Supporting Information

Carboxylic acid tuned nickel(II) clusters: syntheses, structures, solution behaviours and magnetic properties

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Table S1. Crystal Data of **SD/Ni4a**, **SD/Ni5a** and **SD/Ni6b**.

Identification code	**SD/Ni4a**	**SD/Ni5a**	**SD/Ni6b**
Empirical formula	$C_{66}H_{76}N_{16}Ni_4O_{18}$	$C_{62}H_{72}N_{10}Ni_5O_{20}S_6$	$C_{90}H_{106}N_{18}Ni_6O_{24}$
Formula weight	1616.26	1763.20	2176.18
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$C2/c$
a / Å	16.7045(4)	13.897(9)	32.6272(4)
b / Å	25.3661(6)	14.250(9)	13.8653(2)
c / Å	17.6478(3)	21.731(13)	23.2676(3)
α / °	90	106.518(6)	90
β / °	91.667(2)	95.516(6)	108.7600(10)
γ / °	90	96.119(6)	90
Volume / Å^3	7474.7(3)	4066(4)	9966.7(2)
Z	4	2	4
ρ_{calc}g/cm^3	1.436	1.440	1.450
μ/mm^{-1}	1.780	1.360	1.892
F(000)	3360.0	1820.0	4528.0
Radiation	Cu$K\alpha$ (λ = 1.54184)	Mo$K\alpha$ (λ = 0.71073)	Cu$K\alpha$ (λ = 1.54184)
2θ range for data collection / °	7.184–134.158	3.344–52.746	6.988–134.154
Index ranges	$-19 \leqslant h \leqslant 19$, $-30 \leqslant k \leqslant 29$, $-20 \leqslant l \leqslant 20$	$-16 \leqslant h \leqslant 17$, $-17 \leqslant k \leqslant 17$, $-27 \leqslant l \leqslant 27$	$-38 \leqslant h \leqslant 22$, $-14 \leqslant k \leqslant 16$, $-27 \leqslant l \leqslant 27$
Independent reflections	13102 [R_{int} = 0.0684, R_{sigma} = 0.0593]	16589 [R_{int} = 0.1548, R_{sigma} = 0.2032]	8753 [R_{int} = 0.0478, R_{sigma} = 0.0486]
Goodness-of-fit on F^2	1.172	0.921	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0999 wR_2 = 0.2700	R_1 = 0.0702 wR_2 = 0.1634	R_1 = 0.0438 wR_2 = 0.1160
Final R indexes [all data]	R_1 = 0.1225 wR_2 = 0.2942	R_1 = 0.1910 wR_2 = 0.2162	R_1 = 0.0549 wR_2 = 0.1278
Largest diff. peak/hole / e Å^{-3}	1.44/–1.46	1.13/–0.63	0.46/–0.61

Table S2. The selected bond lengths [Å] and angles [°] for **SD/Ni4a**, **SD/Ni5a** and **SD/Ni6b.**

SD/Ni4a			
Ni1—O2	2.043 (3)	Ni3—O8	2.089 (4)
Ni1—O5	2.123 (4)	Ni3—O10	2.076 (3)
Ni1—O6	2.029 (4)	Ni3—O11	2.032 (4)
Ni1—O7	2.060 (3)	Ni3—O12	2.080 (5)
Ni1—O9	2.108 (4)	Ni3—N2	2.068 (18)
Ni1—N11	2.075 (4)	Ni4—O1	1.997 (3)
Ni2—O3	2.009 (3)	Ni4—O7	2.098 (3)
Ni2—O7	2.056 (3)	Ni4—O9	2.104 (4)
Ni2—O8	2.116 (3)	Ni4—O10	2.063 (3)
Ni2—O10	2.091 (3)	Ni4—N4	2.121 (5)
Ni2—N7	2.078 (4)	Ni4—N5	2.051 (4)
Ni2—N9	2.078 (5)	O4—Ni3—N2	86.0 (5)
O2—Ni1—O5	89.83 (15)	O10—Ni3—O8	82.04 (13)
O2—Ni1—O7	92.01 (14)	O10—Ni3—O12	79.85 (14)
O2—Ni1—O9	89.06 (14)	O11—Ni3—O4	174.40 (16)
O2—Ni1—N11	85.97 (16)	O11—Ni3—O8	95.31 (16)
O6—Ni1—O2	172.61 (15)	O11—Ni3—O10	93.56 (15)
O6—Ni1—O5	89.06 (15)	O11—Ni3—O12	89.00 (18)
O6—Ni1—O7	94.97 (14)	O11—Ni3—N2	89.3 (5)
O6—Ni1—O9	94.34 (15)	O12—Ni3—O8	161.60 (15)
O6—Ni1—N11	86.84 (16)	N2—Ni3—O8	113.1 (5)
O7—Ni1—O5	79.34 (13)	N2—Ni3—O10	164.3 (5)
O7—Ni1—O9	81.89 (13)	N2—Ni3—O12	84.7 (5)
O7—Ni1—N11	173.79 (17)	O1—Ni4—O7	92.46 (14)
O9—Ni1—O5	161.15 (14)	O1—Ni4—O9	89.80 (14)
N11—Ni1—O5	94.77 (17)	O1—Ni4—O10	170.33 (15)
N11—Ni1—O9	103.92 (17)	O1—Ni4—N4	99.36 (15)
O3—Ni2—O7	169.04 (15)	O1—Ni4—N5	94.63 (15)
O3—Ni2—O8	90.23 (14)	O7—Ni4—O9	81.10 (14)
O3—Ni2—O10	93.05 (14)	O7—Ni4—N4	165.27 (15)
O3—Ni2—N7	92.84 (14)	O9—Ni4—N4	90.13 (16)
O3—Ni2—N9	98.38 (16)	O10—Ni4—O7	80.64 (13)
O7—Ni2—O8	97.84 (13)	O7—Ni2—N9	89.21 (14)
O7—Ni2—O10	80.97 (13)	O10—Ni2—O8	81.02 (15)
O7—Ni2—N7	79.24 (13)	N7—Ni2—O8	176.81 (14)
N7—Ni2—O10	99.69 (15)	O10—Ni4—O9	95.76 (13)
N9—Ni2—O8	89.00 (16)	O10—Ni4—N4	88.55 (14)
N9—Ni2—O10	164.86 (15)	N5—Ni4—O7	100.09 (15)
N9—Ni2—N7	89.68 (16)	N5—Ni4—O9	175.35 (14)
O4—Ni3—O8	89.36 (15)	N5—Ni4—O10	80.06 (14)
O4—Ni3—O10	90.14 (14)	N5—Ni4—N4	87.76 (17)
O4—Ni3—O12	87.52 (16)		
SD/Ni5a			

Ni1—O1	2.024 (5)	Ni3—O9	1.990 (6)
Ni1—O2	2.099 (5)	Ni3—N4	2.090 (7)
Ni1—O7	2.069 (5)	Ni3—N5	2.070 (7)
Ni1—O13	2.015 (5)	Ni4—O2	2.047 (5)
Ni1—N2	2.077 (6)	Ni4—O7	2.066 (5)
Ni1—N7	2.083 (6)	Ni4—O8	2.026 (5)
Ni2—O1	2.038 (5)	Ni4—O10	1.993 (6)
Ni2—O3	2.103 (5)	Ni4—O11	2.096 (5)
Ni2—O4	2.010 (5)	Ni4—O16	2.018 (5)
Ni2—O5	2.090 (5)	Ni5—O4	2.025 (5)
Ni2—O6	2.043 (5)	Ni5—O14	2.016 (5)
Ni2—O12	1.991 (5)	Ni5—O15	2.089 (7)
Ni3—O1	2.077 (5)	Ni5—O17	2.044 (6)
Ni3—O2	2.014 (5)	Ni5—O20	2.072 (7)
Ni3—O3	2.077 (5)	Ni5—N10	2.064 (8)
O1—Ni1—O2	79.68 (19)	O9—Ni3—O2	170.4 (2)
O1—Ni1—O7	97.17 (19)	O9—Ni3—O3	90.7 (2)
O1—Ni1—N2	79.2 (2)	O9—Ni3—N4	97.9 (3)
O1—Ni1—N7	90.1 (2)	O9—Ni3—N5	94.9 (3)
O7—Ni1—O2	79.18 (19)	N5—Ni3—O1	98.7 (2)
O7—Ni1—N2	175.8 (2)	N5—Ni3—O3	174.1 (3)
O7—Ni1—N7	92.4 (2)	N5—Ni3—N4	88.4 (3)
O13—Ni1—O1	166.5 (2)	O2—Ni4—O7	80.45 (18)
O13—Ni1—O2	90.7 (2)	O2—Ni4—O11	79.44 (19)
O13—Ni1—O7	90.2 (2)	O7—Ni4—O11	159.77 (19)
O13—Ni1—N2	93.8 (2)	O8—Ni4—O2	98.8 (2)
O13—Ni1—N7	100.9 (2)	O8—Ni4—O7	91.9 (2)
N2—Ni1—O2	102.0 (2)	O8—Ni4—O11	93.3 (2)
N2—Ni1—N7	85.6 (2)	O10—Ni4—O2	91.3 (2)
N7—Ni1—O2	165.7 (2)	O10—Ni4—O7	89.1 (2)
O1—Ni2—O3	79.66 (18)	O10—Ni4—O8	169.9 (2)
O1—Ni2—O5	98.54 (19)	O10—Ni4—O11	89.2 (2)
O1—Ni2—O6	91.0 (2)	O10—Ni4—O16	83.1 (2)
O4—Ni2—O1	82.27 (19)	O16—Ni4—O2	170.9 (2)
O4—Ni2—O3	161.93 (19)	O16—Ni4—O7	106.6 (2)
O4—Ni2—O5	89.31 (19)	O16—Ni4—O8	86.9 (2)
O4—Ni2—O6	94.6 (2)	O16—Ni4—O11	93.2 (2)
O5—Ni2—O3	93.38 (19)	O4—Ni5—O15	90.6 (2)
O6—Ni2—O3	85.7 (2)	O4—Ni5—O17	97.1 (2)
O6—Ni2—O5	170.1 (2)	O4—Ni5—O20	176.2 (2)
O12—Ni2—O1	177.2 (2)	O4—Ni5—N10	88.3 (3)
O12—Ni2—O3	98.0 (2)	O14—Ni5—O4	91.5 (2)
O12—Ni2—O4	100.1 (2)	O14—Ni5—O15	91.9 (3)
O12—Ni2—O5	83.1 (2)	O14—Ni5—O17	170.9 (2)
O12—Ni2—O6	87.3 (2)	O14—Ni5—O20	84.8 (2)
O1—Ni3—N4	166.6 (2)	O14—Ni5—N10	84.4 (3)
O2—Ni3—O1	80.44 (18)	O17—Ni5—O15	91.0 (3)
O2—Ni3—O3	94.81 (18)	O17—Ni5—O20	86.6 (2)
O2—Ni3—N4	89.7 (3)	O17—Ni5—N10	92.9 (3)
O2—Ni3—N5	79.4 (2)	O20—Ni5—O15	88.4 (3)
O3—Ni3—O1	79.38 (18)	N10—Ni5—O15	176.1 (3)
O3—Ni3—N4	92.5 (2)	N10—Ni5—O20	92.4 (3)
O9—Ni3—O1	92.9 (2)		
SD/Ni6b			

Ni1—O4	2.0964 (17)	Ni3—O11	1.9934 (17)
Ni1—O10	2.0441 (16)	Ni3—O7	2.161 (2)
Ni1—O10^{i}	2.0897 (17)	Ni3—O1W	2.065 (2)
Ni1—O5	2.0246 (17)	Ni3—O1	1.995 (2)
Ni1—N5	2.097 (2)	Ni3—O9	2.137 (2)
Ni1—N1	2.098 (2)	Ni3—N4	2.062 (2)
Ni2—O4^{i}	2.1118 (17)	O4—Ni2^{i}	2.1119 (17)
Ni2—O10	2.0520 (17)	Ni2—O6^{i}	2.0747 (17)
Ni2—O11	2.0259 (17)	O10—Ni1^{i}	2.0899 (17)
Ni2—O3	2.0571 (17)	Ni2—O2	2.0083 (18)
O4—Ni1—N5	92.27 (7)	O3—Ni2—O4^{i}	92.40 (7)
O4—Ni1—N1	174.98 (8)	O3—Ni2—O6^{i}	173.53 (7)
O10—Ni1—O4	96.68 (6)	O2—Ni2—O4^{i}	98.83 (7)
O10^{i}—Ni1—O4	79.07 (6)	O2—Ni2—O10	174.69 (7)
O10—Ni1—O10^{i}	81.06 (7)	O2—Ni2—O11	100.15 (7)
O10^{i}—Ni1—N5	166.45 (8)	O2—Ni2—O6^{i}	86.08 (7)
O10—Ni1—N5	89.72 (7)	O2—Ni2—O3	87.58 (7)
O10—Ni1—N1	78.32 (7)	O11—Ni3—O7	104.63 (8)
O10^{i}—Ni1—N1	99.55 (8)	O11—Ni3—O1W	88.14 (8)
O5—Ni1—O4	90.04 (7)	O11—Ni3—O1	98.26 (8)
O5—Ni1—O10^{i}	93.13 (7)	O11—Ni3—O9	163.33 (9)
O5—Ni1—O10	170.08 (7)	O11—Ni3—N4	89.03 (8)
O5—Ni1—N5	97.31 (8)	O1W—Ni3—O7	85.09 (9)
O5—Ni1—N1	94.86 (8)	O1W—Ni3—O9	83.80 (9)
N5—Ni1—N1	88.18 (9)	O1—Ni3—O7	156.88 (9)
O10—Ni2—O4^{i}	79.56 (6)	O1—Ni3—O1W	92.56 (10)
O10—Ni2—O6^{i}	88.78 (7)	O1—Ni3—O9	96.66 (9)
O10—Ni2—O3	97.52 (7)	O1—Ni3—N4	90.57 (10)
O11—Ni2—O4^{i}	160.95 (7)	O9—Ni3—O7	60.23 (9)
O11—Ni2—O10	81.39 (7)	N4—Ni3—O7	92.97 (9)
O11—Ni2—O6^{i}	92.36 (7)	N4—Ni3—O1W	176.05 (11)
O11—Ni2—O3	90.03 (7)	N4—Ni3—O9	98.24 (9)
O6^{i}—Ni2—O4^{i}	87.30 (7)	Ni1—O4—Ni2^{i}	96.47 (7)
Symmetry code: (i) −*x*+1, *y*, −*z*+1/2.			

Table S3. The shortest intra- and intermolecular Ni-Ni distances [Å] for **SD/Ni4a**, **SD/Ni5a** and **SD/Ni6b.**

Intramolecular Ni-Ni distances			
SD/Ni4a			
Ni1-Ni2	3.5796(10)	Ni2-Ni4	3.1576(11)
Ni1-Ni4	3.0892(11)	Ni3-Ni4	3.6293(11)
Ni2-Ni3	3.0910(12)		
SD/Ni5a			
Ni1-Ni2	3.4928(18)	Ni2-Ni3	3.1077(23)
Ni1-Ni3	3.1424(20)	Ni2-Ni3	3.4844(21)
Ni1-Ni4	3.0997(22)	Ni3-Ni4	3.5298(25)
SD/Ni6b			
Ni1-Ni1^{i}	3.1403(8)	Ni1-Ni2^{i}	3.1391(8)
Ni1-Ni2	3.5290(6)	Ni2-Ni3	3.4785(9)
Symmetry code: (i) −x+1, y, −z+1/2			
Intermolecular Ni-Ni distances			
SD/Ni4a		9.8558(11)	
SD/Ni5a		9.2197(49)	
SD/Ni6b		6.5294(6)	

Table S4. Identification of the key species in ESI-MS of **SD/Ni6b (1a-1j)**, **SD/Ni5a (2a-2g)** and **SD/Ni4a (3a-3j)**.

Species	Molecular formula	Exp. *m*/*z*	Sim. *m*/*z*
1a	$[Ni_4(bdped)(mba)_5(Hdmpz)_2(H_2O)]^+$	1367.2382	1367.2363
1b	$[Ni_5(bdped)(mba)_7(CH_3CN)]^+$	1528.1329	1528.1366
1c	$[Ni_5(bdped)_3(mba)_2(NO_3)(Hdmpz)(C_2H_6O)_2(CH_3OH)]^+$	1590.2555	1590.3078
1d	$[Ni_5(bdped)(mba)_7(Hdmpz)(CH_3CN)]^+$	1624.2021	1624.2057
1e	$[Ni_5(bdped)_2(mba)_5(Hdmpz)(CH_3OH)_2(H_2O)_2]^+$	1661.3074	1661.2907
1f	$[Ni_5(bdped)_3(mba)_2(NO_3)(Hdmpz)_2(C_2H_6O)_2(CH_3OH)]^+$	1686.3128	1686.3768
1g	$[Ni_5(bdped)(mba)_7(Hdmpz)(CH_3CN)_2(CH_3OH)]^+$	1697.2587	1697.2586
1h	$[Ni_5(bdped)(mba)_7(Hdmpz)_2(CH_3CN)]^+$	1720.2701	1720.2747
1i	$[Ni_5(bdped)(mba)_7(Hdmpz)_2(CH_3CN)_2(CH_3OH)]^+$	1793.3267	1793.3277
1j	$[Ni_5(bdped)_3(mba)_3(Hdmpz)_4(C_2H_6O)(CH_3OH)]^+$	1905.4735	1905.5302
2a	$[Ni_5(bdped)(tca)_6(Hdmpz)_3(C_2H_6O)_4(CH_3OH)]^{2+}$	904.0306	904.0546
2b	$[Ni_5(bdped)(tca)_6(Hdmpz)_4(C_2H_6O)_4(CH_3OH)]^{2+}$	952.0665	952.0890
2c	$[Ni_5(bdped)_2(tca)_4(Hdmpz)_6(CH_3OH)(H_2O)_7]^{2+}$	1016.1877	1016.1895
2d	$[Ni_4(bdped)_2(tca)_3]^+$	1110.9372	1110.9478
2e	$[Ni_5(bdped)_3(tca)_2(Hdmpz)_8(CH_3OH)_2(CH_3CN)(H_2O)_5]^{2+}$	1127.8991	1127.8528
2f	$[Ni_4(bdped)(tca)_4(OH)(CH_3OH)_2(H_2O)_4]^+$	1142.8617	1142.9032
2g	$[Ni_4(bdped)(tca)_5(CH_3OH)(H_2O)_5]^+$	1238.9307	1238.8730
3a	$[Ni_4(bdped)_2(ba)(NO_3)_2(H_2O)_3(CH_3OH)]^+$	1061.0654	1061.0540
3b	$[Ni_4(bdped)_2(ba)_3]^+$	1093.0701	1093.0787
3c	$[Ni_4(bdped)(ba)_5(CH_3OH)]^+$	1119.0390	1119.0356
3d	$[Ni_4(bdped)(ba)_5(Hdmpz)(CH_3OH)]^+$	1215.1079	1215.1046
3e	$[Ni_4(ba)_5(NO_3)_2(Hdmpz)_3(H_2O)_3(CH_3OH)]^+$	1337.1456	1337.1221
3f	$[Ni_4(bdped)_2(ba)_3(Hdmpz)_2(CH_3OH)_2]^+$	1349.3141	1349.2691
3g	$[Ni_4(bdped)_3(ba)(Hdmpz)_2(H_2O)_3(CH_3OH)]^+$	1377.3425	1377.3439
3h	$[Ni_4Na_2(ba)_8(NO_3)(Hdmpz)(CH_3OH)(H_2O)]^+$	1456.0676	1456.0424
3i	$[Ni_4(bdped)(ba)_5(Hdmpz)_4]^+$	1471.3570	1471.2852
3j	$[Ni_4(bdped)_2(ba)(NO_3)_2(Hdmpz)_5(CH_3CN)]^+$	1496.3850	1496.3673

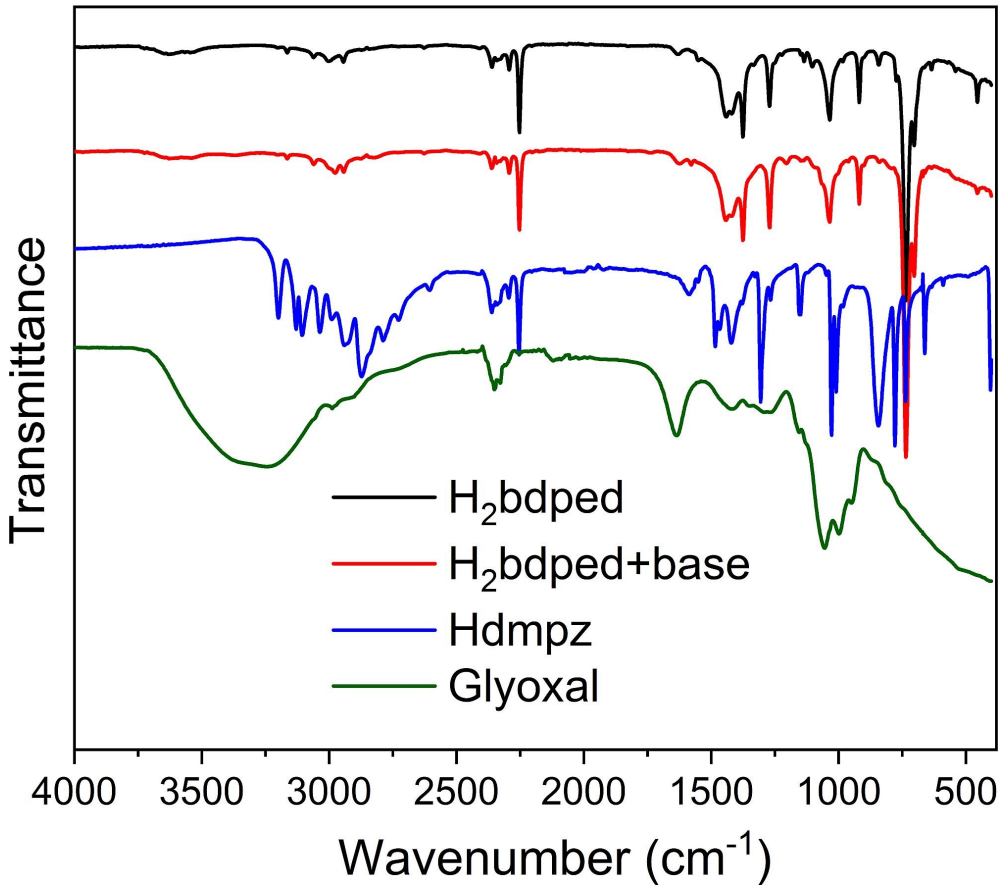

Figure S1. The IR spectra of pure organic ligands in MeCN/DCM.

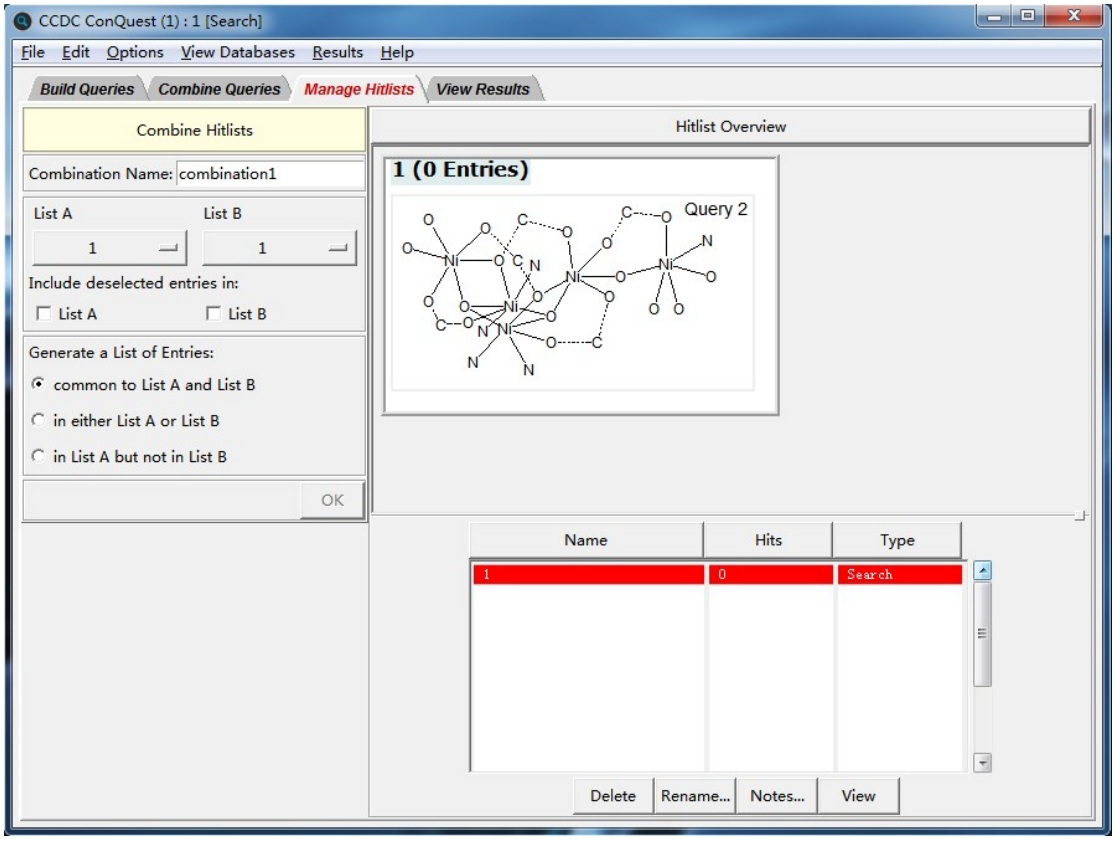

Figure S2. The scheme about searching the topology of Ni_5 core geometry (five nickel(II) ions with bridged parts of ligands including bridging carboxylates) in Cambridge Structural Database (version 2020.3.0).

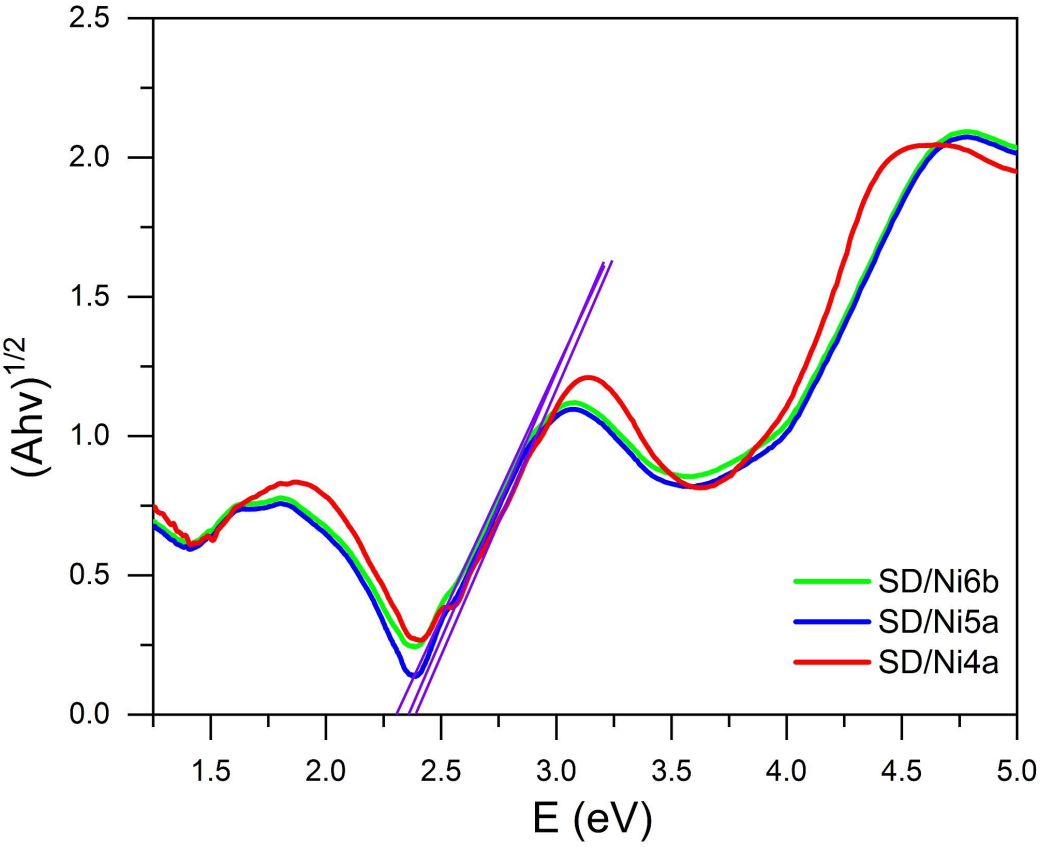

Figure S3. The absorption spectra of **SD/Ni4a**, **SD/Ni5a** and **SD/Ni6b** derived from the diffuse reflectance spectra through the Kubelka-Munk function.

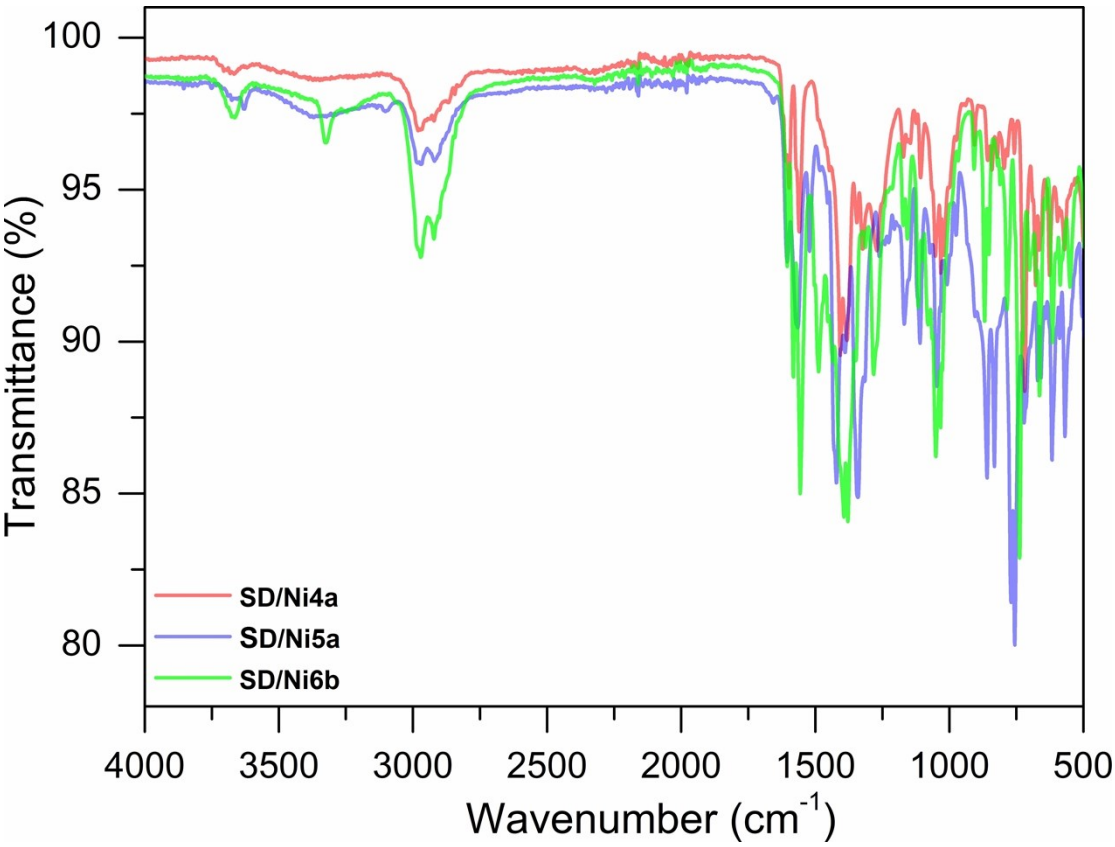

Figure S4. The IR spectra of **SD/Ni4a**, **SD/Ni5a** and **SD/Ni6b**.

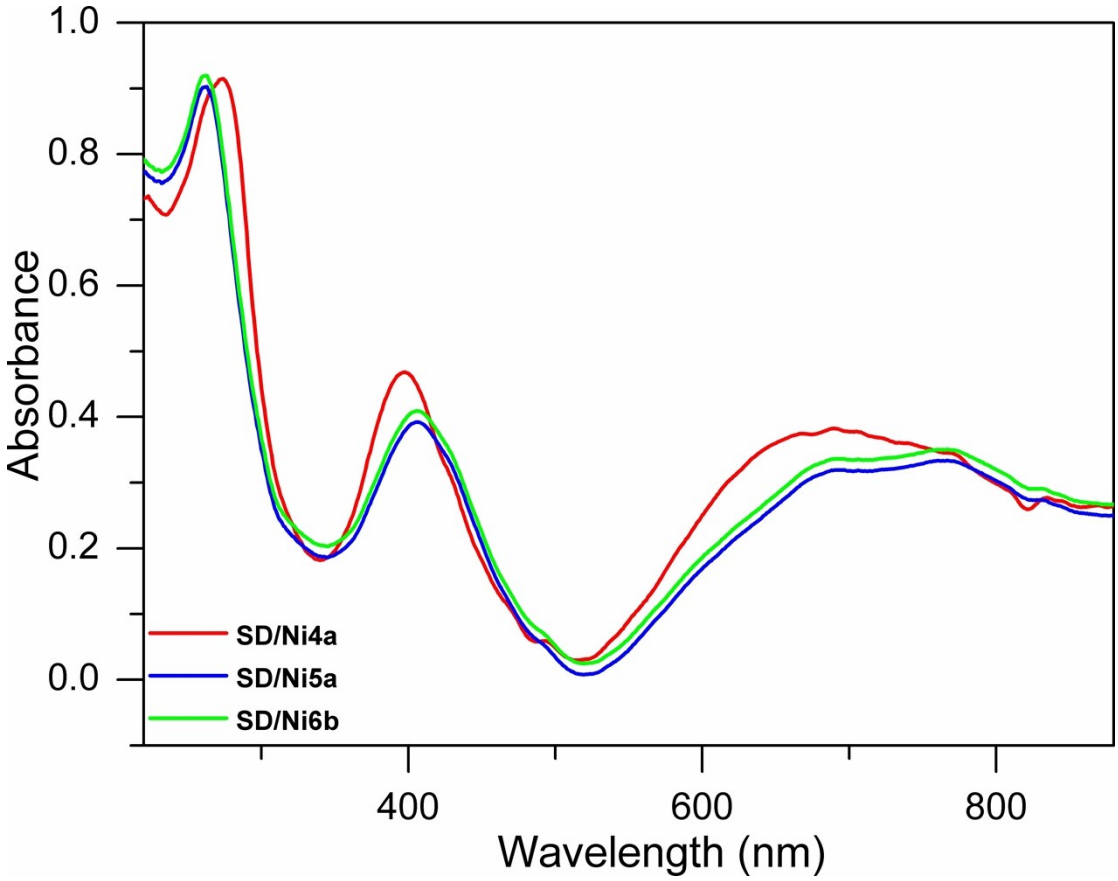

Figure S5. The solid-state UV-Vis spectra of **SD/Ni4a**, **SD/Ni5a** and **SD/Ni6b**.

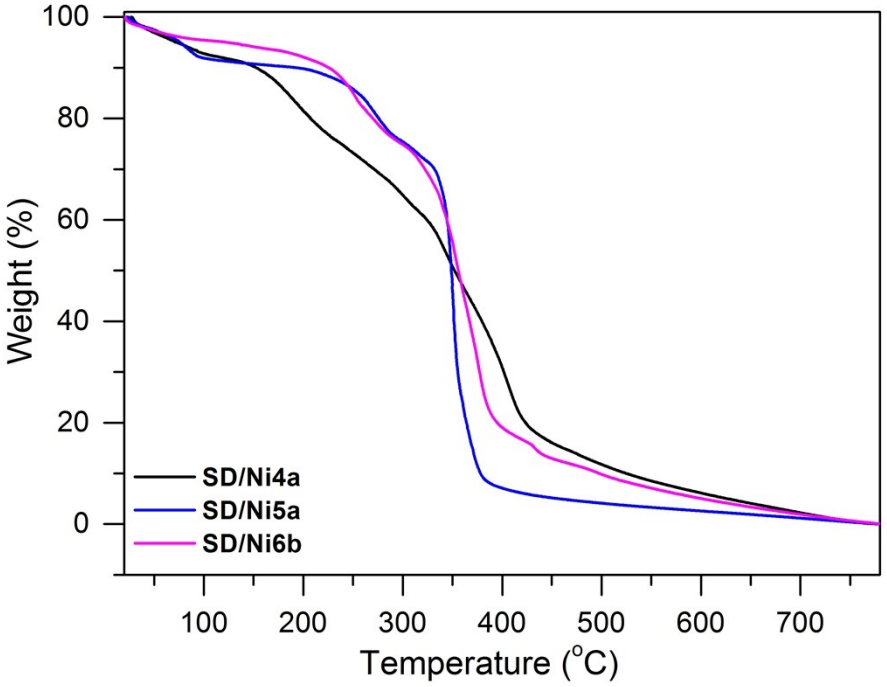

Figure S6. The TGA of **SD/Ni4a**, **SD/Ni5a** and **SD/Ni6b**.

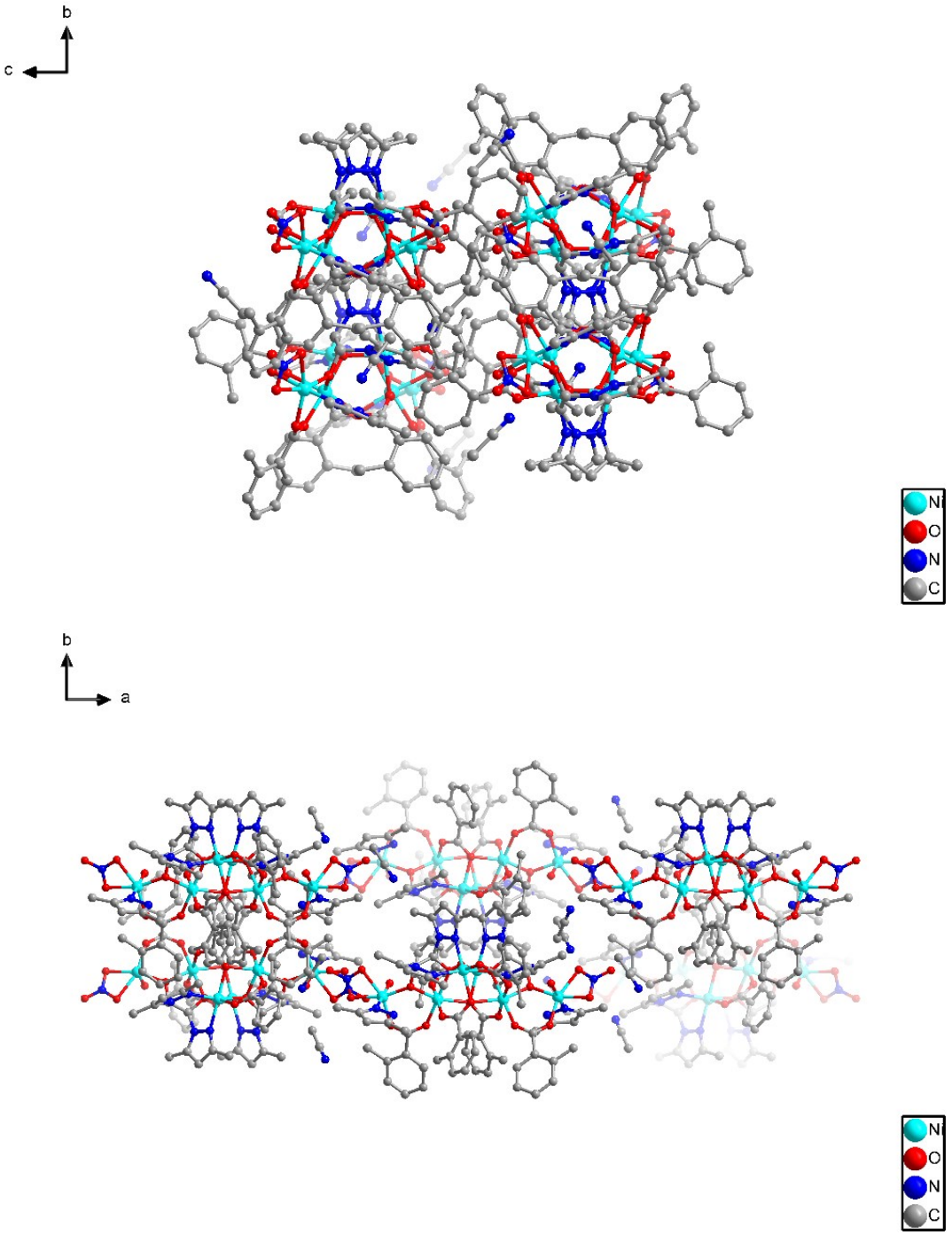

Figure S7. The cluster packing in the unit cell of **SD/Ni6b** viewed along two different directions.

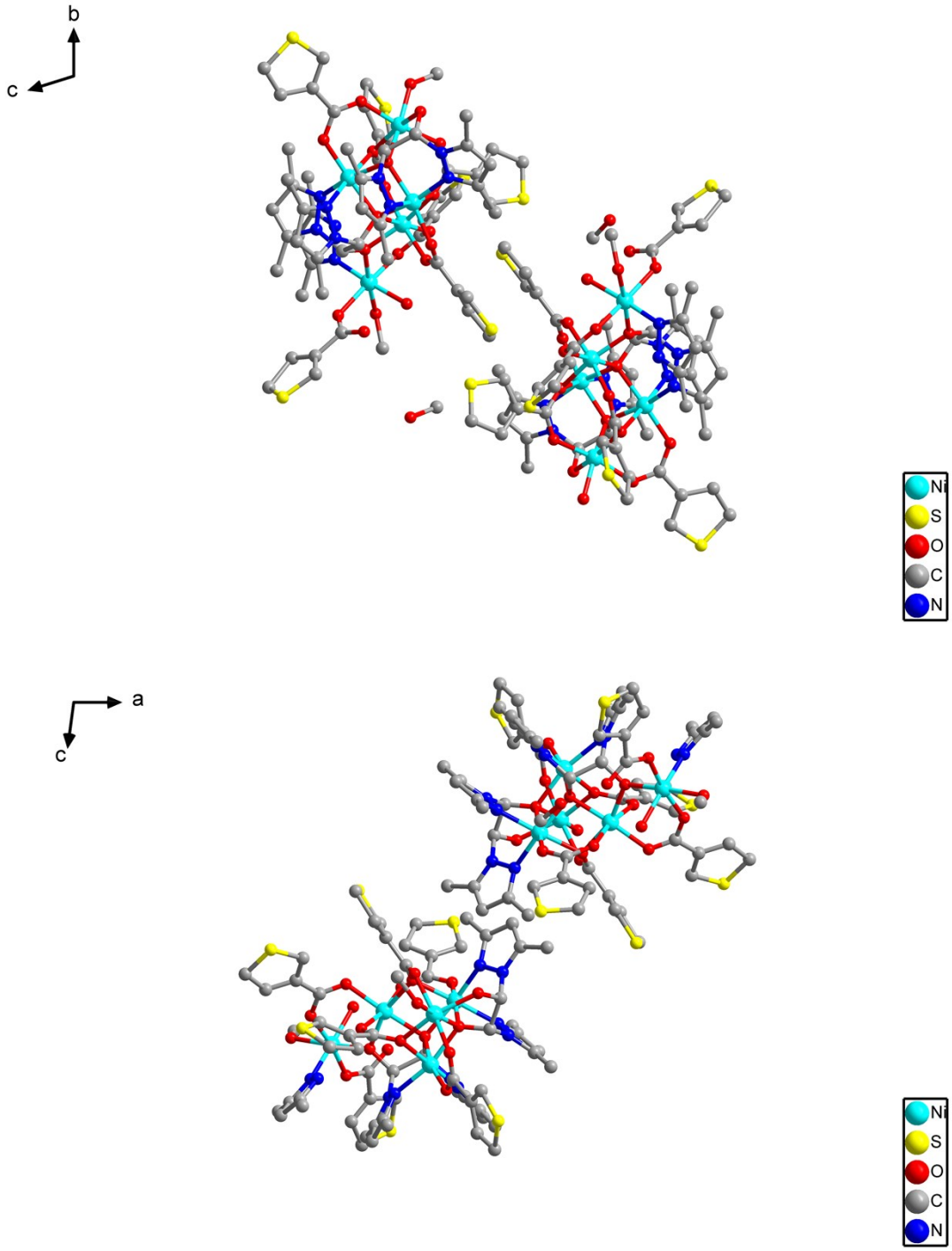

Figure S8. The cluster packing in the unit cell of **SD/Ni5a** viewed along two different directions.

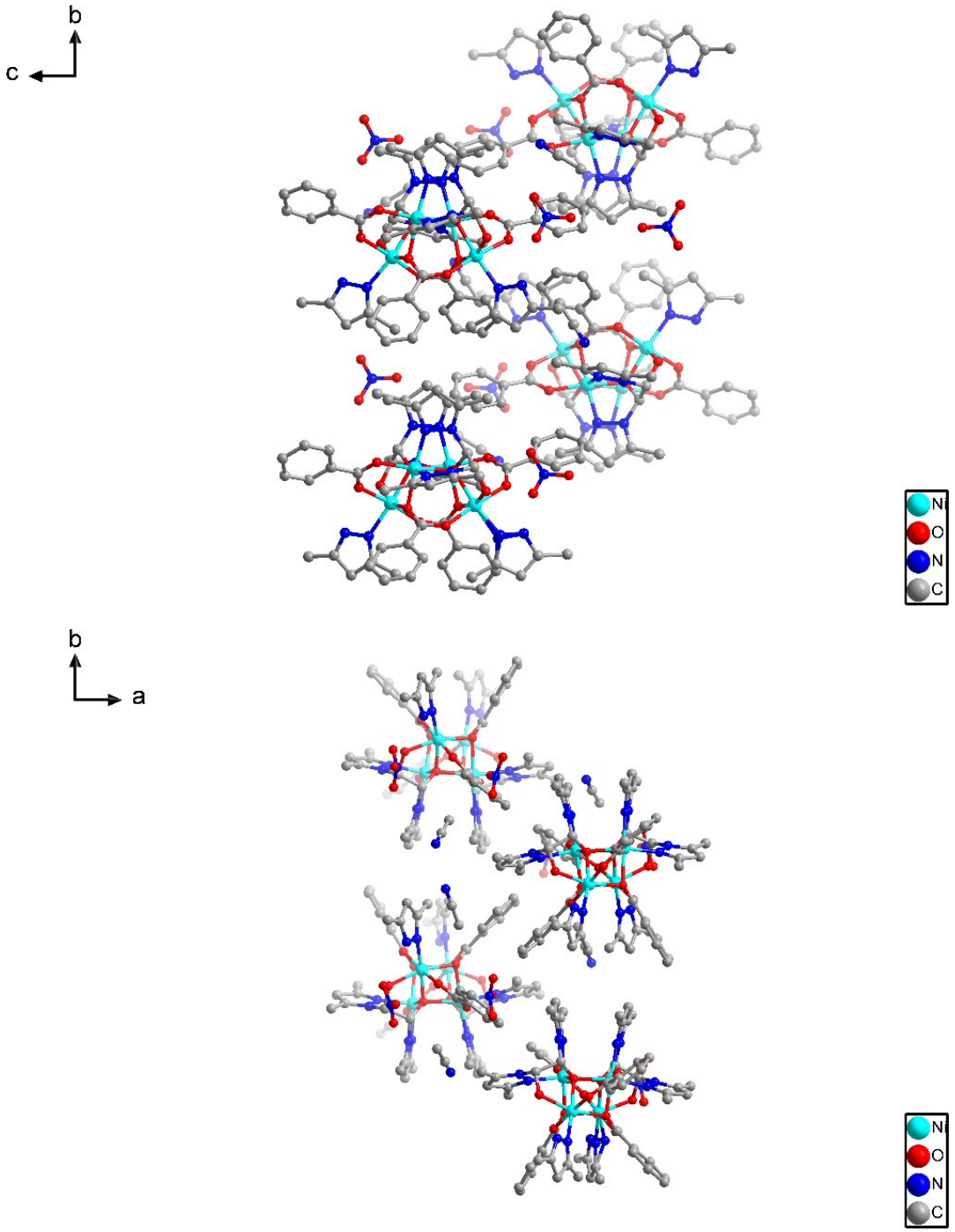

Figure S9. The cluster packing in the unit cell of **SD/Ni4a** viewed along two different directions.

The details of fitting of magnetic data for three compounds

SD/Ni4a:

The only successful fitting attempt was the one including ZFS and two exchange interactions. Some of the fitting attempts are shown in Figure 1 as red lines. The dashed, dotted and dash-dotted lines are attempts including only one J with a positive CF parameter, two Js with a positive CF parameter and one J with a negative CF parameter, respectively. All attempts failed to satisfactory fit the experimental data. Thus, the fit with two Js and a negative CF parameter was adopted (full red line). The fitting parameters with uncertainties are:

$g = 2.2014 \pm 0.0004$

$J_1 = (5.86 \pm 0.02)\ cm^{-1}$

$J_2 = (-2.570 \pm 0.008)\ cm^{-1}$

$D = (-10.2 \pm 0.09)\ cm^{-1}$

SD/Ni5a:

The green lines on Figure 1 show some of the fitting attempts for fitting the Ni5 experimental data. The dash-dotted line represents an attempt including only ZFS, which could not successfully fit the experimental data. In the case of Ni5 attempts with two Js gave satisfactory fit for a positive and a negative CF parameter. However, because of the similarities in the crystal structures between the Ni4 and Ni5 samples, the fit with a negative CF was adopted. Furthermore, the fitting parameters for the fit with a negative CF were closer to those in the Ni4 fit. A similarity between fitting parameters is expected due to the structural similarities between the samples. The fitting parameters with uncertainties are:

$g = 2.1857 \pm 0.0008$

$J_1 = (6.53 \pm 0.02)\ cm^{-1}$

$J_2 = (-0.0441 \pm 0.009)\ cm^{-1}$

$D = (-11.1 \pm 0.3)\ cm^{-1}$

The J_2 fitting parameter is negative even when its uncertainties are considered. The

correlation parameter between J_2 and the CF parameter is calculated by the PHI software to be -0.9 which indicates a strong correlation. However, attempts to omit one of the parameters or fixing its value to a different value to the one yielded by the fit, resulted in a worse quality of the fit. Based on these results and the small uncertainties of the individual parameters, it was concluded that the obtained values of the fitting parameters are valid and related to the properties of the investigated system.

SD/Ni6b:

The blue lines on Figure 1 show some fitting attempts for the Ni6 sample. The dash-dotted line shows the unsuccessful attempt including only exchange interactions without ZFS. Also other attempts, for example including only a positive CF (dashed line) or including a positive CF with one J, yielded fits which were not as good as the fit including ZFS only. Here are the fitting parameters of this fit including uncertainties:

$g = 2.3497 \pm 0.0003$

$D = (-13.23 \pm 0.06)\ cm^{-1}$

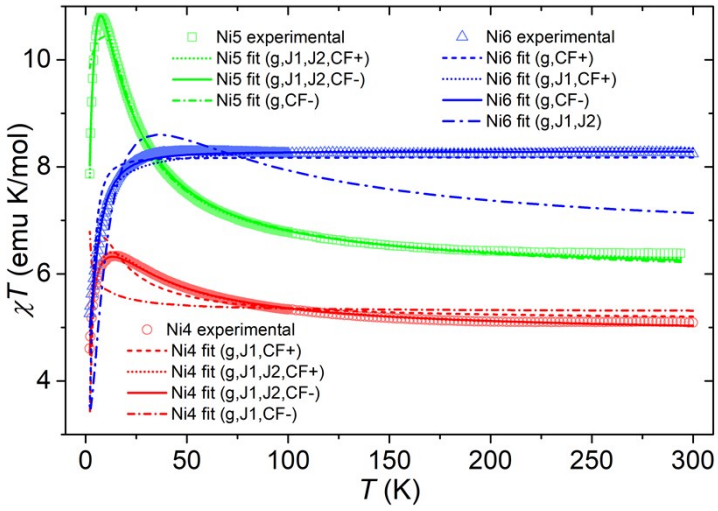

Figure S10. The product χT as a function of temperature. Comparison between the experimental data (circles, squares and triangles) and various fitting attempts (full, dashes, dotted and dash-dotted lines). The full lines represent the best fits obtained.