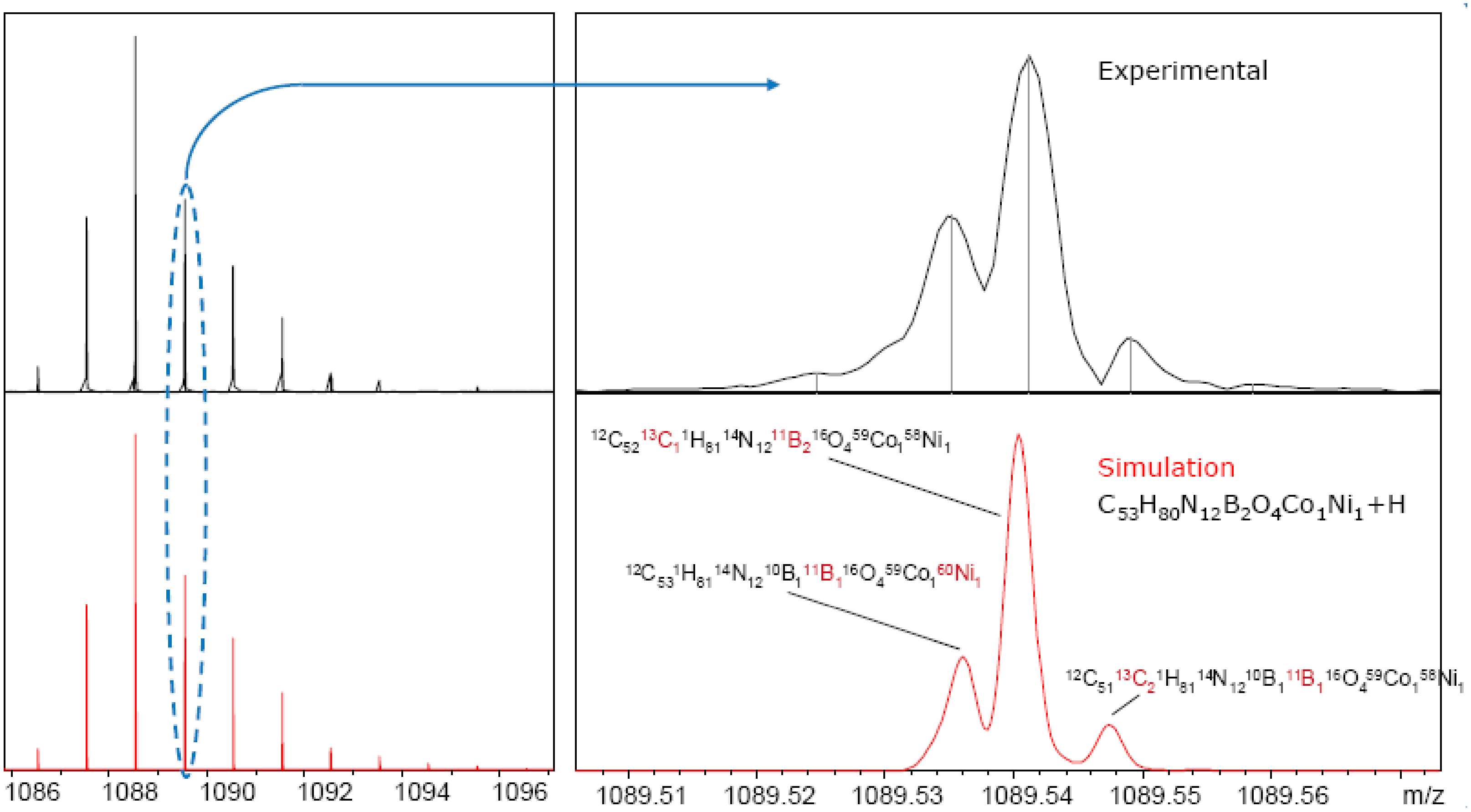

Fig S2. Experimental and calculated fine structure of the peak with m/z 1089.5 for compound **2**.

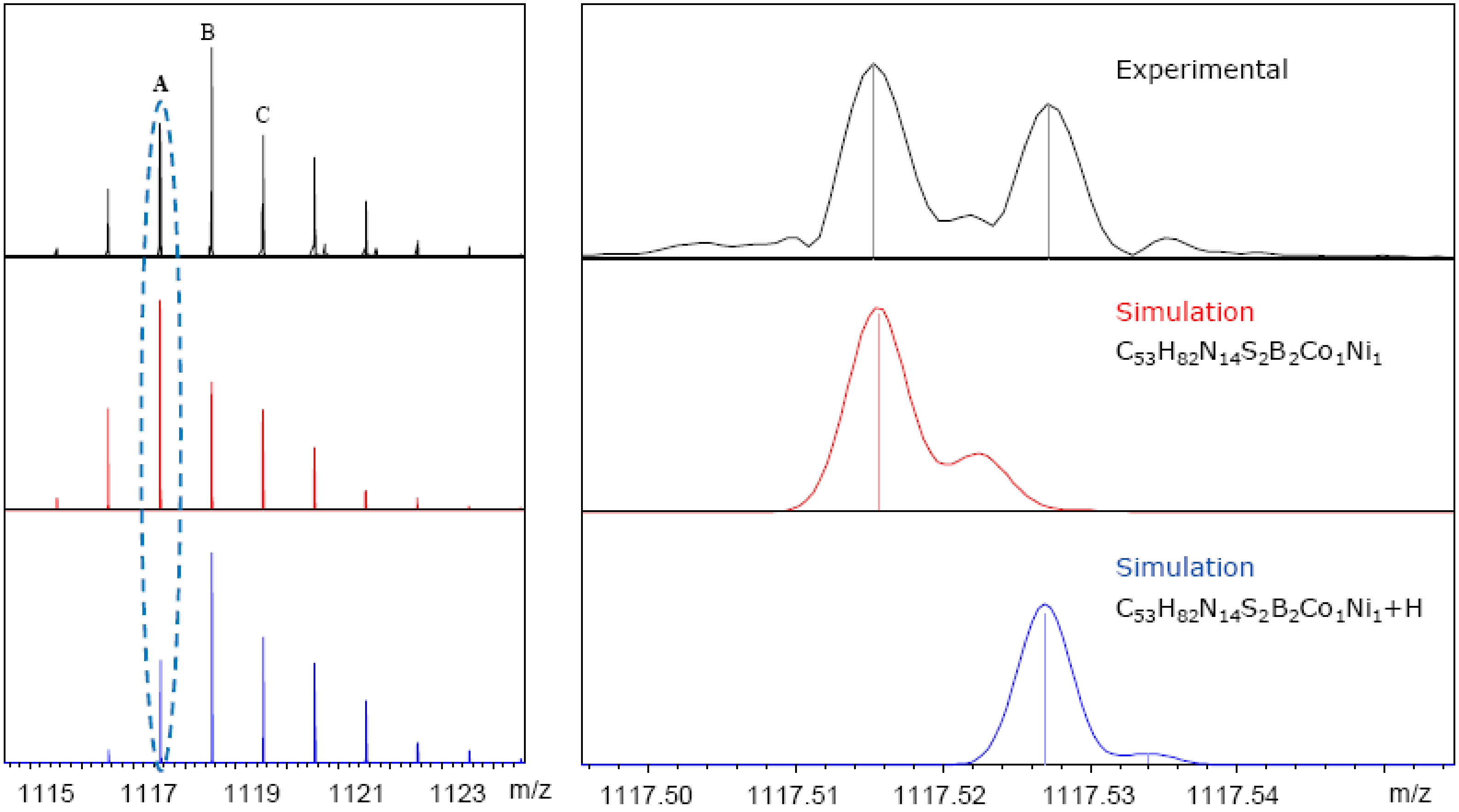

Fig S3. Experimental and calculated fine structure of the peak with m/z 1117.5 for compound **7**.

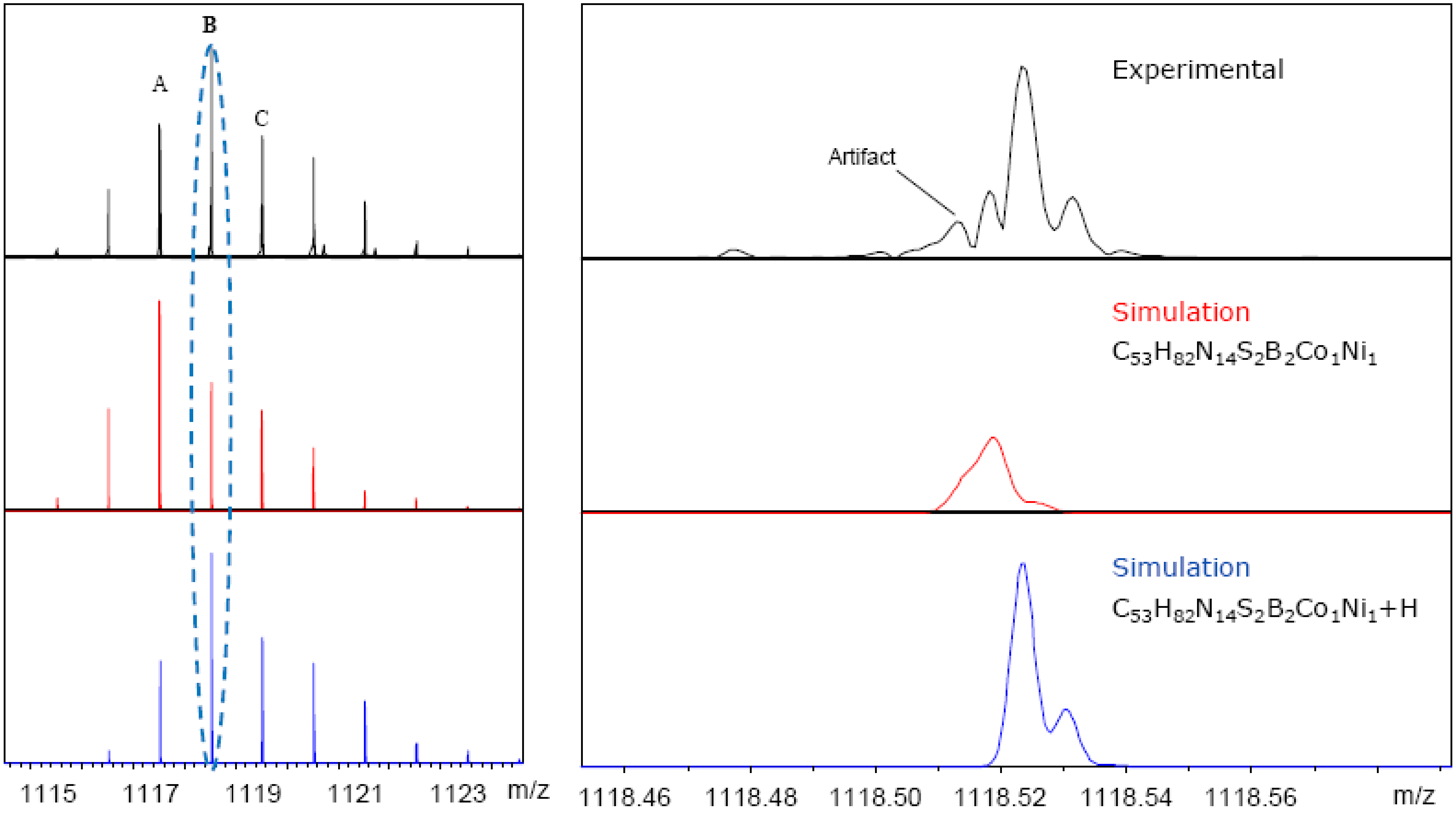

Fig S4. Experimental and calculated fine structure of the peak with m/z 1118.5 for compound **7**.

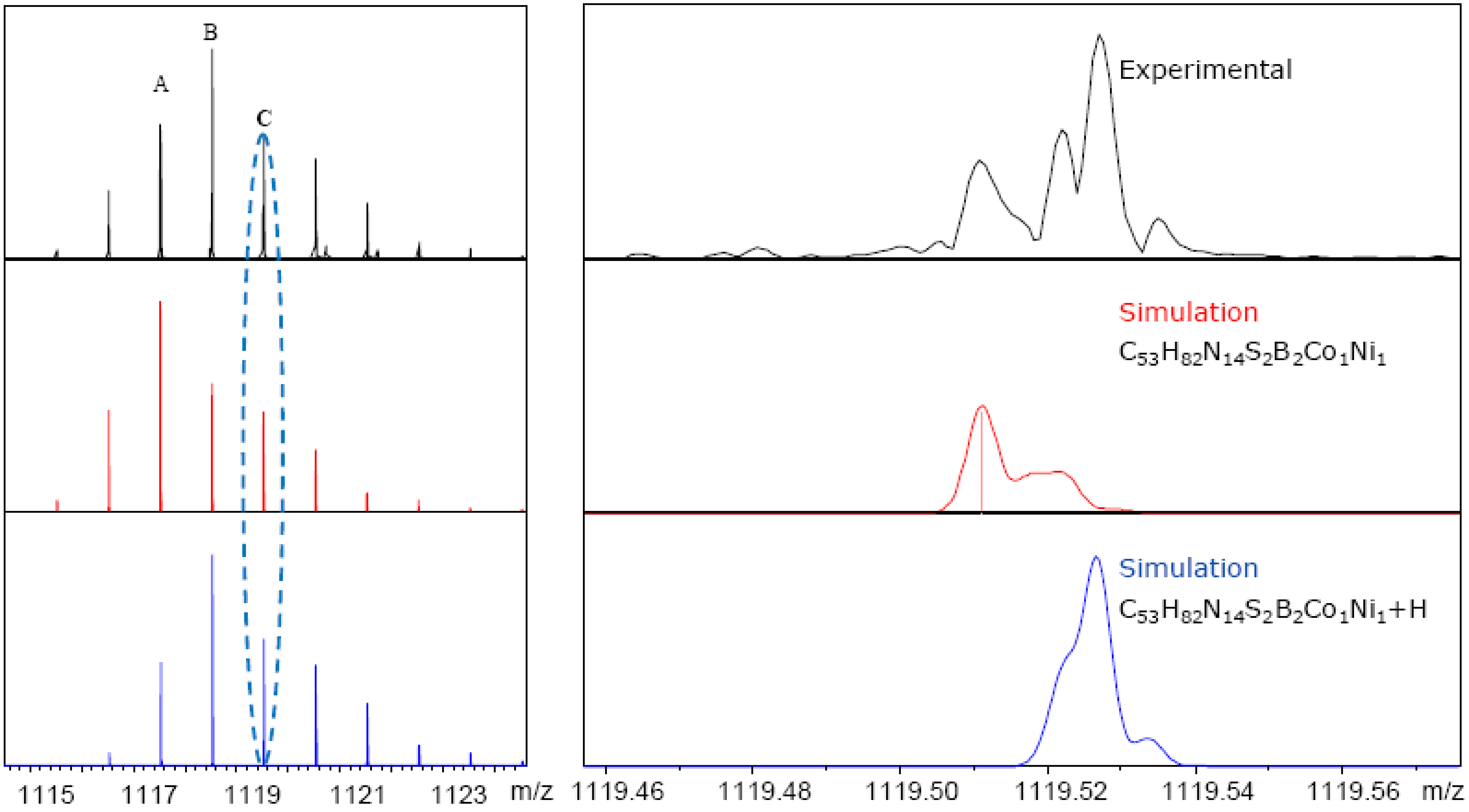

Fig S5. Experimental and calculated fine structure of the peak with m/z 1119.5 for compound **7**.

Description of disorder and pseudosymmetry

In compound **2** a solvent toluene molecule is present and disordered over two orientations with equal occupancies. The C-C bonds of the aromatic rings were constrained to be 1.39 Å and the ring to resemble an ideal hexagon. In the structure of compound **3** one of the cyclohexyl rings shows a large freedom of movement and was refined as disordered over two positions. The occupancy ratio refined to 0.72(2) to 0.28(2). The two moieties were restrained to have similar geometries and the ADPs of disordered atoms were restrained to be isotropic within standard deviations of 0.01 or 0.04 $Å^2$. In compound **4** the oxygen atom and the amide unit of the bridging ligand are disordered with each other in a one to one ratio. These O- and N-atoms in the same location were constrained to have exactly the same position and ADP. In compound **5** the coordinated acetonitrile molecule partially occupies the same space as one of its counterparts in a neighboring molecule, so this position is half occupied. The central ligand is disordered across a twofold axis. The positions of the N and O atoms were indistinguishable and each was refined to reside on the same position and with the same ADP. For compound **6** the central ligand is inversion-disordered in a ratio of 0.575(2) to 0.425(2). The disordered moieties were restrained to have similar geometries. The N- and C-atoms of the bridging ligand were restrained to be isotropic within standard deviations of 0.05 and 0.004 $Å^2$, respectively, and overlapping disordered atoms were constrained to have identical ADPs. In the case of compound **7** (*vide infra*) the central dithiooxamidate ligand is flip-disordered with an occupancy ratio of 0.835(2) to 0.165(2). The major orientation is bonded to Ni *via* the sulfur atoms and to Co *via* the nitrogen atoms. Associated with this is a disorder of a solvent acetonitrile molecule hydrogen-bonded to one of the N-H groups. The atoms of the minor components were restrained to resemble the geometry of the major component within a standard deviation of 0.02 Å, and equivalent atoms were constrained to have identical anisotropic displacement parameters. One of the *tert*-butyl groups is rotationally disordered, and was refined as statically disordered over two positions with an occupancy ratio of 0.34(2) to 0.66(2). Equivalent C-C distances were restrained to be similar for both orientations within a standard deviation of 0.02 Å, and the anisotropic displacement parameters of the methyl carbon atoms were restrained to be isotropic within a standard deviation of 0.02 $Å^2$. In compound **8** an acetonitrile molecule is partially present in a void close to the metal center. This solvating molecule is in close proximity to a symmetry-dependent counterpart of itself, and depending on the presence of either one or two of these acetonitrile molecules, their positions do vary. The sum of the occupancies was restrained so that at least one of the two acetonitrile molecules is present. The occupancies refined to 0.4027(17) for the case when only one acetonitrile is present, and 0.195(3) for the case that two neighboring ones are present. The geometries of the two molecules were restrained to be similar and the ADPs of equivalent atoms to be indentical. The dithiooxamidate is also disordered in **8** across an two fold axis, and two positions in the coordination sphere of each nickel are filled by S and N atoms with occupation factors of 0.50 for each. No restraints or constraints were applied for this disorder. Similarly to **6** and **7**, the X-ray structure shows that only S,S and N,N coordination dithiooxamidate modes are present in **8**.

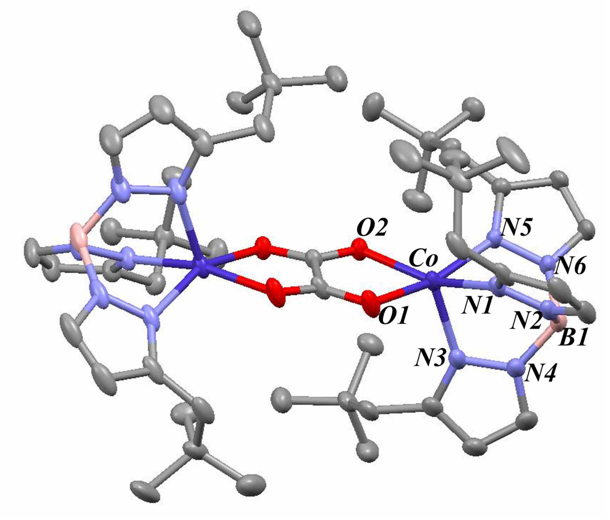

Fig. S6 Molecular structure of **1**. For clarity of presentation, H-atoms are omitted.

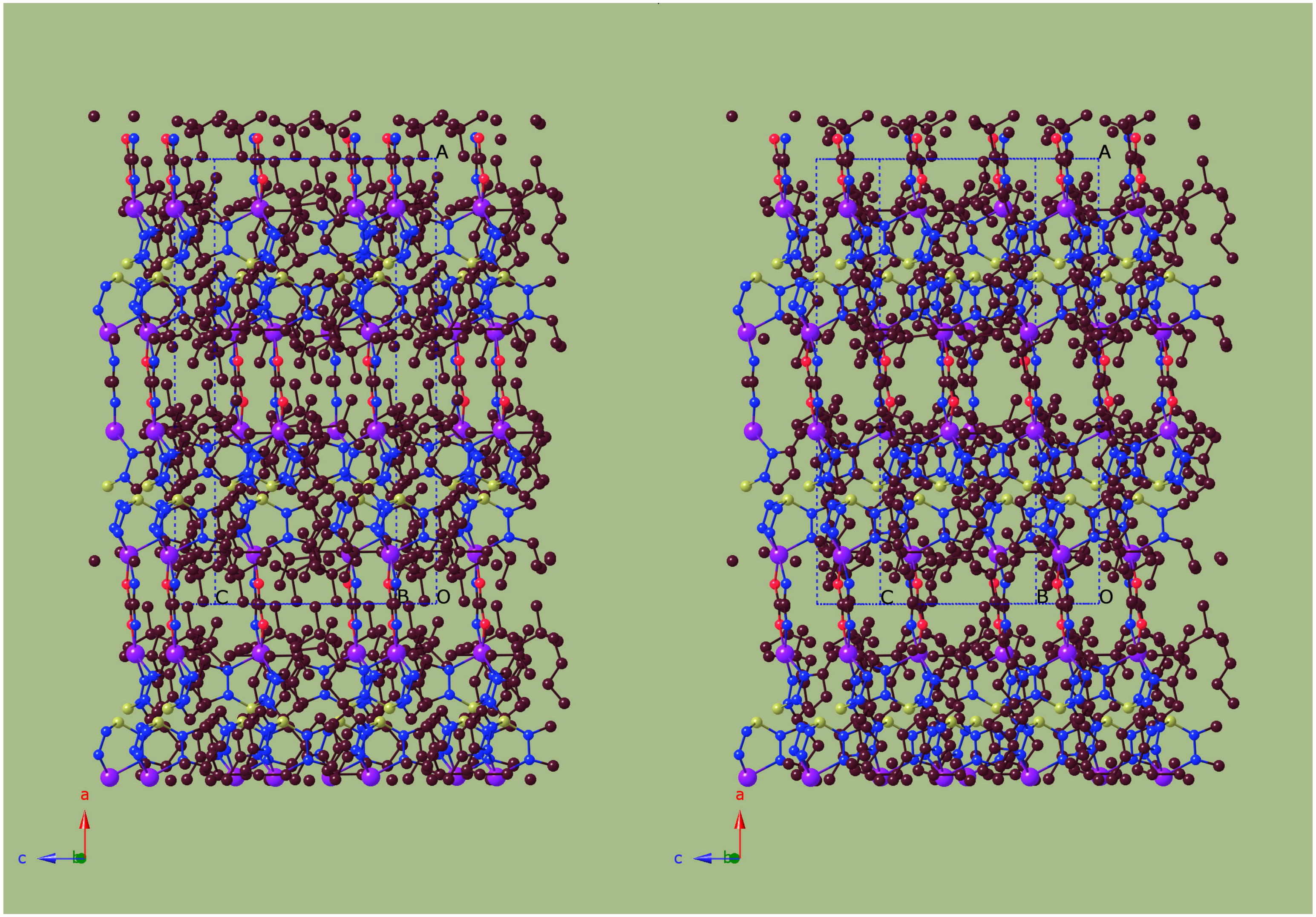

Fig. S7 Inverse stereoview of a fragment of the dicobalt μ-oxamidate lattice (**1**) along the *b*-axis, showing mutual alignment of the Co-Co vectors essentially along the *c*-direction. H-atoms omitted for clarity of presentation.

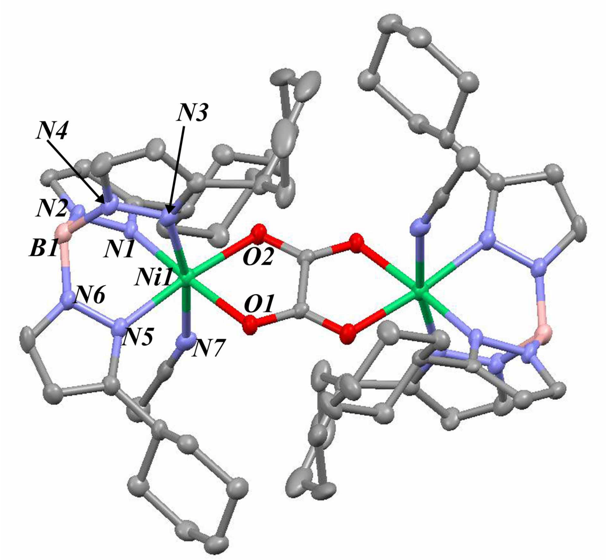

Fig. S8 Molecular structure of **3**. H-atoms omitted for clarity of presentation.

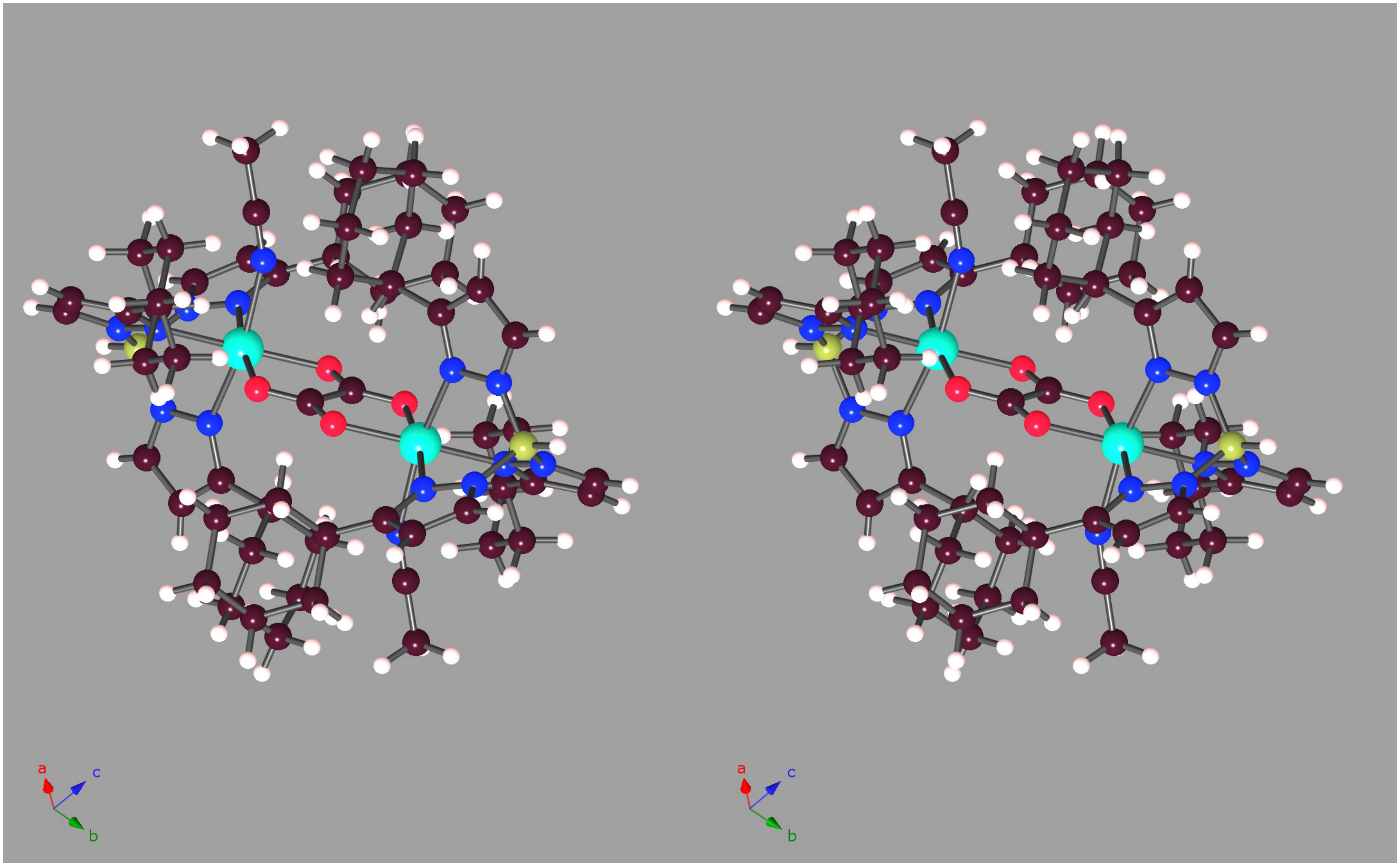

Fig. S9 Inverse stereoview of the dinickel oxalate, **3**; cyclohexyl disorder suppressed.

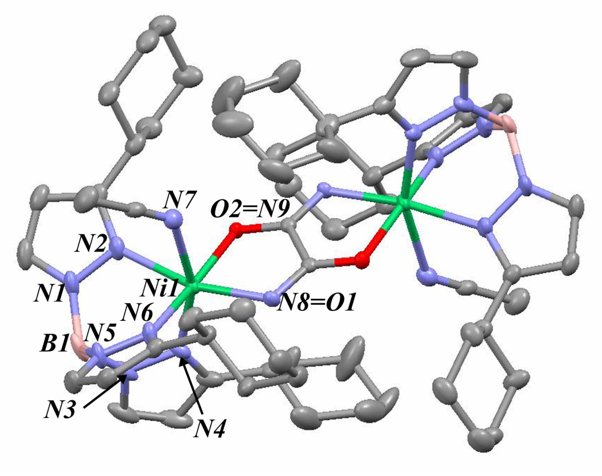

Fig. S10 Molecular structure of **5**. H-atoms omitted for clarity of presentation.

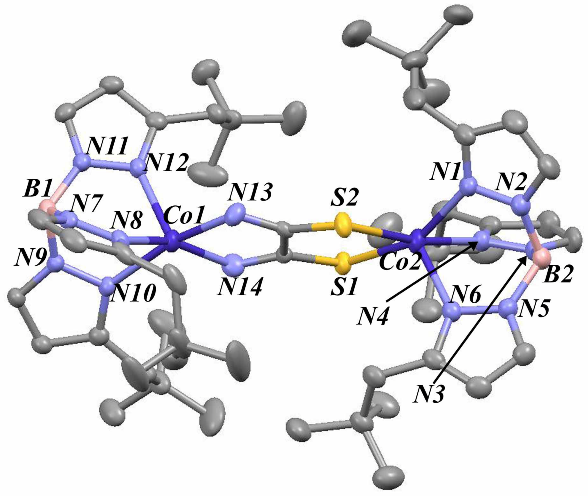

Fig. S11 Molecular structure of **6**. Disorder of dithiooxamidate is not shown. H-atoms omitted for clarity of presentation.

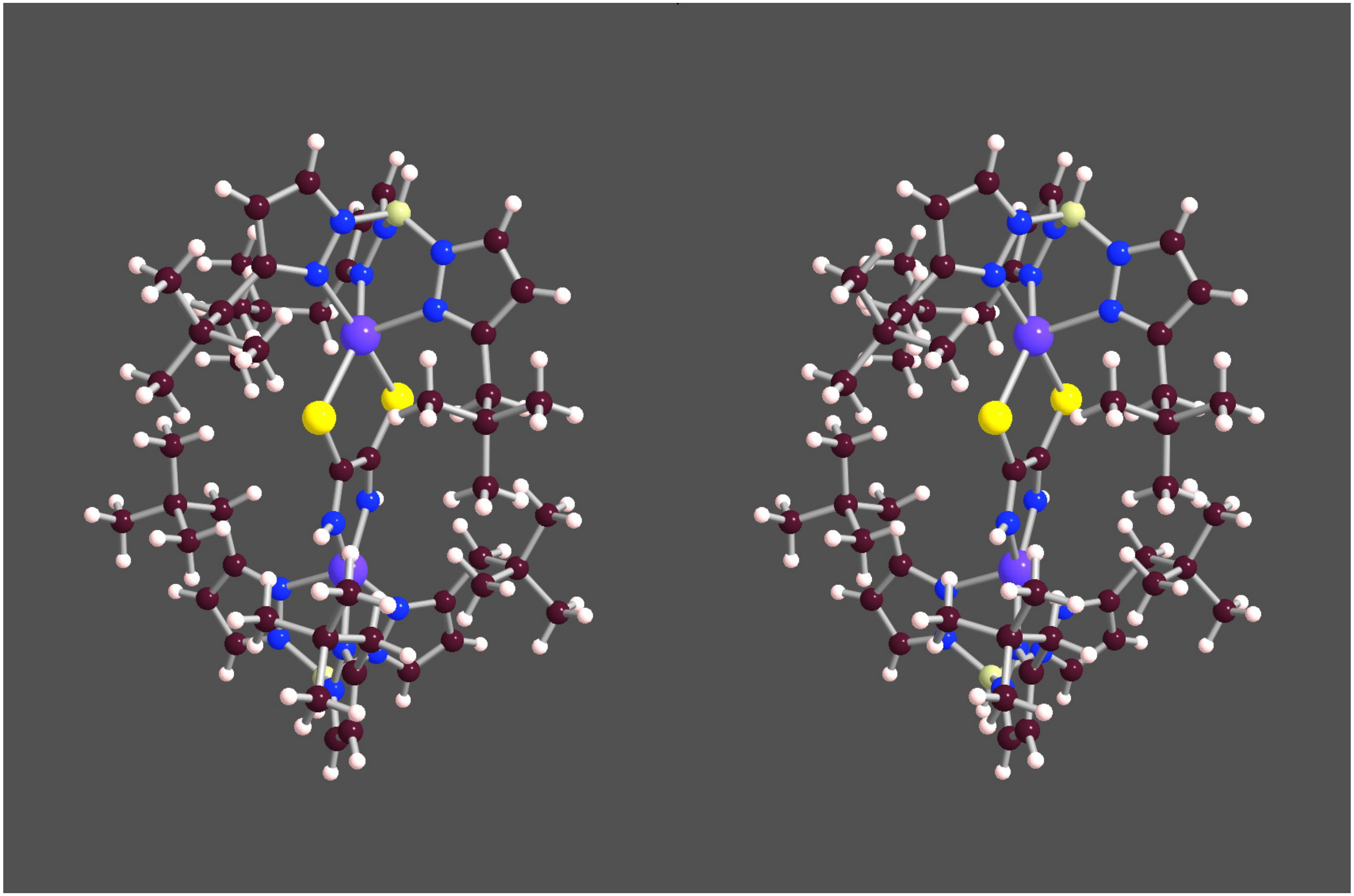

Fig. S12 Inverse stereoview of the dicobalt dithiooxamidate, **6**, N/S disorder suppressed.

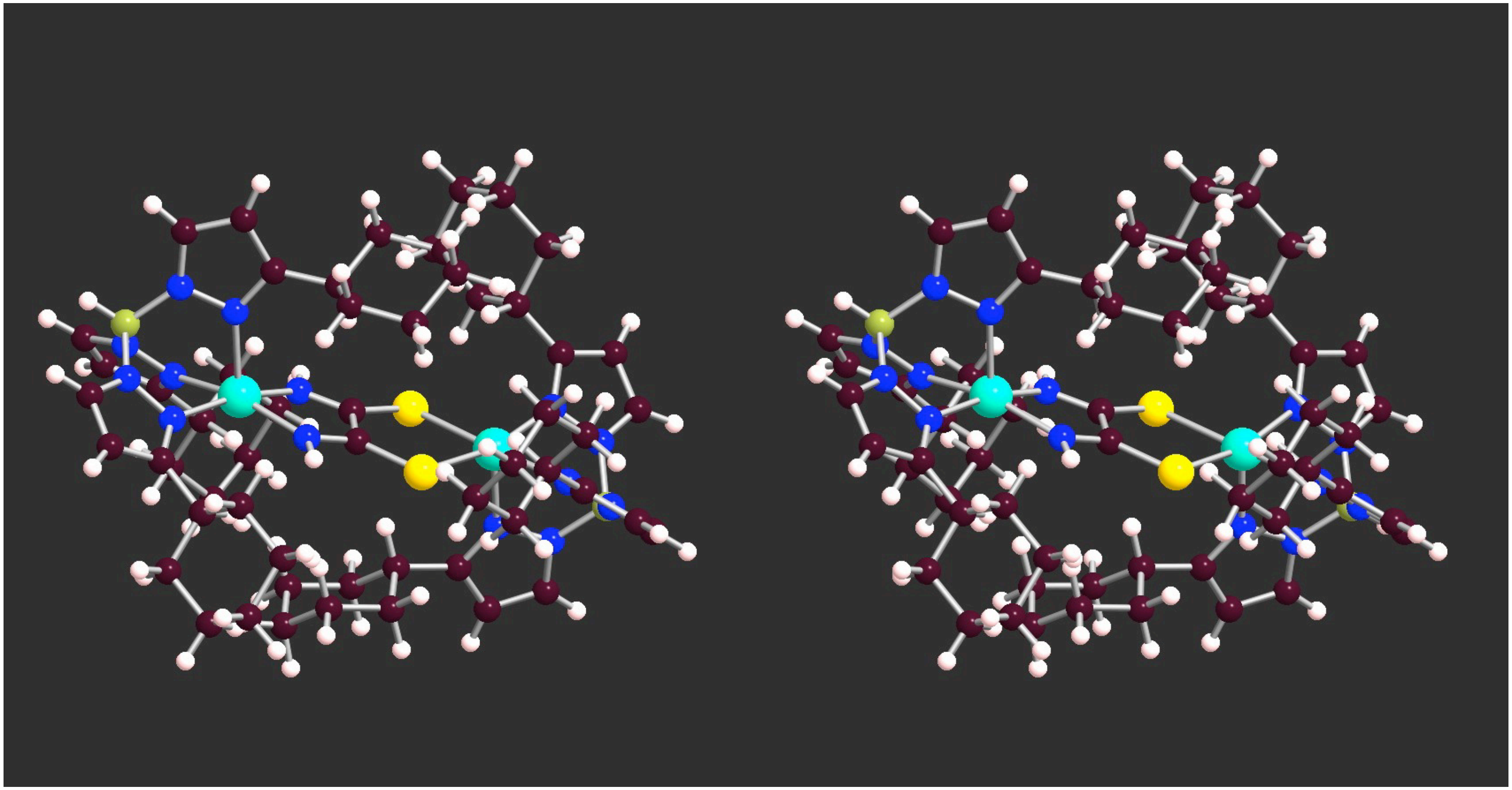

Fig. S13 Inverse stereoview of the dinickel dithiooxamidate, **8**; N/S disorder suppressed.

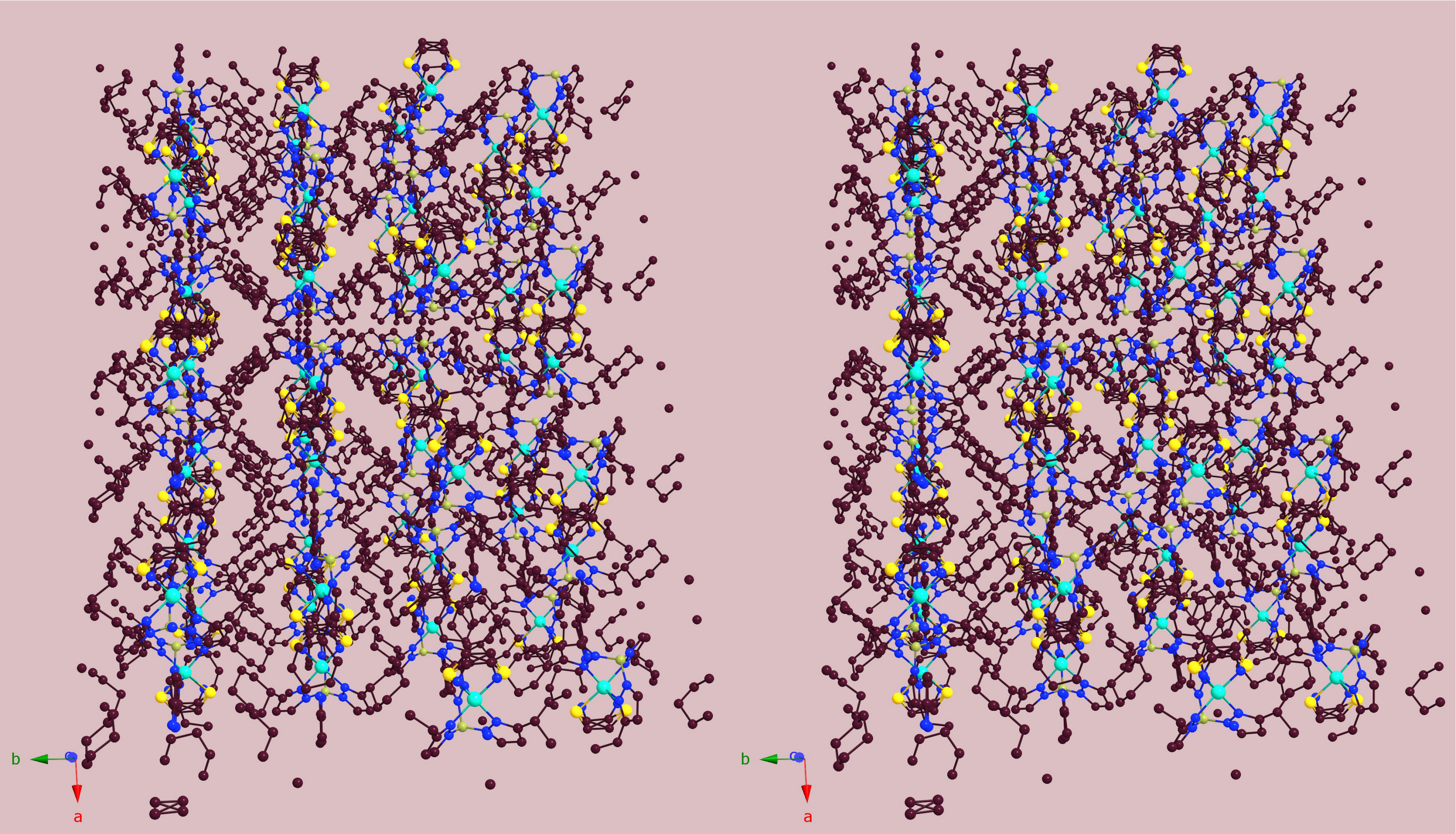

Fig. S14 Inverse stereoview of the dinickel dithiooxamidate (**8**) lattice, viewed along the *c*-axis. Hydrogen atoms are not shown, disorder not suppressed.

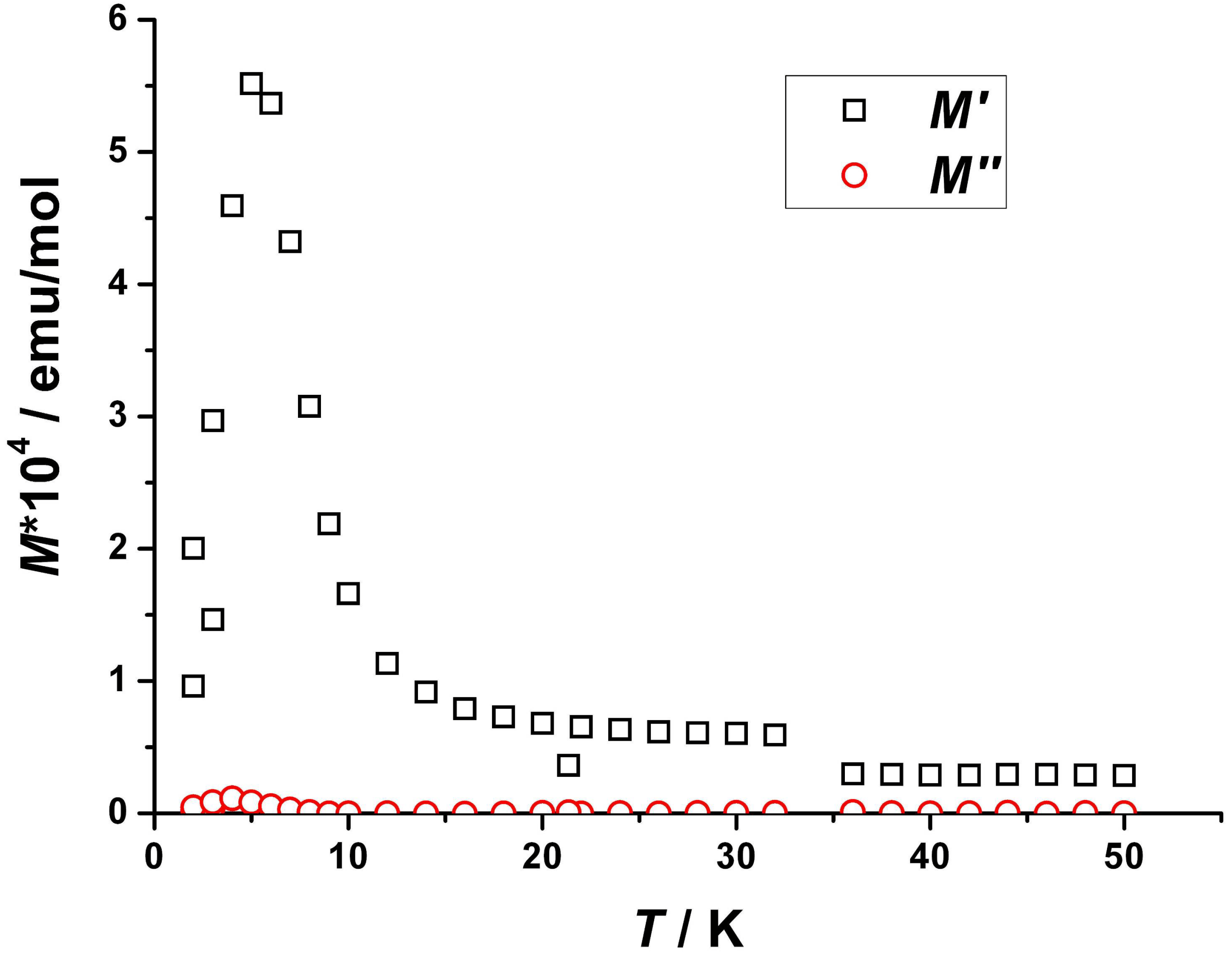

Fig. S15 In-phase (M') and out-of-phase (M'') magnetization *vs*. T plots for **2.**

Table S1 Selected bonds lengths and angles in compounds **1-8.**

Complex **1**

Selected bonds, Å

Co-O(1)	2.0682(13)	Co-N(3)	2.0694(17)
Co-O(2)	2.0836(12)	Co-N(5)	2.0948(15)
Co-N(1)	2.1096(15)	Co-Co	5.438(3)

Selected angles, º

O(1)-Co-N(3)	104.38(6)	O(1)-Co-O(2)	79.37(5)
N(3)-Co-O(2)	110.36(6)	O(1)-Co-N(5)	165.95(6)
N(3)-Co-N(5)	89.55(6)	O(2)-Co-N(5)	97.79(5)
O(1)-Co-N(1)	90.58(6)	N(3)-Co-N(1)	92.50(6)
O(2)-Co-N(1)	156.62(6)	N(5)-Co-N(1)	86.83(6)

Complex **2**

Selected bonds, Å

Ni-N(4)	2.008(4)	Ni-O(2)	2.045(3)
Ni-N(2)	2.047(4)	Ni-O(1)	2.054(3)
Ni-N(6)	2.065(4)	Co-O(3)	2.045(3)
Co-N(12)	2.045(4)	Co-O(4)	2.078(3)
Co-N(8)	2.096(4)	Co-N(10)	2.117(4)
Co-Ni	5.381(3)		

Selected angles, º

N(4)-Ni-O(2)	106.94(13)	N(4)-Ni-N(2)	89.61(14)
O(2)-Ni-N(2)	92.91(13)	N(4)-Ni-O(1)	102.32(13)
O(2)-Ni-O(1)	80.69(12)	N(2)-Ni-O(1)	167.66(13)
N(4)-Ni-N(6)	93.27(14)	O(2)-Ni-N(6)	159.48(14)
N(2)-Ni-N(6)	90.66(14)	O(1)-Ni-N(6)	91.79(13)
O(3)-Co-N(12)	115.85(14)	O(3)-Co-O(4)	79.70(12)
N(12)-Co-O(4)	105.03(15)	O(3)-Co-N(8)	152.91(14)
N(12)-Co-N(8)	91.20(15)	O(4)-Co-N(8)	92.46(13)
O(3)-Co-N(10)	93.03(13)	N(12)-Co-N(10)	90.66(16)
O(4)-Co-N(10)	164.30(15)	N(8)-Co-N(10)	87.76(14)

Complex **3**

Selected bonds, Å

Ni-N(1)	2.040(3)	Ni-N(3)	2.132(3)
Ni-N(5)	2.041(3)	Ni-N(7)	2.252(4)
Ni-O(1)	2.031(2)	Ni-O(2)	2.033(2)

Ni-Ni	5.299(3)		

Selected angles, °

O(1)-Ni-O(2)	81.47(10)	O(1)-Ni-N(1)	172.01(12)
O(2)-Ni-N(1)	92.34(11)	O(1)-Ni-N(5)	93.59(11)
O(2)-Ni-N(5)	174.30(11)	N(1)-Ni-N(5)	92.33(12)
O(1)-Ni-N(3)	97.97(11)	O(2)-Ni-N(3)	95.55(11)
N(1)-Ni-N(3)	87.59(12)	N(5)-Ni-N(3)	87.93(12)
O(1)-Ni-N(7)	91.23(11)	O(2)-Ni-N(7)	92.57(11)
N(1)-Ni-N(7)	83.98(11)	N(5)-Ni-N(7)	84.65(12)
N(3)-Ni-N(7)	168.52(12)		

Complex **4**

Selected bonds, Å

Co-N(7)	2.0558(11)	Co-N(6)	2.0739(12)
Co-O(1)	2.0886(10)	Co-N(2)	2.1094(12)
Co-N(4)	2.1293(12)	Co-Co	5.469(3)

Selected angles, °

N(7)-Co-N(6)	105.18(5)	N(7)-Co-O(1)	79.36(4)
N(6)-Co-O(1)	111.01(4)	N(7)-Co-N(2)	165.40(5)
N(6)-Co-N(2)	89.25(5)	O(1)-Co-N(2)	97.78(4)
N(7)-Co-N(4)	91.05(4)	N(6)-Co-N(4)	92.16(5)
O(1)-Co-N(4)	156.49(4)	N(2)-Co-N(4)	86.10(5)
O(4)-Co-N(10)	164.28(14)	N(8)-Co-N(10)	87.76(14)

Complex **5**

Selected bonds, Å

Ni-N(9)	2.0087(17)	Ni-N(8)	2.0383(17)
Ni-N(7)	2.408(4)	Ni-N(2)	2.082(2)
Ni-N(4)	2.0430(19)	Ni-N(6)	2.081(2)
Ni-Ni	5.382(3)		

Selected angles, °

N(9)-Ni-N(8)	80.95(7)	N(9)-Ni-N(4)	100.79(7)
N(8)-Ni-N(4)	105.35(8)	N(9)-Ni-N(6)	171.06(7)
N(8)-Ni-N(6)	95.95(7)	N(4)-Ni-N(6)	88.11(8)
N(9)-Ni-N(2)	89.83(7)	N(8)-Ni-N(2)	163.50(8)
N(4)-Ni-N(2)	89.75(8)	N(6)-Ni-N(2)	91.09(8)
N(9)-Ni-N(7)	95.29(11)	N(8)-Ni-N(7)	90.02(11)
N(4)-Ni-N(7)	159.23(11)	N(6)-Ni-N(7)	76.26(12)

N(2)-Ni-N(7)	77.16(11)

Complex **6**

Selected bonds, Å

Co(1)-N(14)	1.883(5)	Co(2)-N(13B)	1.869(6)
Co(1)-N(13)	1.956(5)	Co(2)-N(14B)	1.875(6)
Co(1)-N(12)	2.068(2)	Co(2)-N(6)	2.077(2)
Co(1)-N(8)	2.0838(19)	Co(2)-N(1)	2.091(2)
Co(1)-N(10)	2.114(2)	Co(2)-N(4)	2.115(2)
Co(1)-S(2B)	2.4661(18)	Co(2)-S(1)	2.4367(14)
Co(1)-S(1B)	2.484(2)	Co(2)-S(2)	2.4439(14)
Co(1)-Co(2)	5.874(3)		

Selected angles, º

N(14)-Co(1)-N(13)	78.5(2)	N(13B)-Co(2)-N(14B)	79.4(3)
N(14)-Co(1)-N(12)	111.75(17)	N(13B)-Co(2)-N(6)	106.6(2)
N(13)-Co(1)-N(12)	103.12(18)	N(14B)-Co(2)-N(6)	111.8(2)
N(14)-Co(1)-N(8)	154.44(17)	N(13B)-Co(2)-N(1)	90.35(19)
N(13)-Co(1)-N(8)	90.88(17)	N(14B)-Co(2)-N(1)	154.5(2)
N(12)-Co(1)-N(8)	93.21(8)	N(6)-Co(2)-N(1)	93.40(8)
N(14)-Co(1)-N(10)	99.78(16)	N(13B)-Co(2)-N(4)	163.4(2)
N(13)-Co(1)-N(10)	167.38(18)	N(14B)-Co(2)-N(4)	98.8(2)
N(12)-Co(1)-N(10)	89.17(8)	N(6)-Co(2)-N(4)	89.43(8)
N(8)-Co(1)-N(10)	85.49(7)	N(1)-Co(2)-N(4)	84.44(8)
N(14)-Co(1)-S(2B)	81.89(16)	N(13B)-Co(2)-S(1)	82.18(19)
N(13)-Co(1)-S(2B)	5.89(19)	N(14B)-Co(2)-S(1)	3.4(2)
N(12)-Co(1)-S(2B)	97.41(8)	N(6)-Co(2)-S(1)	112.95(7)
N(8)-Co(1)-S(2B)	89.76(7)	N(1)-Co(2)-S(1)	153.65(7)
N(10)-Co(1)-S(2B)	172.10(7)	N(4)-Co(2)-S(1)	95.57(6)
N(14)-Co(1)-S(1B)	4.07(18)	N(13B)-Co(2)-S(2)	9.0(2)
N(13)-Co(1)-S(1B)	82.18(16)	N(14B)-Co(2)-S(2)	83.7(2)
N(12)-Co(1)-S(1B)	112.85(7)	N(6)-Co(2)-S(2)	97.72(6)
N(8)-Co(1)-S(1B)	153.91(8)	N(1)-Co(2)-S(2)	89.57(6)

Complex **7**

Selected bonds, Å

Co(1)-N(8)	2.020(5)	Co(1)-N(7)	2.051(5)
Co(1)-N(11)	2.066(3)	Co(1)-N(13)	2.125(3)
Co(1)-N(9)	2.163(3)	Co(1)-S(1B)	2.381(7)

Co(1)-S(2B)	2.549(6)	Ni(1)-N(1)	2.089(3)
Ni(1)-N(3)	2.058(4)	Ni(1)-N(5)	2.133(3)
Ni(1)-S(1)	2.3443(14)	Ni(1)-S(2)	2.3899(14)
Ni(1)-N(8B)	2.039(7)	Ni(1)-N(7B)	1.794(19)
Co(1)-Ni(1)	5.946(3)		

Selected angles, º

N(8)-Co(1)-N(7)	75.3(2)	N(8)-Co(1)-N(11)	103.13(16)
N(7)-Co(1)-N(11)	109.53(17)	N(8)-Co(1)-N(13)	167.49(16)
N(7)-Co(1)-N(13)	101.48(17)	N(11)-Co(1)-N(13)	89.36(13)
N(8)-Co(1)-N(9)	93.68(15)	N(7)-Co(1)-N(9)	156.47(17)
N(11)-Co(1)-N(9)	93.07(13)	N(13)-Co(1)-N(9)	84.72(12)
N(11)-Co(1)-S(1B)	111.18(17)	N(13)-Co(1)-S(1B)	96.69(18)
N(9)-Co(1)-S(1B)	155.69(16)	N(7)-Co(1)-S(2B)	81.4(2)
N(11)-Co(1)-S(2B)	95.62(16)	N(13)-Co(1)-S(2B)	173.07(16)
S(1B)-Co(1)-S(2B)	86.03(19)	N(8)-Co(1)-S(1B)	79.73
N(9)-Co(1)-S(2B)	90.19	N(7B)-Ni(1)-N(8B)	80.0(6)
N(7B)-Ni(1)-N(3)	107.0(8)	N(8B)-Ni(1)-N(3)	104.8(2)
N(7B)-Ni(1)-N(1)	159.9(8)	N(8B)-Ni(1)-N(1)	93.0(2)
N(3)-Ni(1)-N(1)	92.93(14)	N(7B)-Ni(1)-N(5)	96.1(5)
N(8B)-Ni(1)-N(5)	164.9(2)	N(3)-Ni(1)-N(5)	90.26(14)
N(1)-Ni(1)-N(5)	85.78(14)	N(3)-Ni(1)-S(1)	102.07(10)
N(1)-Ni(1)-S(1)	164.65(10)	N(5)-Ni(1)-S(1)	90.86(11)
N(3)-Ni(1)-S(2)	101.20(10)	N(1)-Ni(1)-S(2)	92.55(10)
N(5)-Ni(1)-S(2)	168.49(11)	S(1)-Ni(1)-S(2)	87.77(5)
S(1)-Ni(1)-N(8B)	86.38	N(7B)-Ni(1)-S(2)	81.65

Complex **8**

Selected bonds, Å

Ni-N(2)	2.0897(17)	Ni-N(4)	2.1106(16)
Ni-N(6)	2.0592(17)	Ni-N(8)	1.908(5)
Ni-N(7)	1.979(6)	Ni-S(1)	2.4296(17)
Ni-S(2)	2.4409(14)	Ni-S(1)	2.4298(17)
Ni-S(2)	2.4407(14)	Ni-Ni	5.932(3)

Selected angles, º

N(8)-Ni-N(7)	77.7(2)	N(8)-Ni-N(6)	104.00(15)
N(7)-Ni-N(6)	108.1(2)	N(8)-Ni-N(2)	91.26(14)
N(7)-Ni-N(2)	159.7(2)	N(6)-Ni-N(2)	90.99(7)

N(8)-Ni-N(4)	168.86(15)	N(7)-Ni-N(4)	98.7(2)
N(6)-Ni-N(4)	87.13(6)	N(2)-Ni-N(4)	88.90(6)
N(8)-Ni-S(1)	82.33(14)	N(7)-Ni-S(1)	6.4(2)
N(6)-Ni-S(1)	102.90(7)	N(2)-Ni-S(1)	165.74(7)
N(4)-Ni-S(1)	94.95(7)	N(8)-Ni-S(2)	10.38(14)
N(7)-Ni-S(2)	82.3(2)	N(6)-Ni-S(2)	93.77(5)
N(2)-Ni-S(2)	89.69(5)	N(4)-Ni-S(2)	178.35(6)
S(1)-Ni-S(2)	86.21(6)		

Electronic Spectra:

The band positions for the nickel(II) complexes **3, 5** and **8** (NiN_4O_2 & NiN_4O or NiN_5O & NiN_4S_2, NiN_6, NiN_5 or NiN_3S_2 chromophores, respectively) are quite close, indicating a perhaps unexpected similarity in separations of electronic levels in nickel(II) chromophores with oxalate and dithiooxamidate. In contrast to the other spectra however, there are intense bands in the case of dithiooxamidate complexes **6 – 8**, with intensity building from near 625 nm and maxima around 333 nm (for **6** and **7**), and 346 nm (**8**). The high energies and intensities (Table 3) of these bands suggest their assignment as LMCTs.[18] They likely obscure the weaker d-d transitions of the CoN_5 or CoN_3S_2 chromophore. The presence of CT bands in the spectra of the dithiooxamidate complexes (**6**, **8**) *vs*. their absence in the spectra of the oxalates and oxamidates (**1 - 5**) is consistent with the lower optical electronegativity of the S-donors.

The spectrum of the heterodinuclear complex **2** is close to a superposition of the spectra of the corresponding homodinuclear analogues **1** and **3** (Table 3), the intensities being about half the values in the latter, which indicates the structural correspondences of the individual metals' chromophores.

18. A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, New York, 1984.

Table S2 Electronic spectra of the complexes in toluene solution or the solid state

Complex	**Chromophore**	**Wavelength, nm (ε, dm^{3}mol^{-1}cm^{-1})**	**Assignment**
1	CoN_3O_2	654 (sh, 15)	$^4E_g \rightarrow {}^4B_{1g}$
		564 (95)	$^4E_g \rightarrow {}^4T_{1g}(P)$
		538 (55)	$^4E_g \rightarrow {}^4T_{1g}(P)$
		473 (45)	$^4E_g \rightarrow {}^4T_{1g}(P)$
2	CoN_3O_2	563 (40)	$^4E_g \rightarrow {}^4T_{1g}(P)$
		535 (sh, 25)	$^4E_g \rightarrow {}^4T_{1g}(P)$
	NiN_3O_2	862 (20)	$^3B_1 \rightarrow {}^3B_2$ or $^3A_2$
		676 (30)	$^3B_1 \rightarrow {}^3E$
		412 (165)	$^3B_1 \rightarrow {}^3A_2$ or $^3E(P)$
3	NiN_4O_2	870 (45)	$^3B_1 \rightarrow {}^3B_2$ or $^3A_2$
		678 (50)	$^3B_1 \rightarrow {}^3E$
		411 (300)	$^3B_1 \rightarrow {}^3A_2$ or $^3E(P)$
4[b]	CoN_4O	660	$^4E_g \rightarrow {}^4B_{1g}$
		560	$^4E_g \rightarrow {}^4T_{1g}(P)$
		520	$^4E_g \rightarrow {}^4T_{1g}(P)$
		455	$^4E_g \rightarrow {}^4T_{1g}(P)$
5[b]	NiN_5O and NiN_4O	876	$^3B_1 \rightarrow {}^3B_2$ or $^3A_2$
		641	$^3B_1 \rightarrow {}^3E$
		400	$^3B_1 \rightarrow {}^3A_2$ or $^3E(P)$
6	CoN_3S_2 and CoN_5	510 (sh, 300)	CT
7	NiN_3S_2 and NiN_5[a]	645 (115)	$^3B_1 \rightarrow {}^3E$
8	NiN_4S_2, NiN_6, NiN_5 and NiN_3S_2	893 (50)	$^3B_1 \rightarrow {}^3B_2$ or $^3A_2$
		625 (130)	$^3B_1 \rightarrow {}^3E$
		417 ($2.3 \cdot 10^3$)	CT
		346 ($7.3 \cdot 10^3$)	CT

[a] no bands assignable to Co-containing chromophores were apparent; [b] electronic spectra for solid samples.