Electronic Supplementary Information (ESI) for

Crystal Structure, Magnetic Properties and Theoretical Study of a Bithiazolebis(oxamate)-containing [Ni^{II}_3] Helicate

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Infrared Spectra

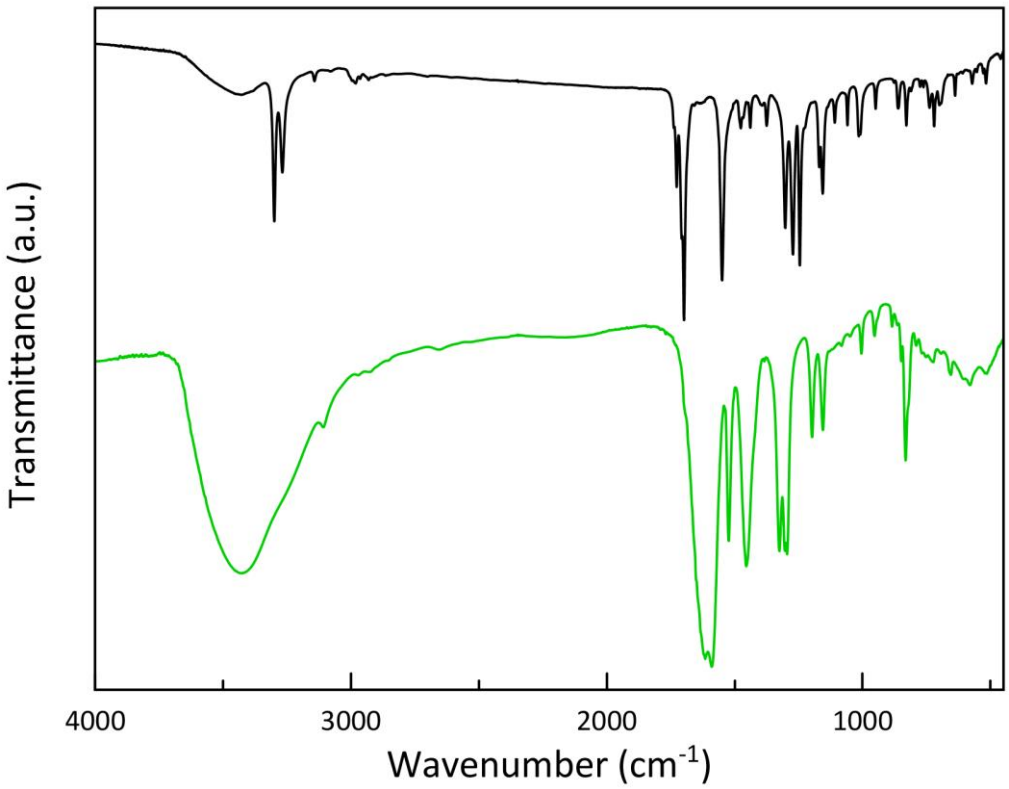

Figure S1. FT-IR spectra of **1** (green), and H_2Et_2dabtzox proligand (black).

Thermogravimetric Analysis

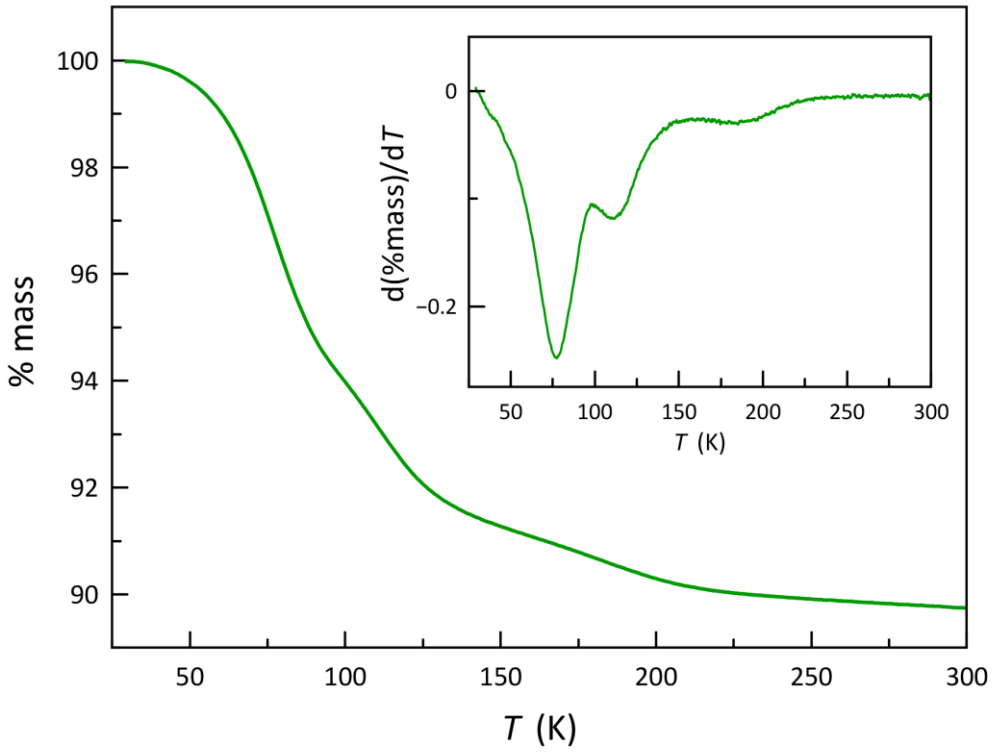

Figure S2. TGA profile of **1** (green) under N_2 atmosphere. The inset shows the first derivative of the TGA curve.

Powder X-Ray diffractograms

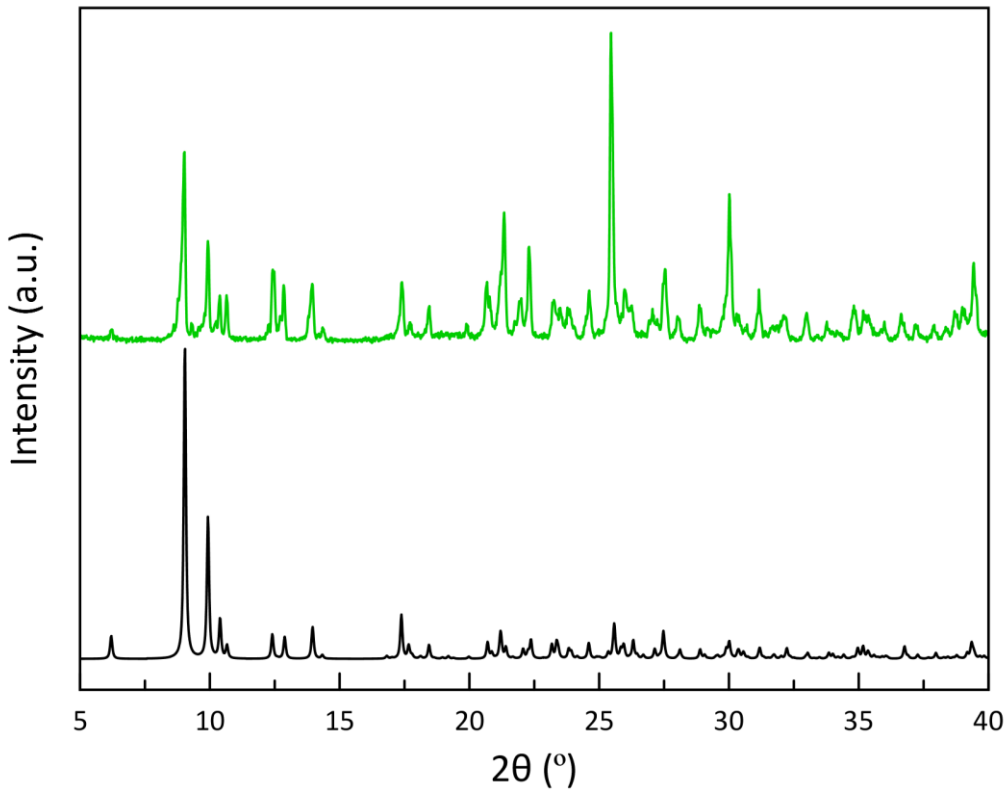

Figure S3. Experimental (green) powder X-ray diffractogram pattern and the calculated one (black) for **1**.

Crystallographic Data and Analysis

Table S1. Selected bond lengths (A) for **1*.**

Ni1—N1	2.053 (4)	Na1—O2v	2.382 (4)
Ni1—N4^{i}	2.041 (4)	Na1—O2^{vi}	2.551 (5)
Ni1—N5	2.099 (4)	Na1—O8	2.329 (6)
Ni1—O1	2.082 (4)	Na1—O9	2.455 (5)
Ni1—O5^{i}	2.070 (4)	Na1—O3W	2.381 (6)
Ni1—O7	2.069 (4)	Na2—O4^{i}	2.541 (5)
Ni2—N2	2.112 (4)	Na2—O5^{i}	2.494 (5)
Ni2—N2^{i}	2.112 (4)	Na2—O7^{vi}	2.428 (5)
Ni2—N3	2.118 (4)	Na2—O8^{vi}	2.939 (6)
Ni2—N3^{i}	2.118 (4)	Na2—O1W	2.400 (6)
Ni2—N6	2.141 (4)	Na2—O2W	2.328 (7)
Ni2—N6^{i}	2.141 (4)	Na2—O3W	2.607 (6)
Ni1i—N1^{i}	2.053 (4)	Na3—O2^{ii}	2.422 (5)
Ni1i—N4	2.041 (4)	Na3—O3^{ii}	2.456 (4)
Ni1i—N5^{i}	2.099 (4)	Na3—O4	2.343 (5)
Ni1i—O1^{i}	2.082 (4)	Na3—O6	2.455 (5)
Ni1i—O5	2.070 (4)	Na3—O4W	2.324 (8)
Ni1i—O7^{i}	2.069 (4)	Na3—O5W	2.473 (6)

*Symmetry code: (i) = 1-*x*, *y*, ½-*z*; (ii) = 1-*x*, *y*-1, ½-*z*; (v) = *x*, 1-*y*, ½+*z*; (vi) = ½-*x*, *y*-½, ½-*z*.

Table S2. Selected bond angles (deg) for **1**

N1—Ni1—N4^{i}	101.9 (2)	O2^{v}—Na1—O8	126.9 (2)
N1—Ni1—N5	102.1 (2)	O2^{v}—Na1—O9	106.4 (2)
N1—Ni1—O1	78.7 (2)	O2^{v}—Na1—O3W	128.8 (2)
N1—Ni1—O5^{i}	169.3 (2)	O2^{vi}—Na1—O8	102.7 (2)
N1—Ni1—O7	90.9 (2)	O2^{vi}—Na1—O9	165.5 (2)
N4^{i}—Ni1—N5	96.5 (2)	O2^{vi}—Na1—O3W	91.2 (2)
N4^{i}—Ni1—O1	90.8 (2)	O8—Na1—O9	69.0 (2)
N4^{i}—Ni1—O5^{i}	80.1 (2)	O8—Na1—O3W	103.2 (2)
N4^{i}—Ni1—O7	167.1 (2)	O9—Na1—O3W	79.7 (2)
N5—Ni1—O1	172.3 (2)	O4^{i}—Na2—O5^{i}	52.14 (13)
N5—Ni1—O5^{i}	88.0 (2)	O4^{i}—Na2—O7^{vi}	114.9 (2)
N5—Ni1—O7	79.2 (2)	O4^{i}—Na2—O8^{vi}	71.08 (14)
O1—Ni1—O5^{i}	90.8 (2)	O4^{i}—Na2—O1W	144.7 (2)
O1—Ni1—O7	93.1 (2)	O4^{i}—Na2—O2W	85.4 (2)
O5^{i}—Ni1—O7	87.5 (2)	O4^{i}—Na2—O3W	92.7 (2)
N2—Ni2—N3	78.62 (16)	O5^{i}—Na2—O7^{vi}	162.8 (2)
N2—Ni2—N6	92.90 (17)	O5^{i}—Na2—O8^{vi}	122.9 (2)
N2—Ni2—N2^{i}	95.2 (2)	O5^{i}—Na2—O1W	92.6 (2)
N2—Ni2—N3^{i}	96.25 (16)	O5^{i}—Na2—O2W	90.9 (2)
N2—Ni2—N6^{i}	168.80 (16)	O5^{i}—Na2—O3W	92.5 (2)
N3—Ni2—N6	92.94 (17)	O7^{vi}—Na2—O8^{vi}	47.84 (14)
N3—Ni2—N2^{i}	96.25 (16)	O7^{vi}—Na2—O1W	99.9 (2)

N3—Ni2—N3^{i}	172.5 (2)	O7^{vi}—Na2—O2W	99.6 (2)
N3—Ni2—N6^{i}	92.81 (17)	O7^{vi}—Na2—O3W	75.9 (2)
N6—Ni2—N2^{i}	168.81 (16)	O8^{vi}—Na2—O1W	143.6 (2)
N6—Ni2—N3^{i}	92.81 (17)	O8^{vi}—Na2—O2W	77.8 (2)
N6—Ni2—N6^{i}	80.3 (2)	O8^{vi}—Na2—O3W	96.0 (2)
N2i—Ni2—N3^{i}	78.62 (16)	O1W—Na2—O2W	95.2 (2)
N2^{i}—Ni2—N6^{i}	92.90 (17)	O1W—Na2—O3W	89.7 (2)
N3^{i}—Ni2—N6^{i}	92.95 (17)	O2W—Na2—O3W	173.9 (2)
N1^{i}—Ni1^{i}—N4	101.9 (2)	O2^{ii}—Na3—O3^{ii}	69.11 (14)
N1^{i}—Ni1^{i}—N5	102.1 (2)	O2^{ii}—Na3—O4	117.9 (2)
N1^{i}—Ni1^{i}—O1^{i}	78.7 (2)	O2^{ii}—Na3—O6	172.0 (2)
N1^{i}—Ni1^{i}—O5	169.3 (2)	O2^{ii}—Na3—O4W	89.3 (3)
N1^{i}—Ni1^{i}—O7^{i}	90.9 (2)	O2^{ii}—Na3—O5W	84.6 (2)
N4—Ni1^{i}—N5^{i}	96.5 (2)	O3^{ii}—Na3—O4	90.5 (2)
N4—Ni1^{i}—O1^{i}	90.8 (2)	O3^{ii}—Na3—O6	112.0 (2)
N4—Ni1^{i}—O5	80.1 (2)	O3^{ii}—Na3—O4W	95.9 (3)
N4—Ni1^{i}—O7^{i}	167.1 (2)	O3^{ii}—Na3—O5W	141.4 (2)
N5^{i}—Ni1^{i}—O1^{i}	172.3 (2)	O4—Na3—O6	70.1 (2)
N5^{i}—Ni1^{i}—O5	88.0 (2)	O4—Na3—O4W	152.4 (3)
N5^{i}—Ni1^{i}—O7^{i}	79.2 (2)	O4—Na3—O5W	77.0 (2)
O1^{i}—Ni1^{i}—O5	90.8 (2)	O6—Na3—O4W	82.7 (3)
O1^{i}—Ni1^{i}—O7^{i}	93.1 (2)	O6—Na3—O5W	98.0 (2)
O5—Ni1^{i}—O7^{i}	87.5 (2)	O4W—Na3—O5W	112.1 (3)

$O2^{v}$—Na1—$O2^{vi}$	88.0 (2)

*Symmetry code: (i) = 1-*x*, *y*, ½-*z*; (ii) = 1-*x*, *y*-1, ½-*z*; (v) = *x*, 1-*y*, ½+*z*; (vi) = ½-*x*, *y*-½, ½-*z*.

Table S3. Metrics for the hydrogen bonds in **1** (D and A state for donor and acceptor atoms, respectively).

D-A groups/molecule	**1**				
water-oxamate	O1W-H1W···O8	0.99	2.00	2.945(7)	158
water-oxamate	O1W-H2W···$O3^{vi}$	1.00	2.01	2.899(7)	148
water-water	O2W-H3W···$O5W^{x}$	0.99	2.02	2.840(9)	138
water-oxamate	O2W-H4W···$O6^{x}$	1.00	1.91	2.904(7)	172
water-oxamate	O3W-H5W···$O1^{vi}$	0.99	1.98	2.945(7)	163
water-water	O3W-H6W···$O1W^{vi}$	0.99	2.00	2.971(8)	168
water-oxamate	O4W-H7W···$S3^{ix}$	0.85	2.77	3.52()	148
water-oxamate	O4W-H8W···$O9^{ix}$	0.85	2.29	2.83()	122
water-oxamate	O5W-H9W···O1	0.99	1.90	2.782(6)	146
water-oxamate	O5W-H10W···$O8^{ix}$	0.85	2.18	3.001(8)	163

*Symmetry code: (vi) = ½-*x*, *y*-½, ½-*z*; (ix) = 1-*x*, -*y*, 1-*z*; (x) = *x*-½, ½-*y*, *z*-½.

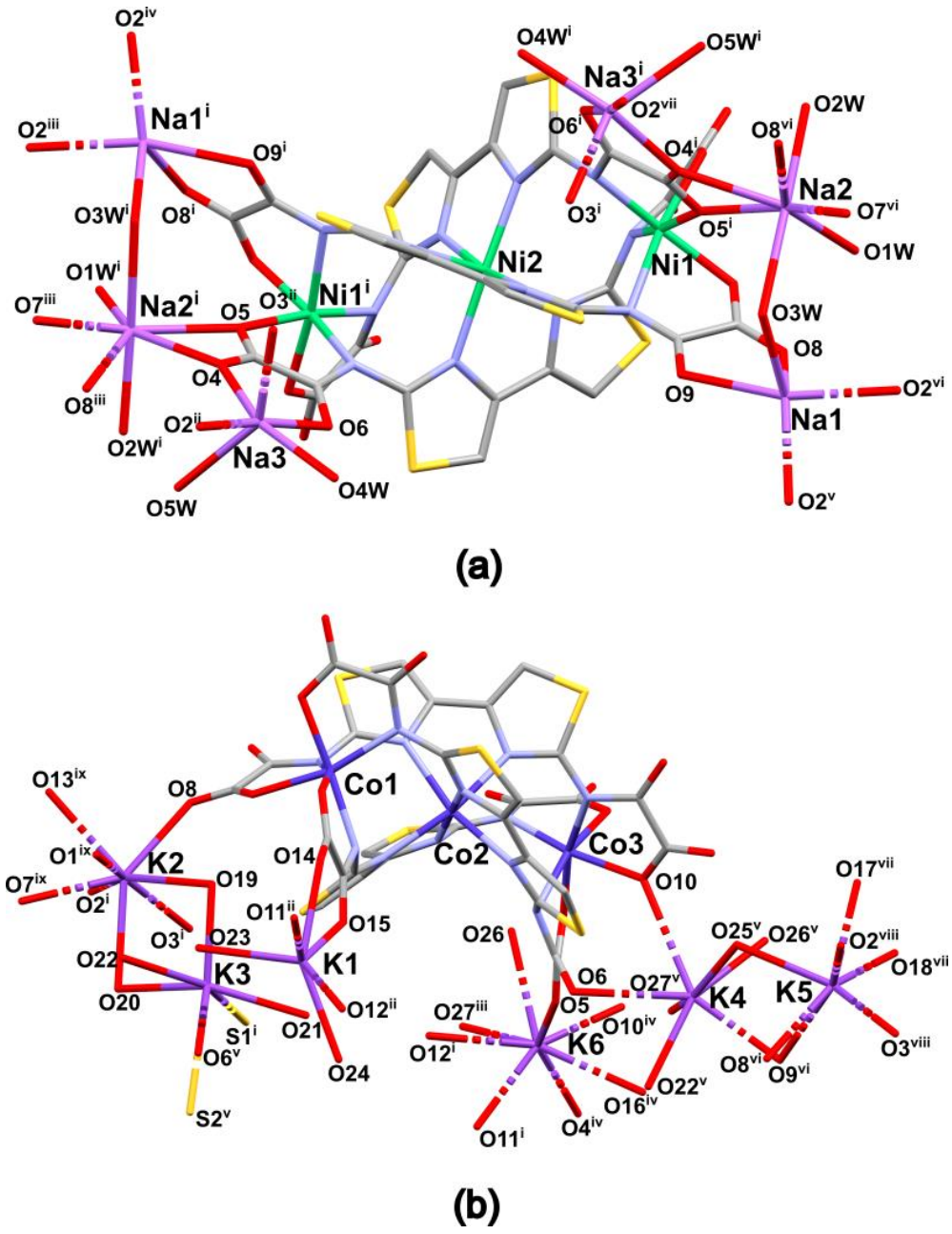

Figure S4. Perspective views of **1** (a) and **2** (b) showing the complete coordination sphere for the involved metal ions. All non-hydrogen atoms were drawn at the 50% probability level and the hydrogen atoms were omitted for clarity [Symmetry code: **1** (i) = 1-*x*, *y*, ½-*z*; (ii) = 1-*x*, *y*-1, ½-*z*; (iii) = ½+*x*, *y*-½, *z*; (iv) = 1-*x*,1-*y*,-*z*; (v) = *x*, 1-*y*, ½+*z*; (vi) = ½-*x*, *y*-½, ½-*z*; (vii) = *x*, *y*-1, *z*. **2** (i)= *x*, 1+*y*, *z*; (ii) = 1-*x*, -*y*, 1-*z*; (iii) = ½+*x*, 1.5-*y*, *z*-½; (iv) = 1.5-*x*, ½+*y*, ½-*z*; (v) = 1-*x*, 1-*y*, 1-*z*; (vi) = *x*-½, ½-*y*, ½-*z*; (vii) = 1.5-*x*, *y*-½, ½-*z*; v(iii) = *x*-½, *y*-½, *z*-½; (ix) = 1.5-*x*, ½+*y*, 1.5-z].

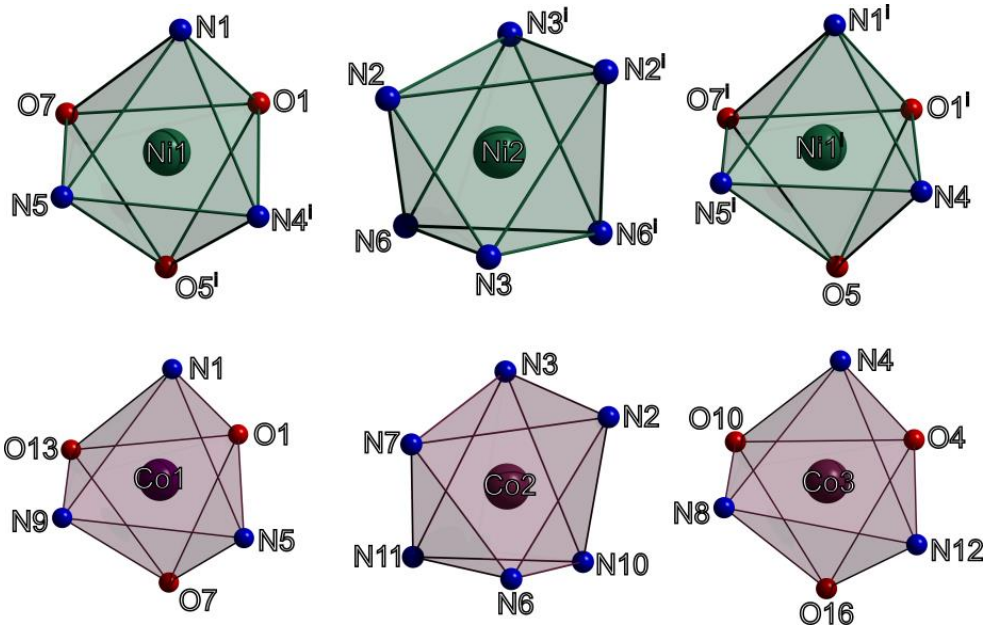

Figure S5. Coordination polyhedra of Ni^{II} (top) and Co^{II} (bottom) ions in **1** and **2**, respectively [Symmetry code (i) = 1-*x*, *y*, ½-*z*].

Table S4. Analyses of the coordination geometry for each M^{II} ion in the structures of **1** (M = Ni) and **2** (M = Co) in The SHAPE program[1] was used to calculate the deviation parameter in relation to each idealized coordinated geometry.

Deviation parameters calculated with SHAPE					
SHAPE code[a]	Ni1	Ni2	Co1	Co2	Co3
OC-6	22.626	16.715	17.776	17.806	17.548
TPR-6	26.684	22.656	22.351	23.411	23.388

[a]OC-6: O_h, octahedron; TPR-6: D_{3h}, trigonal prism.

[1] Alvarez, S.; Alemany, P.; Casanova, D.; Cirrea, J.; Llunell, M.; Avnir, D. Shape Maps and Polyhedral Interconversion Paths in Transition Metal Chemistry. *Coord. Chem. Rev*. **2005**, *249*, 1693–1708

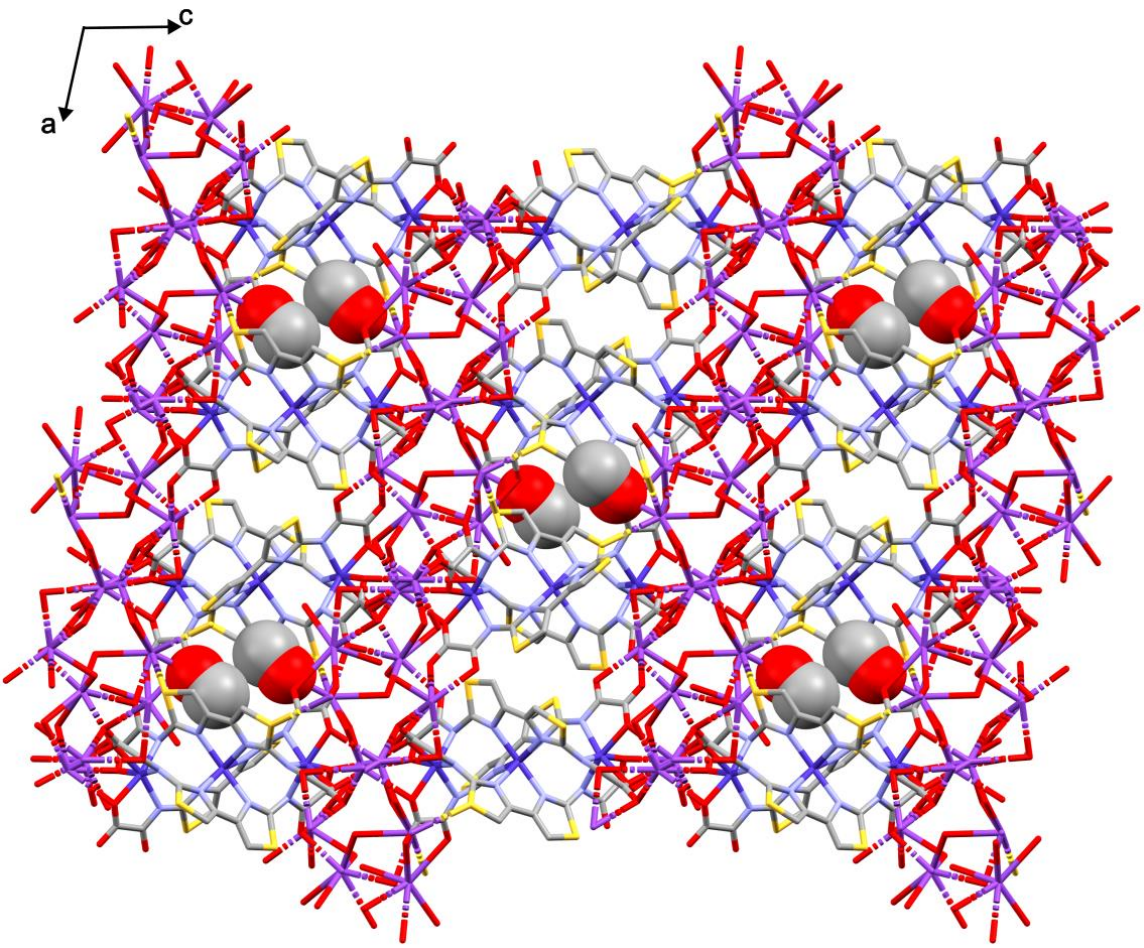

Figure S6. Perspective view of the crystal packing of **2** along the crystallographic *b* axis showing the methanol molecules of crystallization as space-filling representation.

Magnetic Data and Analysis

Table S5. Calculated spin configurations and their relative energies as a function of different J_i constants. The spin configuration used as a reference is the one with the maximum multiplicity generated from the parallel alignment of all local spin moments of the Ni^{II} ions. Only the centers with an antiparallel (negative) alignment of their spin moment are noted. The notation in Scheme 2 is used (see main text). When the second-neighbor magnetic couplings are not considered, J_2 terms should be removed.

Spin configuration	S	J_1[a]	J_2[a]	Relative energy[a]
{1}	1	3	3	+7.33
{2}	1	6	0	+17.34
{3}	1	3	3	+7.33

[a]Values in cm^{-1}.

Table S6. Energy of the calculated quartet (Q_i) and triplet (D_i) excited states and their contributions to the *D* and *E* values for **1** and **2** obtained from CASSCF/NEVPT2 calculations. D_{SS} is the spin-spin contribution to the axial *zfs* parameter, and D_T and D_S stand for the sum of spin-orbit contributions coming from quartet and doublet excited states

Ni1/Ni3					Ni2				
State	Energy[a]	*S*	*D*[a]	*E*[a]	State	Energy[a]	*S*	*D*[a]	*E*[a]
D_{SS}		1	+0.035	+0.009	D_{SS}		1	–0.011	–0.001
D_T		1	–4.473	–0.549	D_T		1	+1.649	+0.017
D_S		0	+0.678	–0.090	D_S		0	–0.187	+0.035
T_1	10071.8	1	–36.330	+2.596	T_1	10429.0	1	+20.183	–20.233
T_2	10240.1	1	+20.351	–20.377	T_2	12916.7	1	+20.358	+20.304
T_3	10673.4	1	+11.519	+17.252	T_3	12974.9	1	–38.894	–0.056
T_4	16655.8	1	+0.003	–0.016	T_4	19759.1	1	+0.002	+0.002
T_5	17063.5	1	–0.017	–0.000	T_5	20006.7	1	+0.000	+0.000
T_6	18010.1	1	+0.003	–0.003	T_6	21153.7	1	–0.000	–0.000
T_7	27390.5	1	+0.000	–0.000	T_7	30681.7	1	–0.000	–0.000
T_8	28717.6	1	+0.000	–0.001	T_8	30968.9	1	+0.000	+0.000
T_9	29102.8	1	–0.002	+0.000	T_9	31962.6	1	+0.000	+0.000
S_1	16606.7	0	–0.000	–0.000	S_1	16688.5	0	–0.000	+0.000
S_2	16565.8	0	–0.000	–0.000	S_2	16689.9	0	–0.000	–0.000
S_3	25924.9	0	+14.350	–0.044	S_3	26864.9	0	–6.965	–6.961
S_4	26515.6	0	–6.925	+6.840	S_4	26948.6	0	–6.861	+6.950
S_5	26888.2	0	–6.747	–6.706	S_5	27119.1	0	+13.639	+0.046

[a]Values in cm^{-1}.

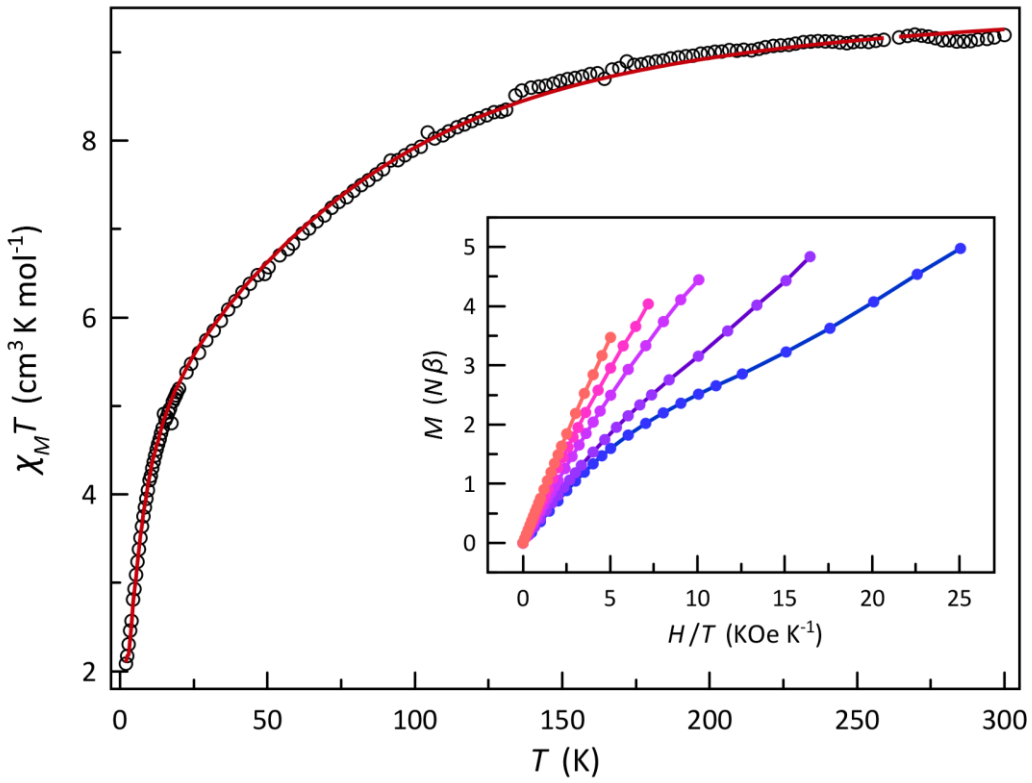

Figure S7. Temperature dependence of $\chi_M T$ for **2**. The solid lines are the best-fit curves The insets show the *M vs H*/*T* plot in the temperature range of 2.0–10 K (from blue to red colours). The solid lines are only eye-guides. Originally published by Kalinke *et al*. (reference 24 from the main text).

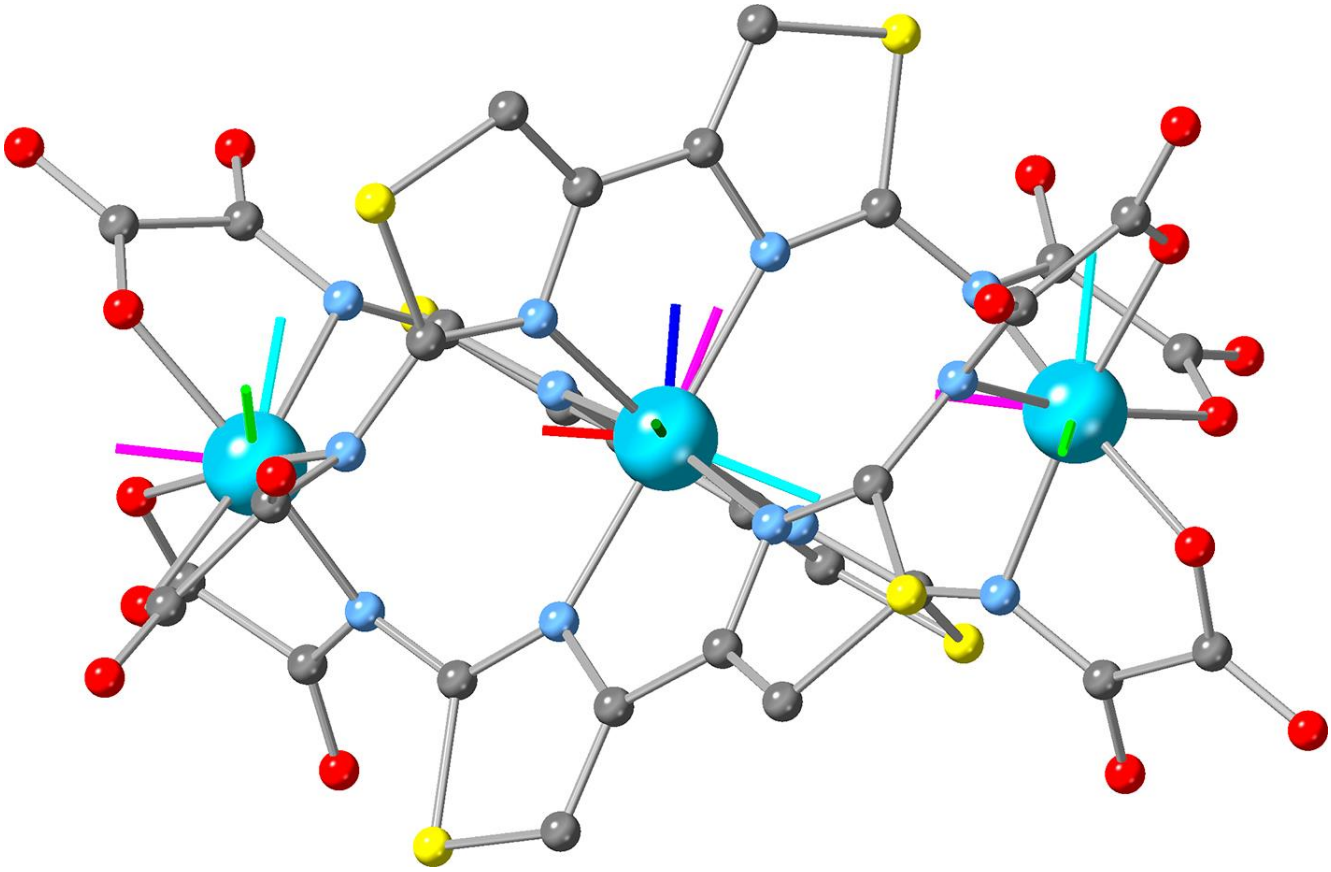

Figure S8. Relative orientations of the experimental coordination sphere geometry for the Ni^{II} sites in **1**, their calculated local (*x* = cyan, *y* = green, *z* = magenta) and global (*x* = blue, *y* = dark green, *z* = red) *D* tensors. The global *D* tensor was calculated for the *S* = 3 ground spin state. Color code: light blue (nickel), dark blue (nitrogen); red (oxygen), black (carbon), and yellow (sulphur) Hydrogen atoms were hidden for clarity.