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The Stepwise Substitution in the Hierarchical Building of $\{Co_{11}Cd_6\}$ Cluster-Based MOFs from $\{Co_{14}\}$ Precursor

Table of content:

1. Experimental Details

Materials and physical measurements

The reagents and solvents employed were commercially available and used as received without further purification. The FT-IR spectra were recorded from KBr pellets containing 1% of the compound over the range 400–4000 cm^{-1} on a Perkin–Elmer one FT-IR spectrophotometer. The C, H, and N micro analyses were carried out on a Perkin–Elmer Vario EL III CHNS elemental analyzer. All ultraviolet−visible light (UV-vis) absorption spectra were performed on a Shimadzu ModelUV-2700 spectrophotometer. Powder X-ray diffraction (PXRD) spectra were measured at 293 K on a Rigaku D/max-IIIA diffractometer (Cu-Kα, λ = 1.54056 Å). The samples were prepared by crushing single crystals and scanned from 5 to 50° at a rate of 5°/min. The calculated diffraction patterns were generated with Mercury software. The TG-DTA analyses were performed on a Labsysevo TG-DTA/DSC from room temperature to 1000 °C under a constant flow of dry nitrogen gas at a rate of 5 °C/min. To further confirm the relative molar ratios of cobalt and cadmium, the inductively coupled plasma mass spectrometry (ICP-MS) used for the elemental analyses of the metals in the bimetallic cluster were carried out with a PekinElmer FLexar-NexION 300X instrument. To measure Scanning electron microscopy (SEM) and energy-dispersed X-ray spectroscopy (EDX), the crystal sample was tiled onto a conductive carbon foil supported on an aluminum stub. The investigations were performed with an LEO 1530 Gemini (Zeiss, operated at 1 kV) or with a Quanta 200 (FEI, operated at 5 kV) equipped with an EDX spectrometer (EDAX). HRESI-MS measurements were conducted on a Thermo Exactive instrument at a capillary temperature of 275 K. A liquots of the solution were injected into the device at 0.3 mL/h. And the data were collected in positive ion mode. The spectrometer had previously been calibrated with standard tune mix to give a precision of about 2 ppm in the region of m/z 800~2000; the tube lens voltage was set at 150 V and the skimmer voltage at 25 V. The in-source energy was set to a range of 0 eV with a gas flow rate at 10% of the maximum.

1.1. Synthesis of $\{Co_{14}\}$ precursor (**1**):

1 has previously been prepared by a solvothermal technique : A mixture of 5,5'-di(pyridin-2-yl)-3,3'-bi(1,2,4-triazole) (H_2dpbt) (0.087 g, 0.3 mmol), $CoCl_2 \cdot 6H_2O$ (0.214 g, 0.9 mmol), and triethylamine (0.6 mmol, *ca.* 2 equiv per H_2dpbt) in MeOH(11 mL) was sealed in a 25 mL Teflon-lined autoclave and heated at 130 °C in an oven for 3 days. Then it was allowed to be cooled to ambient temperature over 24 h, giving blue-green strip crystals of **1** in a yield of 31 % (base on H_2dpbt). Elemental analysis (%) calcd for $Co_{14}C_{102}H_{116}N_{48}O_{18}Cl_{12}$: C, 34.48; H, 3.29; N, 18.92; Found: C, 34.89; H, 3.08; N, 19.17. IR data for **1** (KBr, cm^{-1}): 3410(s), 1621(m), 1478(m), 1449(m), 1418(m), 1310(m), 1271(m), 1034(m), 803(m), 726(s).

1.2. The photograph and ICP-MS monitor of the filtrate solution of $\{Co_{14}\}$ precursor:

We selected a small number of washed $\{Co_{14}\}$ precursor crystals (ca. 10 mg) and soak them in the solution of CH_3OH and CH_3CH_2CN (10:1, v/v) for different times at room temperature. After filtration, the color of the filtrate was compared with each other. The gradually deepening of the color of the solution proved that the Co^{2+} ions in the $\{Co_{14}\}$ precursor were continuously detached (**Figure S1, S2**).

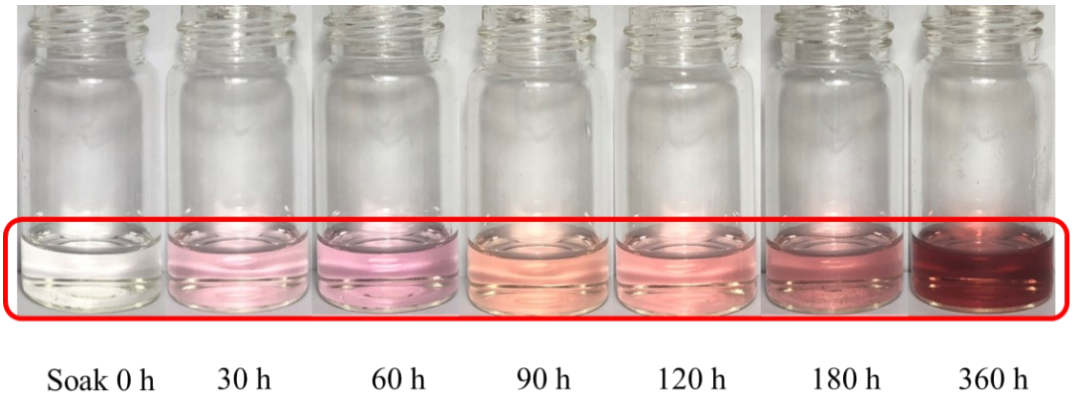


Figure S1. The change of color of $\{Co_{14}\}$ solution in different soaking time

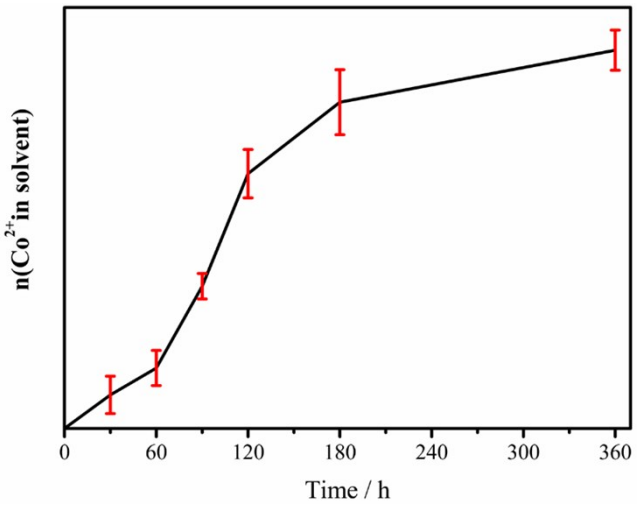
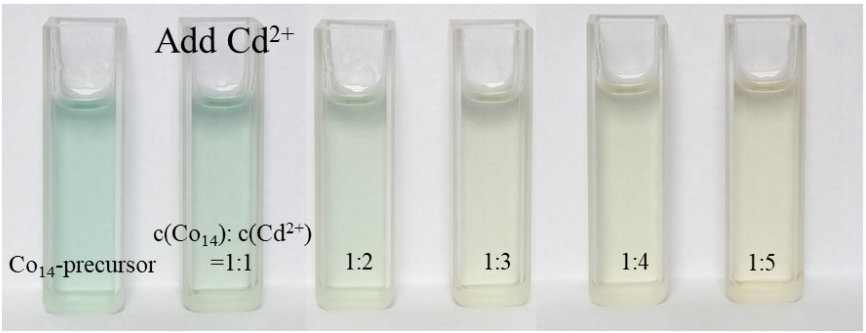


Figure S2. The Curve of n (Co^{2+} in solvent) in {Co_{14}} precursor soaking solution at different times

(a)



(b)

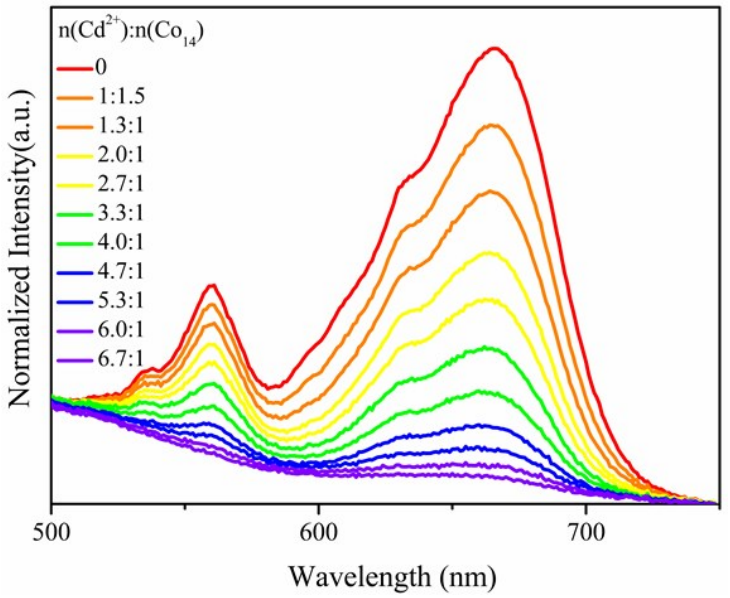


Figure S3. (a) The color change of the solution after adding Cd^{2+} to the DMF solution of the $\{Co_{14}\}$ precursor; (b) UV titration curve of adding Cd^{2+} to the DMF solution of the $\{Co_{14}\}$ precursor.

2. Structural Details

2.1 Crystal structure determinations.

Single crystal X-ray diffraction data collection for **1-de($CoCl_2$)$_3$** and **2** were conducted on an Agilent Supernova diffractometer (Mo, λ = 0.71073Å) at room temperature. The data were processed using CrysAlisPro. (Version 1.171.35.211). The structures were solved by direct methods using SHELXTL program[1] and refined with a full-matrix least-squares technique within the ShelXL2015 and OLEX II.[2,3,4] Hydrogen atoms of the ligand were generated geometrically; other non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed geometrically and refined as riding atoms. The crystallographic details are summarized in Table S1. Selected bond distances and bond angles are listed in Tables S2. The ratio of Co^{2+} to Cd^{2+} was determined by ICP and single-crystal X-ray diffraction data, and their positions in the Co/Cd bimetallic cluster were identified on the basis of single-crystal X-ray diffraction results. Solvent molecules are significantly disordered and could not be modeled properly due to the lack of well defined atomic positions, thus the SQUEEZE procedure implemented in Platon[5] was used to calculate the solvent disorder volume and remove its contribution to the overall intensity data. Thermogravimetric analysis corroborates the rationality of SQUEEZE calculations for complexes **1** and **2**. (**Figure S13**)

For **1-de($CoCl_2$)$_3$**, SQUEEZE gives 1170 electrons/unit cell for the voids. If these electrons are all from CH_3CH_2OH (26 e^-), each unit cell has 45 (cal. 1170/26) CH_3CH_2OH molecules, and each formula unit has 23 CH_3CH_2OH molecules (since Z = 2). So the suitable formula for this compound should be $[Co_{11}(\mu_3\text{-}OCH_3)_4(dpbt)_6Cl_6]\cdot 23\ CH_3CH_2OH$.

For **2**, the contributions of some 166 electrons were removed from the formula unit. And as Z = 4 in this case, this could correspond with the removal of solvent such as 14.5 MeOH from the unit. So the suitable formula for this compound should be $\{[Co_{11}Cd_6(OCH_3)_4(dpbt)_6Cl_{18}(DMF)_{1.75}]\cdot 3.5MeOH\}_n$.

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Centre, with reference numbers 1991481-1991482 for **1-de($CoCl_2$)$_3$** and **2**. CIF files for three compounds can be found in the Supporting Information, or the crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal and Structure Refinement Data for **1-de($CoCl_2$)$_3$** and **2** (Squeezed)

	1-de($CoCl_2$)$_3$	**2**
Empirical formula	$Co_{11}C_{88}H_{60}Cl_6N_{48}O_4$	$Co_{11}Cd_6C_{93.25}H_{72}Cl_{18}N_{49.75}O_{5.75}$
Formula weight	2714.77	3945.21
Crystal system	Triclinic	Monoclinic
Space group	*P-1*	*P21/n*
a (Å)	14.817 (2)	22.5985 (6)
b (Å)	17.216 (2)	19.7687 (5)
c (Å)	32.637 (5)	33.4937 (10)
α (°)	85.312(2)	90.00
β (°)	83.893 (2)	98.555 (5)
γ (°)	72.737 (2)	90.00
V/(Å ^{3})	7894.7 (19)	14796.6 (7)
Z	2	4
D_c (Mg m^{-3})	1.142	1.770

$F(000)$	2710	7661
Reflections collected / unique	78920/29084	103273/27043
R_{int}	0.0662	0.0999
Goodness-of-fit on F^2	1.042	1.027
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0622$ $\omega R_2 = 0.0833$	$R_1 = 0.0926$ $\omega R_2 = 0.2552$
R indices (all data)	$R_1 = 0.0884$ $\omega R_2 = 0.1916$	$R_1 = 0.1309$ $\omega R_2 = 0.2907$

Table S2. Selected bond lengths (Å) and angles (°) of **1-de($CoCl_2$)$_3$** and **2**.

1-de($CoCl_2$)$_3$			
Atomic Distances [Å]			
Co1—O1	2.104 (3)	Co6—Cl3	2.186 (3)
Co1—O3	2.115 (3)	Co6—Cl4	2.206 (2)
Co1—O4	2.077 (3)	Co6—N42	2.030 (4)
Co1—N4	2.250 (4)	Co6—N45	2.049 (4)
Co1—N22	2.180 (4)	Co7—N31	2.046 (4)
Co1—N46	2.242 (4)	Co7—N32	2.223 (4)
Co2—O2	2.098 (3)	Co7—N33	2.223 (4)
Co2—O3	2.121 (3)	Co7—N35	2.056 (4)
Co2—O4	2.092 (3)	Co7—N41	2.227 (4)

Co2—N30	2.210 (4)	Co7—N43	2.047 (4)
Co2—N36	2.220 (4)	Co8—Cl1	2.200 (3)
Co2—N44	2.245 (4)	Co8—Cl2	2.2302 (19)
Co3—O1	2.098 (3)	Co8—N34	2.035 (4)
Co3—O2	2.089 (3)	Co8—N37	2.044 (4)
Co3—O4	2.154 (3)	Co9—N15	2.085 (4)
Co3—N6	2.229 (4)	Co9—N16	2.213 (4)
Co3—N12	2.247 (4)	Co9—N17	2.212 (5)
Co3—N28	2.189 (4)	Co9—N19	2.058 (4)
Co4—O1	2.133 (3)	Co9—N39	2.041 (4)
Co4—O2	2.127 (3)	Co9—N40	2.291 (4)
Co4—O3	2.083 (3)	Co10—N7	2.089 (4)
Co4—N14	2.150 (4)	Co10—N8	2.307 (5)
Co4—N20	2.221 (4)	Co10—N9	2.238 (5)
Co4—N38	2.320 (4)	Co10—N11	2.067 (4)
Co5—N1	2.231 (5)	Co10—N25	2.213 (5)
Co5—N3	2.058 (4)	Co10—N27	2.070 (4)
Co5—N23	2.042 (4)	Co11—Cl5	2.211 (3)
Co5—N24	2.219 (5)	Co11—Cl6	2.201 (2)
Co5—N47	2.074 (4)	Co11—N2	2.036 (4)
Co5—N48	2.211 (5)	Co11—N5	2.042 (5)

Bond Angles [°]

O1—Co1—O3	82.22 (12)	N24—Co5—N1	92.78 (18)
O1—Co1—N4	94.59 (13)	N47—Co5—N1	112.33 (18)
O1—Co1—N22	94.61 (14)	N47—Co5—N24	151.98 (18)
O1—Co1—N46	174.58 (13)	N47—Co5—N48	74.89 (16)
O3—Co1—N4	171.27 (14)	N48—Co5—N1	92.60 (18)
O3—Co1—N22	97.17 (14)	N48—Co5—N24	92.42 (18)
O3—Co1—N46	92.73 (13)	Cl3—Co6—Cl4	112.05 (13)
O4—Co1—O1	81.55 (12)	N42—Co6—Cl3	111.74 (16)
O4—Co1—O3	81.78 (12)	N42—Co6—Cl4	117.84 (15)
O4—Co1—N4	89.73 (14)	N42—Co6—N45	81.35 (16)
O4—Co1—N22	176.11 (14)	N45—Co6—Cl3	112.33 (16)
O4—Co1—N46	95.82 (14)	N45—Co6—Cl4	118.24 (16)
N22—Co1—N4	91.17 (15)	N31—Co7—N32	76.29 (16)
N22—Co1—N46	87.96 (15)	N31—Co7—N33	112.66 (16)
N46—Co1—N4	90.12 (15)	N31—Co7—N35	85.85 (17)
O2—Co2—O3	80.91 (13)	N31—Co7—N41	150.41 (17)
O2—Co2—N30	97.81 (14)	N31—Co7—N43	84.90 (16)
O2—Co2—N36	92.50 (14)	N32—Co7—N41	90.97 (16)
O2—Co2—N44	171.14 (14)	N33—Co7—N32	93.69 (16)
O3—Co2—N30	173.51 (13)	N33—Co7—N41	94.49 (15)
O3—Co2—N36	96.53 (13)	N35—Co7—N32	153.85 (17)
O3—Co2—N44	90.26 (13)	N35—Co7—N33	75.56 (16)

O4—Co2—O2	82.45 (12)	N35—Co7—N41	113.30 (16)
O4—Co2—O3	81.29 (12)	N43—Co7—N32	111.17 (17)
O4—Co2—N30	92.24 (14)	N43—Co7—N33	152.77 (16)
O4—Co2—N36	174.75 (14)	N43—Co7—N35	85.64 (16)
O4—Co2—N44	96.95 (13)	N43—Co7—N41	74.85 (15)
N30—Co2—N36	89.87 (15)	Cl1—Co8—Cl2	114.36 (11)
N30—Co2—N44	91.05 (14)	N34—Co8—Cl1	115.66 (15)
N36—Co2—N44	87.81 (14)	N34—Co8—Cl2	112.46 (14)
O1—Co3—O4	79.88 (12)	N34—Co8—N37	80.73 (16)
O1—Co3—N6	93.71 (13)	N37—Co8—Cl1	114.07 (16)
O1—Co3—N12	92.19 (13)	N37—Co8—Cl2	115.38 (14)
O1—Co3—N28	172.71 (14)	N15—Co9—N16	76.07 (16)
O2—Co3—O1	82.31 (12)	N15—Co9—N17	149.09 (17)
O2—Co3—O4	81.17 (12)	N15—Co9—N40	112.54 (17)
O2—Co3—N6	175.18 (15)	N16—Co9—N40	87.99 (16)
O2—Co3—N12	92.86 (14)	N17—Co9—N16	89.64 (18)
O2—Co3—N28	96.69 (14)	N17—Co9—N40	93.84 (16)
O4—Co3—N6	95.49 (14)	N19—Co9—N15	84.89 (17)
O4—Co3—N12	170.61 (13)	N19—Co9—N16	115.10 (17)
O4—Co3—N28	92.83 (14)	N19—Co9—N17	76.49 (16)
N6—Co3—N12	90.00 (15)	N19—Co9—N40	154.48 (17)
N28—Co3—N6	86.91 (15)	N39—Co9—N15	84.48 (16)

N28—Co3—N12	95.07 (15)	N39—Co9—N16	146.84 (18)
O1—Co4—N14	96.59 (13)	N39—Co9—N17	119.16 (17)
O1—Co4—N20	94.49 (13)	N39—Co9—N19	89.12 (16)
O1—Co4—N38	171.55 (13)	N39—Co9—N40	74.89 (15)
O2—Co4—O1	80.60 (12)	N7—Co10—N8	74.55 (17)
O2—Co4—N14	96.01 (14)	N7—Co10—N9	116.32 (18)
O2—Co4—N20	172.52 (14)	N7—Co10—N25	145.88 (18)
O2—Co4—N38	92.08 (13)	N9—Co10—N8	88.94 (19)
O3—Co4—O1	82.29 (12)	N11—Co10—N7	86.67 (17)
O3—Co4—O2	81.11 (13)	N11—Co10—N8	148.72 (18)
O3—Co4—N14	177.03 (14)	N11—Co10—N9	77.09 (17)
O3—Co4—N20	92.70 (14)	N11—Co10—N25	120.02 (18)
O3—Co4—N38	92.47 (13)	N11—Co10—N27	87.51 (16)
N14—Co4—N20	90.13 (15)	N25—Co10—N8	87.82 (18)
N14—Co4—N38	88.32 (15)	N25—Co10—N9	91.77 (17)
N20—Co4—N38	92.37 (14)	N27—Co10—N7	85.00 (17)
N3—Co5—N1	74.79 (17)	N27—Co10—N8	114.82 (18)
N3—Co5—N24	113.21 (18)	N27—Co10—N9	152.4 (2)
N3—Co5—N47	86.32 (17)	N27—Co10—N25	76.12 (16)
N3—Co5—N48	151.56 (18)	Cl6—Co11—Cl5	113.64 (11)
N23—Co5—N1	151.28 (19)	N2—Co11—Cl5	115.77 (17)
N23—Co5—N3	85.18 (17)	N2—Co11—Cl6	115.58 (16)

N23—Co5—N24	76.22 (17)	N2—Co11—N5	80.36 (18)
N23—Co5—N47	86.15 (17)	N5—Co11—Cl5	110.55 (17)
N23—Co5—N48	114.01 (18)	N5—Co11—Cl6	116.89 (17)

2 Symmetry code: (A) -x+1, -y+1, -z; (B) -x+3/2, y-1/2, -z-1/2; (C) -x+2, -y+1, -z; (D) -x+3/2, y+1/2, -z-1/2.

Atomic Distances [Å]

Cd1—Cl8	2.403 (4)	Co2—N38	2.273 (9)
Cd1—Cl9	2.589 (3)	Co3—O1	2.105 (7)
Cd1—Cl10	2.543 (3)	Co3—O3	2.116 (7)
Cd1—N2	2.340 (9)	Co3—O4	2.085 (7)
Cd1—N5	2.332 (9)	Co3—N14	2.259 (9)
Cd2—Cl9	2.558 (3)	Co3—N20	2.235 (9)
Cd2—Cl10	2.661 (4)	Co3—N28	2.191 (8)
Cd2—Cl11	2.371 (12)	Co4—O1	2.086 (7)
Cd2—N42A	2.385 (9)	Co4—O2	2.128 (7)
Cd2—N45A	2.328 (9)	Co4—O3	2.119 (7)
Cd2—O5	2.284 (11)	Co4—N30	2.217 (8)
Cd3—Cl5	2.421 (4)	Co4—N36	2.189 (9)
Cd3—Cl6	2.553 (5)	Co4—N46	2.245 (8)
Cd3—N26	2.334 (10)	Co5—N7	2.052 (9)
Cd3—N29	2.331 (9)	Co5—N8	2.173 (9)
Cd3—O6	2.58 (3)	Co5—N9	2.224 (10)

Cd3—O7	2.23 (3)	Co5—N11	2.077 (9)
Cd3—O7'	2.31 (3)	Co5—N41	2.223 (11)
Cd4—Cl1	2.651 (8)	Co5—N43	2.058 (9)
Cd4—Cl2	2.292 (12)	Co6—N1	2.212 (10)
Cd4—Cl3	2.514 (5)	Co6—N3	2.065 (9)
Cd4—N10	2.348 (10)	Co6—N23	2.060 (10)
Cd4—N13	2.348 (10)	Co6—N24	2.197 (11)
Cd4—Cl4	2.642 (10)	Co6—N39	2.054 (11)
Cd4—Cl4'	2.634 (8)	Co6—N40	2.214 (11)
Cd5—Cl12	2.562 (4)	Co7—N15	2.042 (10)
Cd5—Cl13	2.443 (5)	Co7—N16	2.173 (10)
Cd5—N34	2.362 (10)	Co7—N17	2.180 (10)
Cd5—N37	2.351 (11)	Co7—N19	2.061 (10)
Cd5—Cl14	2.619 (10)	Co7—N25	2.266 (11)
Cd5—Cl15	2.516 (9)	Co7—N27	2.075 (10)
Cd6B—Cl3	2.444 (7)	Co8—N31	2.055 (9)
Cd6'B—Cl3	2.564 (6)	Co8—N32	2.185 (9)
Cd6C—Cl12	2.567 (5)	Co8—N33	2.190 (11)
Cd6'C—Cl12	2.706 (5)	Co8—N35	2.075 (10)
Cd6'—Cl24	2.26 (3)	Co8—N47	2.045 (8)
Co1—O1	2.105 (6)	Co8—N48	2.227 (11)
Co1—O2	2.085 (7)	Co9—Cl1B	2.411 (11)

Co1—O4	2.089 (7)	Co9—Cl6	2.308 (6)
Co1—N6	2.249 (8)	Co9—Cl7	2.324 (10)
Co1—N12	2.254 (8)	Co9—Cl4'B	2.505 (9)
Co1—N44	2.200 (8)	Co10—Cl13	2.527 (7)
Co2—O2	2.101 (7)	Co10—Cl16	2.52 (2)
Co2—O3	2.078 (7)	Co10—Cl17	2.678 (9)
Co2—O4	2.132 (7)	Co11—Cl17	2.381 (7)
Co2—N4	2.201 (9)	Co12—Cl17	2.612 (10)
Co2—N22	2.248 (9)	Co12—Cl22	2.69 (3)
Bond Angles [°]			
Cl8—Cd1—Cl9	109.07 (14)	O7'—Cd3—Cl5	99.1 (9)
Cl8—Cd1—Cl10	111.23 (14)	O7'—Cd3—Cl6	96.5 (8)
Cl10—Cd1—Cl9	88.26 (11)	O7'—Cd3—N26	86.6 (9)
N2—Cd1—Cl8	112.6 (2)	O7'—Cd3—N29	149.6 (10)
N2—Cd1—Cl9	86.7 (2)	Cl12—Cd5—Cl14	86.9 (2)
N2—Cd1—Cl10	135.1 (2)	Cl13—Cd5—Cl12	119.75 (19)
N5—Cd1—Cl8	106.5 (3)	Cl13—Cd5—Cl14	123.2 (4)
N5—Cd1—Cl9	142.7 (2)	Cl13—Cd5—Cl15	111.2 (3)
N5—Cd1—Cl10	89.0 (2)	N34—Cd5—Cl12	88.2 (3)
N5—Cd1—N2	69.6 (3)	N34—Cd5—Cl13	102.8 (3)
Cl9—Cd2—Cl10	86.40 (11)	N34—Cd5—Cl14	129.1 (4)
Cl11—Cd2—Cl9	87.3 (3)	N34—Cd5—Cl15	145.7 (4)

Cl11—Cd2—Cl10	172.1 (3)	N37—Cd5—Cl12	136.1 (3)
Cl11—Cd2—N42A	94.9 (4)	N37—Cd5—Cl13	102.1 (3)
N42A—Cd2—Cl9	111.1 (2)	N37—Cd5—N34	69.0 (3)
N42A—Cd2—Cl10	82.9 (2)	N37—Cd5—Cl14	80.4 (3)
N45A—Cd2—Cl9	175.5 (2)	N37—Cd5—Cl15	98.7 (4)
N45A—Cd2—Cl10	97.4 (2)	Cl15—Cd5—Cl12	79.1 (3)
N45A—Cd2—Cl11	89.1 (3)	Cl3D—Cd6—Cl12C	91.6 (2)
N45A—Cd2—N42A	71.9 (3)	Cl3D—Cd6—N18	89.1 (3)
O5—Cd2—Cl9	87.3 (3)	Cl3D—Cd6—Cl4D	70.1 (3)
O5—Cd2—Cl10	88.6 (3)	Cl12C—Cd6—Cl4D	87.9 (3)
O5—Cd2—Cl11	95.9 (4)	N18—Cd6—Cl12C	156.6 (3)
O5—Cd2—N42i	159.1 (3)	N18—Cd6—Cl4D	114.2 (3)
O5—Cd2—N45i	90.4 (3)	N21—Cd6—Cl3D	130.6 (4)
Cl5—Cd3—Cl6	105.88 (18)	N21—Cd6—Cl12C	124.4 (4)
Cl5—Cd3—O6	174.7 (9)	N21—Cd6—N18	70.6 (4)
Cl6—Cd3—O6	78.8 (8)	N21—Cd6—Cl4D	77.9 (4)
N26—Cd3—Cl5	104.7 (3)	Cl3D—Cd6'—Cl12C	85.91 (18)
N26—Cd3—Cl6	148.3 (3)	Cl24—Cd6'—Cl3D	84.5 (7)
N26—Cd3—O6	71.0 (8)	Cl24—Cd6'—Cl12C	90.5 (8)
N29—Cd3—Cl5	105.2 (3)	Cl24—Cd6'—N18	93.4 (8)
N29—Cd3—Cl6	94.1 (3)	Cl24—Cd6'—N21	155.7 (8)
N29—Cd3—N26	69.9 (3)	N18—Cd6'—Cl3D	91.8 (3)

N29—Cd3—O6	76.6 (9)	N18—Cd6'—Cl12C	175.3 (3)
O7—Cd3—Cl5	117.3 (9)	N18—Cd6'—N21	69.5 (4)
O7—Cd3—Cl6	92.9 (9)	N21—Cd6'—Cl3D	112.1 (3)
O7—Cd3—N26	80.2 (10)	N21—Cd6'—Cl12C	107.6 (3)
O7—Cd3—N29	133.0 (9)	Cl15C—Cd6'—N18	102.2 (4)
O7—Cd3—O6	59.4 (13)	Cl15C—Cd6'—N21	100.5 (5)
O1—Co1—N6	171.1 (3)	N43—Co5—N8	148.3 (4)
O1—Co1—N12	92.4 (3)	N43—Co5—N9	112.1 (4)
O1—Co1—N44	96.7 (3)	N43—Co5—N11	84.3 (3)
O2—Co1—O1	81.8 (3)	N43—Co5—N41	74.8 (3)
O2—Co1—O4	81.4 (3)	N1—Co6—N40	89.8 (4)
O2—Co1—N6	94.1 (3)	N3—Co6—N1	75.8 (4)
O2—Co1—N12	174.1 (3)	N3—Co6—N24	147.8 (5)
O2—Co1—N44	93.1 (3)	N3—Co6—N40	115.8 (4)
O4—Co1—O1	81.3 (3)	N23—Co6—N1	114.1 (4)
O4—Co1—N6	90.2 (3)	N23—Co6—N3	84.4 (3)
O4—Co1—N12	96.8 (3)	N23—Co6—N24	75.2 (4)
O4—Co1—N44	174.4 (3)	N23—Co6—N40	152.6 (4)
N6—Co1—N12	91.5 (3)	N24—Co6—N1	90.0 (4)
N44—Co1—N6	91.4 (3)	N24—Co6—N40	92.5 (5)
N44—Co1—N12	88.6 (3)	N39—Co6—N1	149.5 (4)
O2—Co2—O4	80.1 (3)	N39—Co6—N3	86.1 (4)

O2—Co2—N4	96.0 (3)	N39—Co6—N23	87.7 (4)
O2—Co2—N22	173.5 (3)	N39—Co6—N24	117.1 (4)
O2—Co2—N38	92.0 (3)	N39—Co6—N40	76.1 (4)
O3—Co2—O2	82.5 (3)	N15—Co7—N16	76.4 (4)
O3—Co2—O4	81.4 (3)	N15—Co7—N17	118.4 (4)
O3—Co2—N4	176.0 (3)	N15—Co7—N19	86.7 (4)
O3—Co2—N22	92.3 (3)	N15—Co7—N25	150.7 (4)
O3—Co2—N38	94.1 (3)	N15—Co7—N27	86.2 (4)
O4—Co2—N4	94.7 (3)	N16—Co7—N17	92.6 (4)
O4—Co2—N22	95.3 (3)	N16—Co7—N25	91.6 (4)
O4—Co2—N38	171.3 (3)	N17—Co7—N25	88.3 (4)
N4—Co2—N22	89.0 (3)	N19—Co7—N16	152.8 (4)
N4—Co2—N38	89.7 (3)	N19—Co7—N17	76.8 (4)
N22—Co2—N38	92.3 (3)	N19—Co7—N25	112.7 (4)
O1—Co3—O3	81.7 (3)	N19—Co7—N27	84.6 (4)
O1—Co3—N14	90.3 (3)	N27—Co7—N16	114.8 (4)
O1—Co3—N20	172.7 (3)	N27—Co7—N17	147.6 (4)
O1—Co3—N28	97.6 (3)	N27—Co7—N25	74.6 (4)
O3—Co3—N14	172.0 (3)	N31—Co8—N32	76.7 (3)
O3—Co3—N20	95.7 (3)	N31—Co8—N33	149.6 (4)
O3—Co3—N28	92.3 (3)	N31—Co8—N35	84.6 (4)
O4—Co3—O1	81.5 (3)	N31—Co8—N48	114.5 (4)

O4—Co3—O3	81.6 (3)	N32—Co8—N33	91.3 (4)
O4—Co3—N14	96.2 (3)	N32—Co8—N48	89.2 (4)
O4—Co3—N20	91.4 (3)	N33—Co8—N48	92.8 (4)
O4—Co3—N28	174.0 (3)	N35—Co8—N32	116.7 (4)
N20—Co3—N14	92.1 (3)	N35—Co8—N33	75.9 (4)
N28—Co3—N14	89.7 (3)	N35—Co8—N48	151.5 (4)
N28—Co3—N20	89.3 (3)	N47—Co8—N31	84.9 (3)
O1—Co4—O2	81.2 (3)	N47—Co8—N32	148.7 (4)
O1—Co4—O3	82.0 (3)	N47—Co8—N33	116.2 (4)
O1—Co4—N30	95.0 (3)	N47—Co8—N35	86.0 (4)
O1—Co4—N36	175.7 (3)	N47—Co8—N48	75.6 (3)
O1—Co4—N46	90.5 (3)	Cl1B—Co9—Cl4'B	91.3 (3)
O2—Co4—N30	172.0 (3)	Cl6—Co9—Cl1B	110.3 (3)
O2—Co4—N36	94.4 (3)	Cl6—Co9—Cl7	114.1 (3)
O2—Co4—N46	94.9 (3)	Cl6—Co9—Cl4'B	114.1 (3)
O3—Co4—O2	80.9 (3)	Cl7—Co9—Cl1B	113.6 (4)
O3—Co4—N30	91.6 (3)	Cl7—Co9—Cl4'B	111.4 (4)
O3—Co4—N36	97.2 (3)	Cl13—Co10—Cl17	101.3 (2)
O3—Co4—N46	171.9 (3)	Cl16—Co10—Cl13	120.4 (6)
N30—Co4—N46	92.1 (3)	Cl16—Co10—Cl17	89.7 (5)
N36—Co4—N30	89.3 (3)	Cl17—Co11—Cl20	105.6 (5)
N36—Co4—N46	90.0 (3)	Cl17—Co11—Cl19	117.8 (3)

N7—Co5—N8	76.5 (3)	Cl18—Co11—Cl17	110.1 (5)
N7—Co5—N9	153.6 (4)	Cl18—Co11—Cl20	101.5 (7)
N7—Co5—N11	88.0 (4)	Cl18—Co11—Cl19	120.9 (4)
N7—Co5—N41	115.8 (4)	Cl19—Co11—Cl20	97.1 (5)
N7—Co5—N43	85.7 (3)	Cl17—Co12—Cl22	96.6 (7)
N8—Co5—N9	94.3 (4)	Cl17—Co12—Cl21	96.7 (9)
N8—Co5—N41	89.4 (4)	Cl21—Co12—Cl22	132.4 (10)
N11—Co5—N8	120.5 (4)	Cl23—Co12—Cl22	91.2 (11)
N11—Co5—N9	75.3 (3)	Cl23—Co12—Cl17	114.3 (9)
N11—Co5—N41	146.4 (4)	Cl23—Co12—Cl21	123.4 (13)
N41—Co5—N9	88.4 (4)		

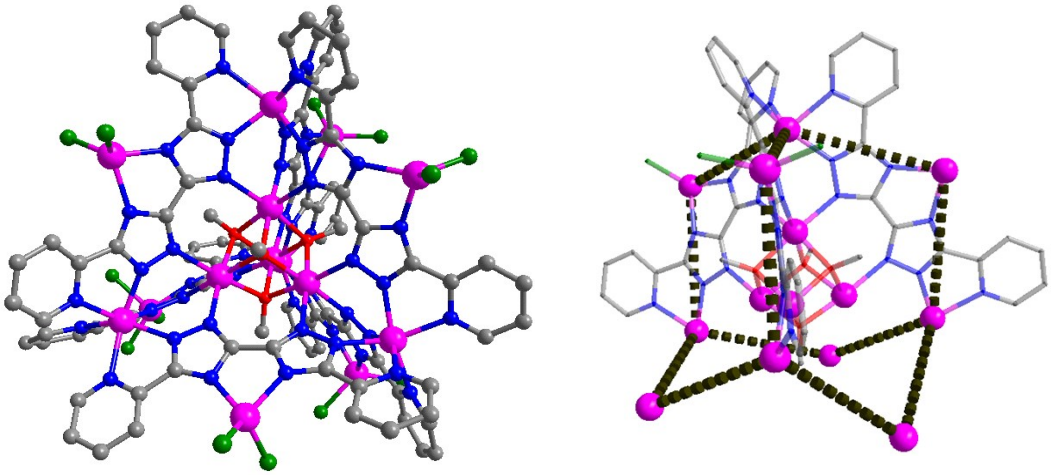


Figure S4. The molecular structure and the [Co_4O_4 cubic alkane ⊂Co_{10} adamantane] skeleton of **1**.

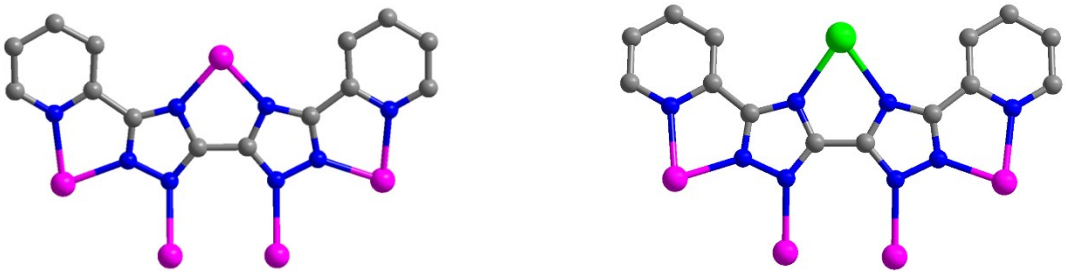


Figure S5. The coordination pattern of ligand in **1-de($CoCl_2$)$_3$** (left) and **2** (right).

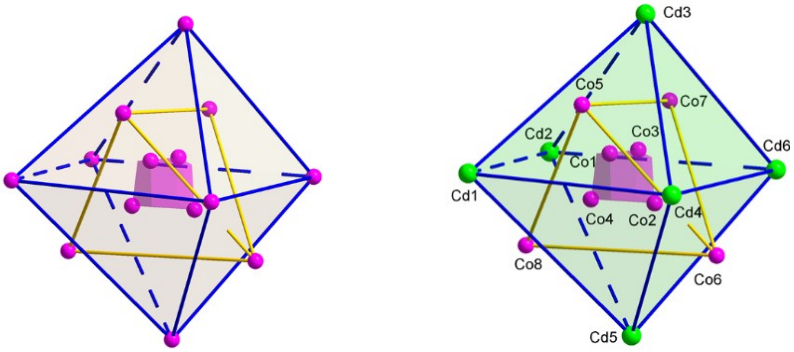


Figure S6. the metal frame diagram of [Co_4⊂Co_4⊂M_6 (M=Co for **1** (left), and M=Cd for **2** (right)].

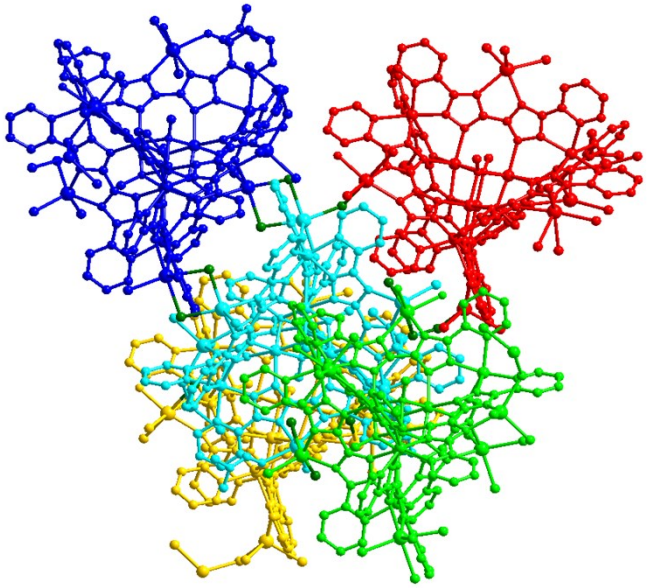


Figure S7. The 3-D cluster-based MOFs structure of **2**;

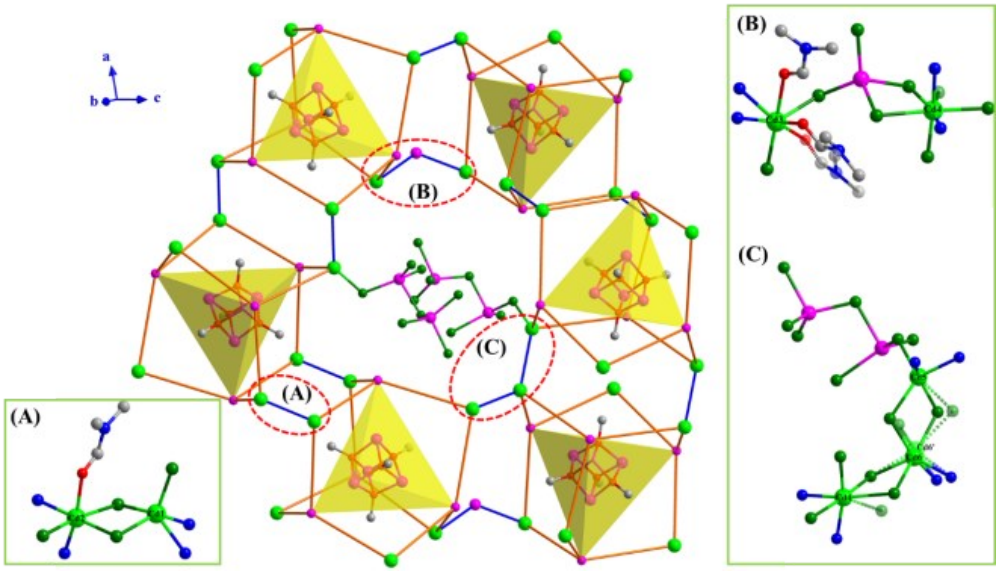


Figure S8. The schematic diagram of main framework shown the connected modes and the coordination environment of rest Co(II) atoms.

3. Measurement Details

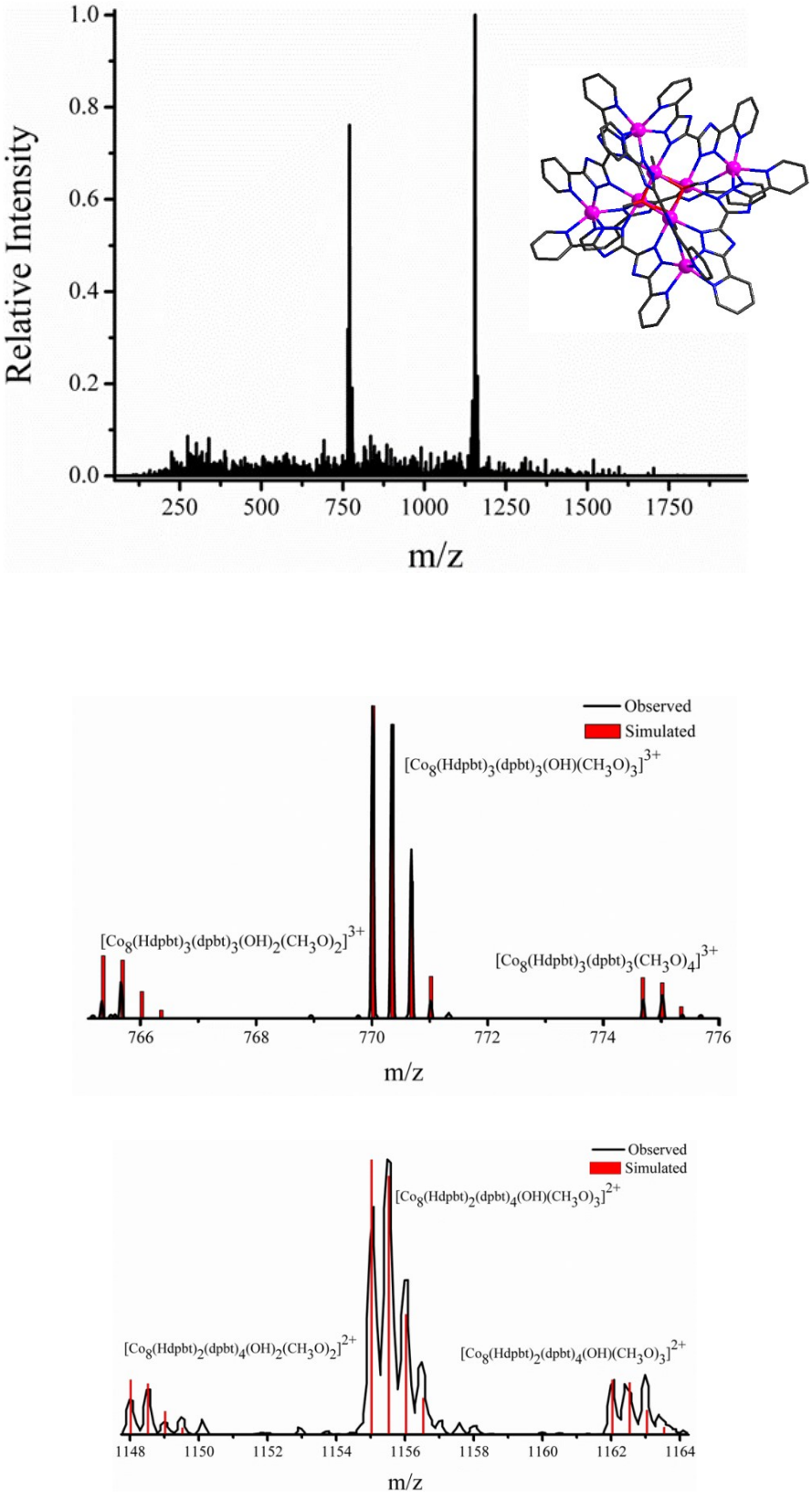


Figure S9. Positive HRESI-MS spectra of {Co_{14}} precursor in DMF (In-Source CID

= 0 eV) and schematic diagram of the {Co_8} core structure.

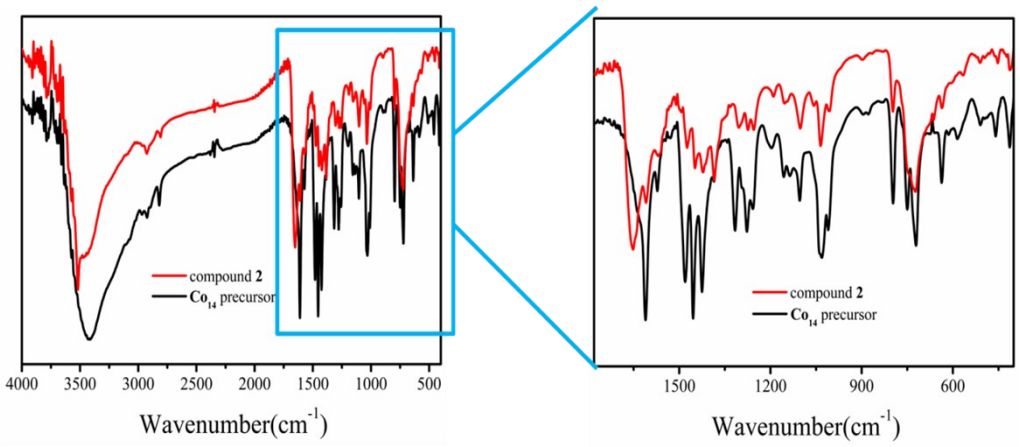


Figure S10. Comparison chart of infrared spectrum and local comparison chart of {Co_{14}} precursor with compound **1** and **2**.

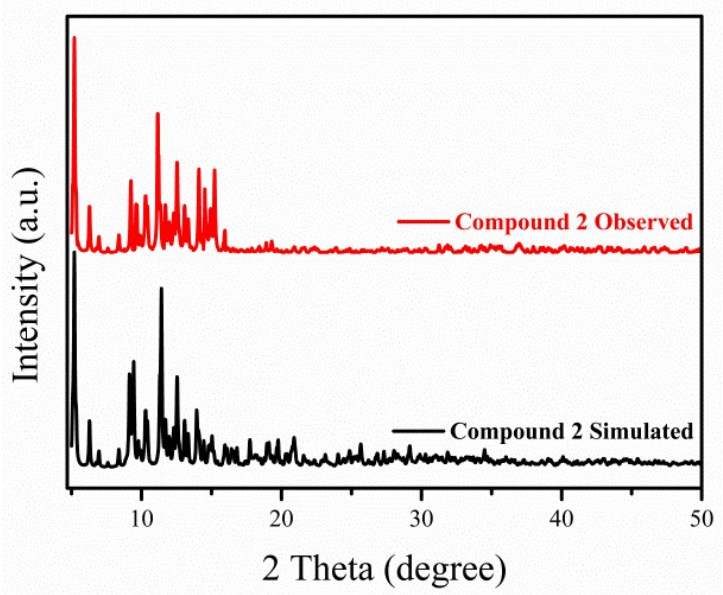
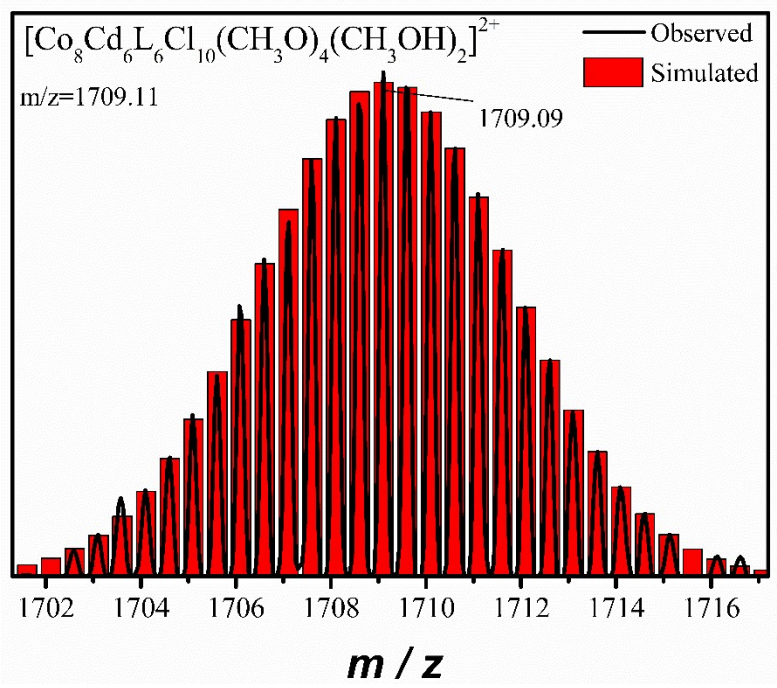


Figure S11. X-ray powder diffraction patterns of **2**

Table S3. Major species assigned in the HRESI-MS of compound **2** in positive mode.

Compound **2** (In-Source CID 0 eV)			
	Peaks	Obs. m/z	Calc. m/z
$[Co_8Cd_6]$-a	$[Co_8Cd_6L_6Cl_{10}(CH_3O)_4(CH_3OH)_2]^{2+}$	1709.09	1709.11
$[Co_8Cd_6]$-b	$[Co_8Cd_6L_6Cl_9(CH_3O)_4(CH_3CN)(CH_3CH_2OH)]^{3+}$	1150.44	1150.43
$[Co_8Cd_6]$-c	$[Co_8Cd_6L_6Cl_9(CH_3O)_4(H_2O)_2]^{3+}$	1118.40	1118.40
Compound **2** (In-Source CID 20 eV)			
	Peaks	Obs. m/z	Calc. m/z
$[Co_8Cd_6]$-a	$[Co_8Cd_6L_6Cl_{10}(CH_3O)_4(CH_3OH)_2]^{2+}$	1709.10	1709.11
$[Co_8Cd_6]$-b	$[Co_8Cd_6L_6Cl_9(CH_3O)_4(CH_3CN)(CH_3CH_2OH)]^{3+}$	1150.44	1150.43
$[Co_8Cd_5]$-a	$[Co_8Cd_5L_6Cl_8(CH_3O)_4(H_2O)(CH_3CN)]^{2+}$	1614.19	1614.18
$[Co_8Cd_5]$-b	$[Co_8Cd_5L_6Cl_8(CH_3O)_4(DMF)(CH_3OH)(CH_3CN)]^{2+}$	1658.72	1658.71
	$[Co_8Cd_5L_6Cl_8(CH_3O)_4(H_2O)(DMF)(CH_3CN)]^{2+}$	1651.68	1651.71
$[Co_8Cd_5]$-c	$[Co_8Cd_5L_6Cl_7(CH_3O)_4(DMF)(CH_3OH)_2(CH_3CN)]^{3+}$	1114.15	1114.17
	$[Co_8Cd_5L_6Cl_7(CH_3O)_4(H_2O)_2(CH_3OH)(CH_3CN)_2]^{3+}$	1095.16	1095.16
	$[Co_8Cd_5L_6Cl_7(CH_3O)_4(H_2O)(CH_3OH)(CH_3CN)_2]^{3+}$	1089.16	1089.15
	$[Co_8Cd_5L_6Cl_7(CH_3O)_4(H_2O)_2(CH_3CN)_2]^{3+}$	1084.49	1084.47
$[Co_8Cd_5]$-d	$[Co_8Cd_5L_6Cl_7(CH_3O)_4(H_2O)(CH_3CN)]^{3+}$	1064.80	1064.79
	$[Co_8Cd_5L_6Cl_7(CH_3O)_4(H_2O)_2]^{3+}$	1057.21	1057.22
Compound **2** (In-Source CID 40 eV)			
	Peaks	Obs. m/z	Calc. m/z
$[Co_8Cd_6]$-a	$[Co_8Cd_6L_6Cl_{10}(CH_3O)_4(CH_3OH)_2]^{2+}$	1709.10	1709.11
$[Co_8Cd_5]$-a	$[Co_8Cd_5L_6Cl_8(CH_3O)_4(H_2O)(CH_3CN)]^{2+}$	1614.88	1615.18
$[Co_8Cd_5]$-b	$[Co_8Cd_5L_6Cl_8(CH_3O)_4(DMF)(CH_3OH)(CH_3CN)]^{2+}$	1658.73	1658.71
	$[Co_8Cd_5L_6Cl_8(CH_3O)_4(H_2O)(DMF)(CH_3CN)]^{2+}$	1651.68	1651.71
$[Co_8Cd_5]$-c	$[Co_8Cd_5L_6Cl_7(CH_3O)_4(DMF)(CH_3OH)_2(CH_3CN)]^{3+}$	1114.15	1114.17
$[Co_8Cd_4]$-a	$[Co_8Cd_4L_6Cl_6(OH)(CH_3O)_3(DMF)_2]^{2+}$	1523.26	1523.26
$[Co_8Cd_4]$-b	$[Co_8Cd_4L_6Cl_6(CH_3O)_4(DMF)_2]^{2+}$	1566.80	1566.79
$[Co_8Cd_4]$-c	$[Co_8Cd_4L_6Cl_5(CH_3O)_4(H_2O)(DMF)(CH_3CN)]^{3+}$	1028.20	1028.20

$[Co_8Cd_4]$-d	$[Co_8Cd_4L_6Cl_5(CH_3O)_4(H_2O)]^{3+}$	1003.85	1003.85
	$[Co_8Cd_4L_6Cl_5(CH_3O)_4(CH_3CH_2OH)]^{3+}$	996.17	996.18
Compound **2** (In-Source CID 60 eV)			
	Peaks	Obs. m/z	Calc. m/z
$[Co_8Cd_4]$-a	$[Co_8Cd_4L_6Cl_6(OH)(CH_3O)_3(DMF)_2]^{2+}$	1523.26	1523.26
$[Co_8Cd_4]$-b	$[Co_8Cd_4L_6Cl_6(CH_3O)_4(DMF)_2]^{2+}$	1566.80	1566.79
$[Co_8Cd_4]$-c	$[Co_8Cd_4L_6Cl_5(CH_3O)_4(H_2O)(DMF)(CH_3CN)]^{3+}$	1028.20	1028.20
$[Co_8Cd_3]$-a	$[Co_8Cd_3L_6Cl_4(CH_3O)_4(H_2O)(CH_3CN)]^{2+}$	1431.33	1431.34
$[Co_8Cd_3]$-b	$[Co_8Cd_3L_6Cl_4(CH_3O)_4(H_2O)(DMF)(CH_3OH)]^{2+}$	1495.36	1495.39
	$[Co_8Cd_3L_6Cl_4(CH_3O)_4(DMF)(CH_3OH)]^{2+}$	1486.42	1486.38
	$[Co_8Cd_3L_6Cl_4(CH_3O)_4(DMF)(CH_3OH)]^{2+}$	1475.37	1475.38
$[Co_8Cd_3]$-c	$[Co_8Cd_3L_6Cl_4(CH_3O)_4(OH)]^{2+}$	1394.79	1394.81
$[Co_8Cd_3]$-d	$[Co_8Cd_3L_6Cl_4(CH_3O)_3(OH)(DMF)(H_2O)_2]^{2+}$	1449.31	1449.35
Compound **2** (In-Source CID 80 eV)			
	Peaks	Obs. m/z	Calc. m/z
$[Co_8Cd_4]$-a	$[Co_8Cd_4L_6Cl_6(OH)(CH_3O)_3(DMF)_2]^{2+}$	1523.26	1523.26
$[Co_8Cd_4]$-b	$[Co_8Cd_4L_6Cl_6(CH_3O)_4(DMF)_2]^{2+}$	1566.80	1566.79
$[Co_8Cd_3]$-a	$[Co_8Cd_3L_6Cl_4(CH_3O)_4(H_2O)(CH_3CN)]^{2+}$	1431.33	1431.34
$[Co_8Cd_3]$-b	$[Co_8Cd_3L_6Cl_4(CH_3O)_4(DMF)(CH_3OH)]^{2+}$	1475.37	1475.38
$[Co_8Cd_2]$-a	$[Co_8Cd_2L_6Cl_2(CH_3O)_4(H_2O)_2(CH_3OH)_2]^{2+}$	1357.92	1357.94
$[Co_8Cd_2]$-b	$[Co_8Cd_2L_6Cl(CH_3O)_4(H_2O)(DMF)(CH_3OH)]^{3+}$	917.98	917.99
	$[Co_8Cd_2L_6Cl(CH_3O)_4(DMF)(CH_3OH)]^{3+}$	907.28	907.31
Compound **2** (In-Source CID 100 eV)			
	Peaks	Obs. m/z	Calc. m/z
$[Co_8Cd_2]$-a	$[Co_8Cd_2L_6Cl_2(CH_3O)_4(H_2O)_2(CH_3OH)_2]^{2+}$	1357.92	1357.94


[Co8Cd6L6Cl10(CH3O)4(CH3OH)2]2+
Observed
Simulated
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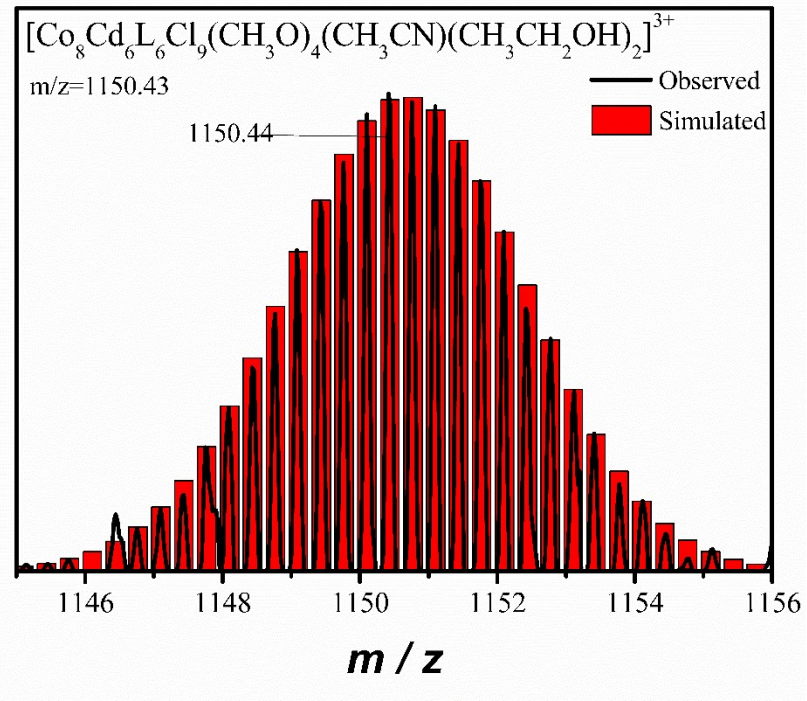
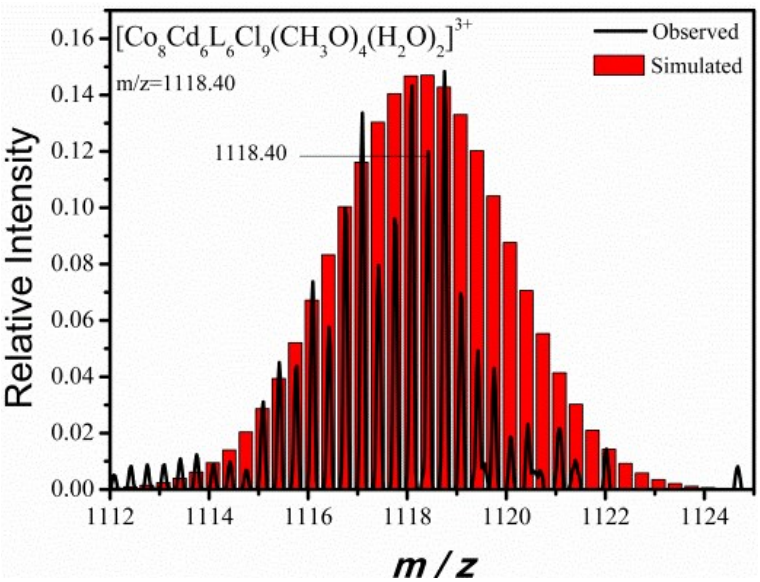
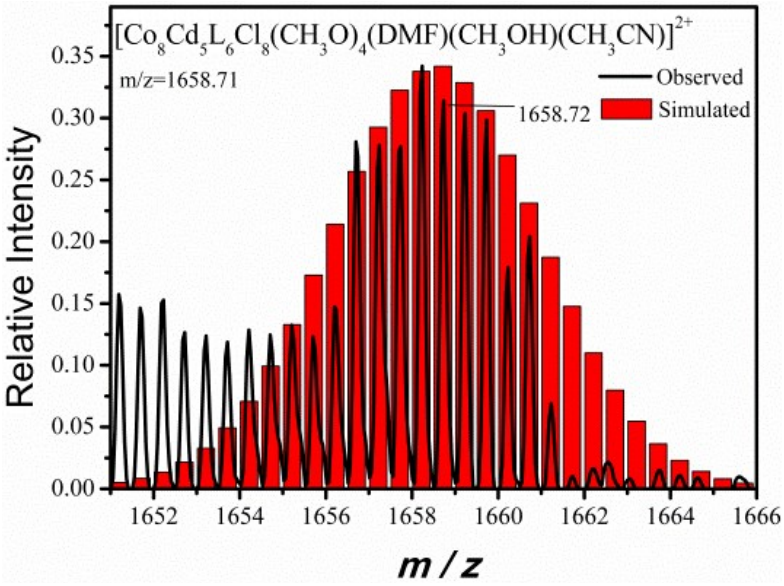
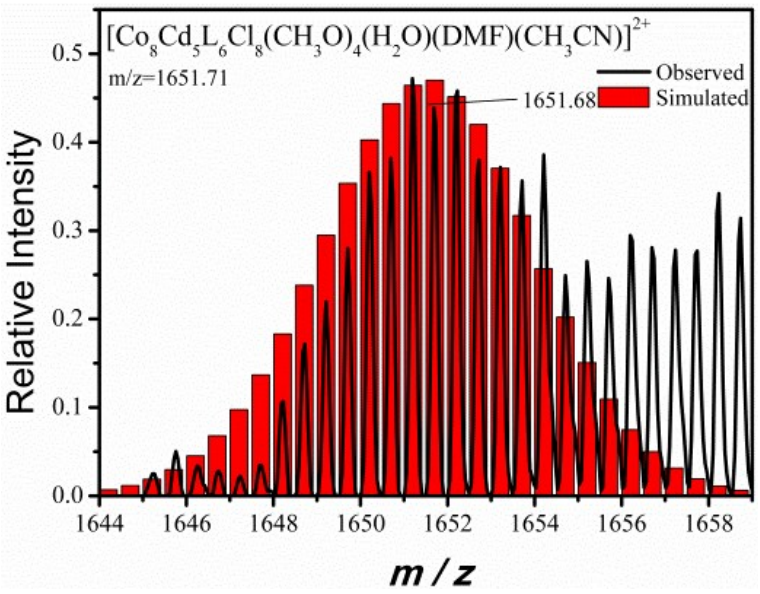
1709.09
1702
1704
1706
1708
1710
1712
1714
1716
m / z

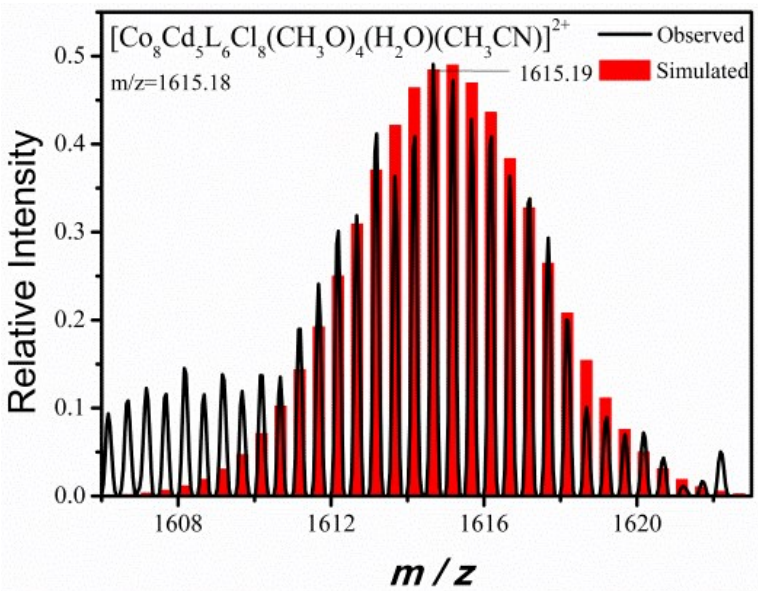

[Co8Cd6L6Cl9(CH3O)4(CH3CN)(CH3CH2OH)2]3+
m/z=1150.43
Observed
Simulated
1150.44
1146
1148
1150
1152
1154
1156
m / z

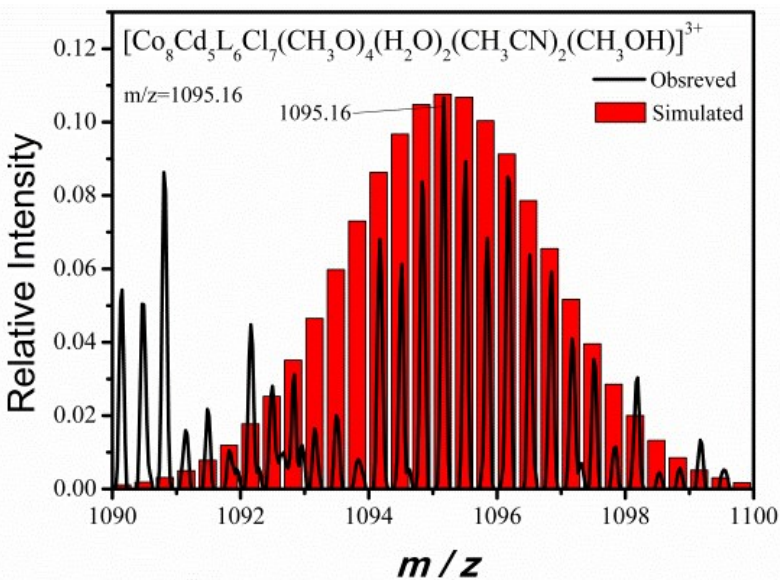


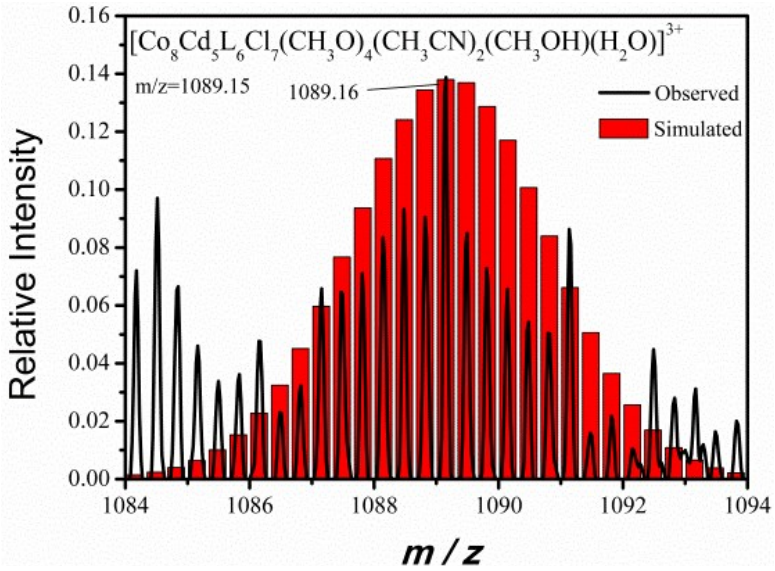
Peaks of cation fragment $\{Co_8Cd_5\}$

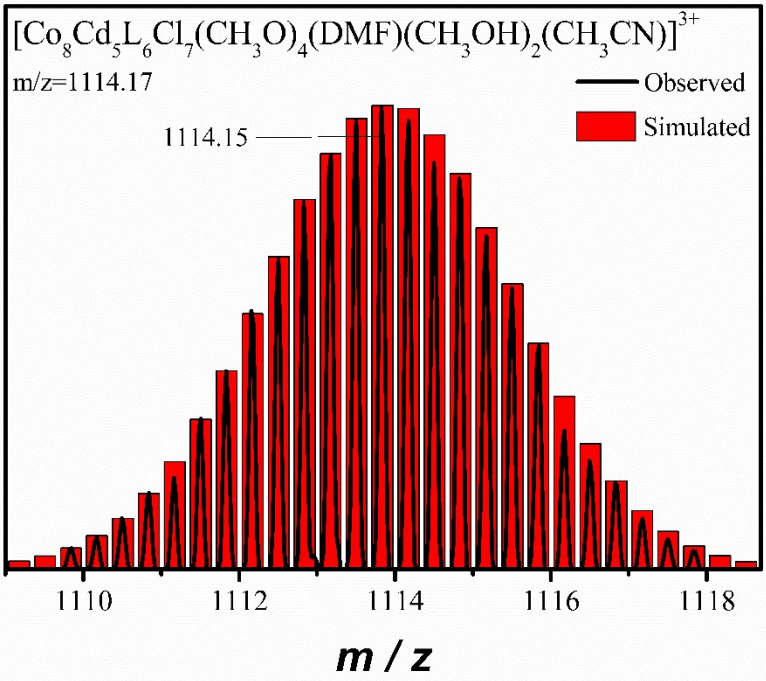


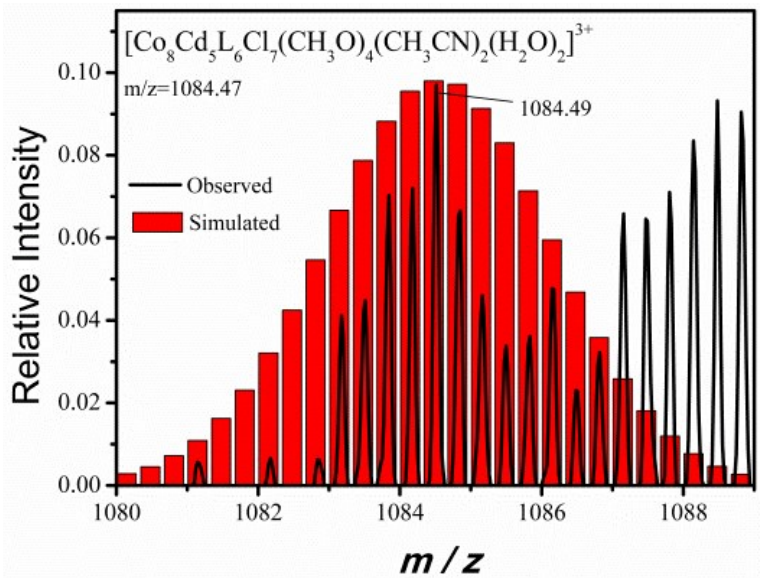

[Co8Cd5L6Cl8(CH3O)4(H2O)(DMF)(CH3CN)]2+
m/z=1651.71
Observed
Simulated
1651.68
Relative Intensity
m / z

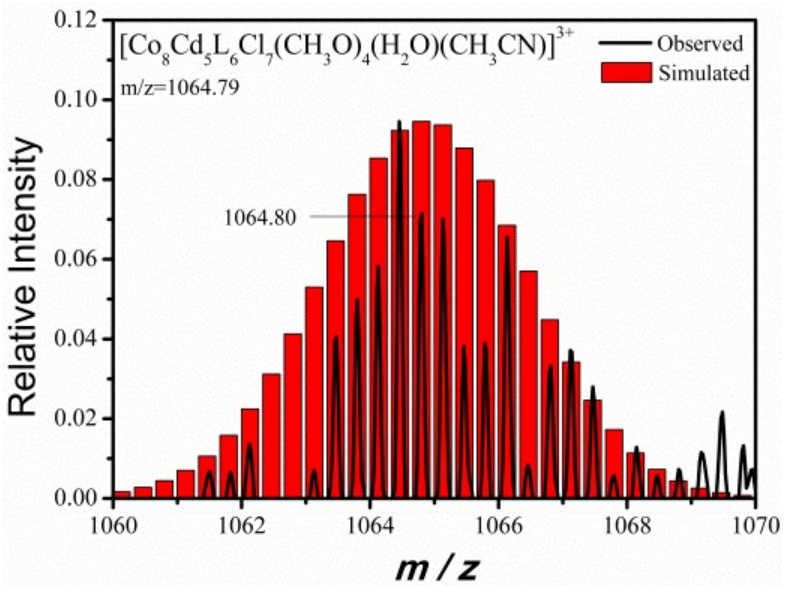

[Co8Cd5L6Cl8(CH3O)4(H2O)(CH3CN)]2+
m/z=1615.18
Observed
Simulated
1615.19
Relative Intensity
m / z

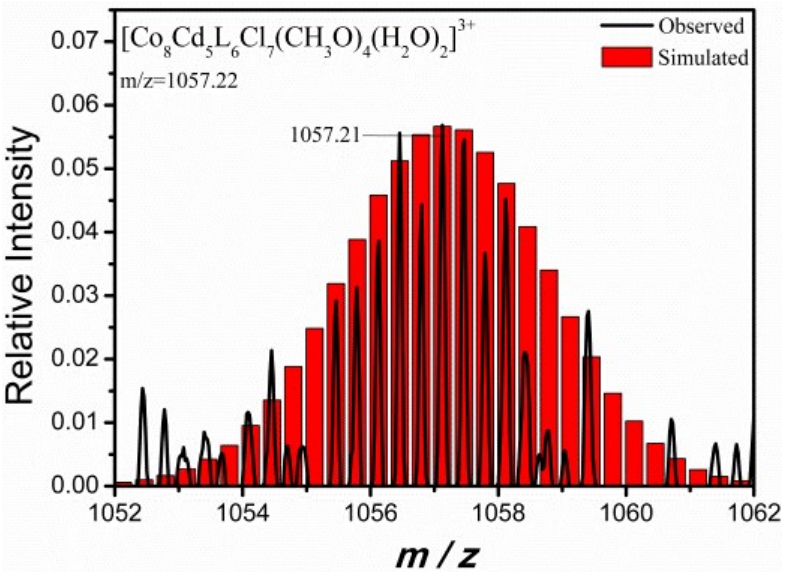

[Co8Cd5L6Cl7(CH3O)4(H2O)2(CH3CN)2(CH3OH)]3+
m/z=1095.16
Obsreved
Simulated
1095.16
Relative Intensity
m / z


[Co8Cd5L6Cl7(CH3O)4(CH3CN)2(CH3OH)(H2O)]3+
m/z=1089.15
1089.16
Observed
Simulated
Relative Intensity
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
1084
1086
1088
1090
1092
1094
m / z

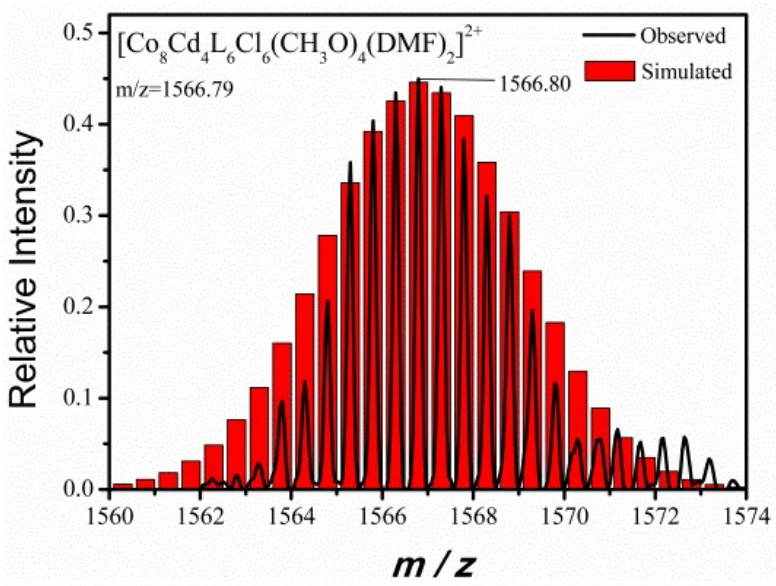

[Co8Cd5L6Cl7(CH3O)4(DMF)(CH3OH)2(CH3CN)]3+
m/z=1114.17
1114.15
Observed
Simulated
1110
1112
1114
1116
1118
m / z

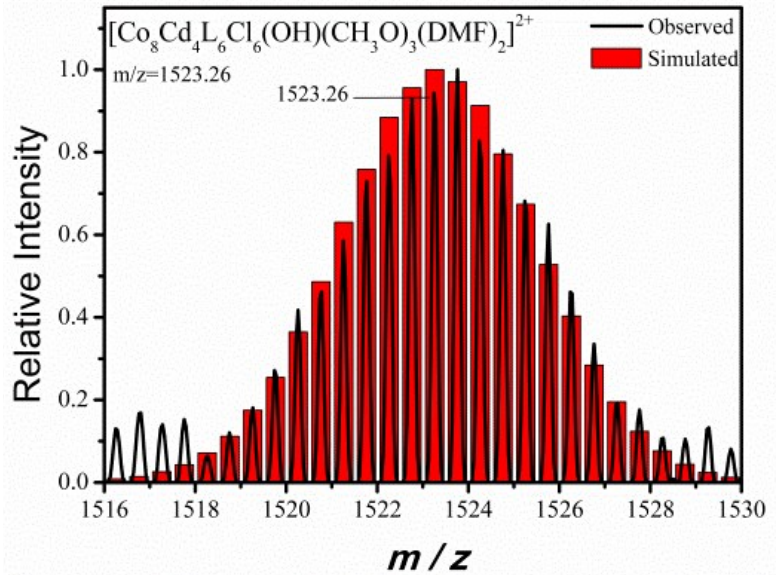

[Co8Cd5L6Cl7(CH3O)4(CH3CN)2(H2O)2]3+
m/z=1084.47
1084.49
Observed
Simulated
Relative Intensity
m / z

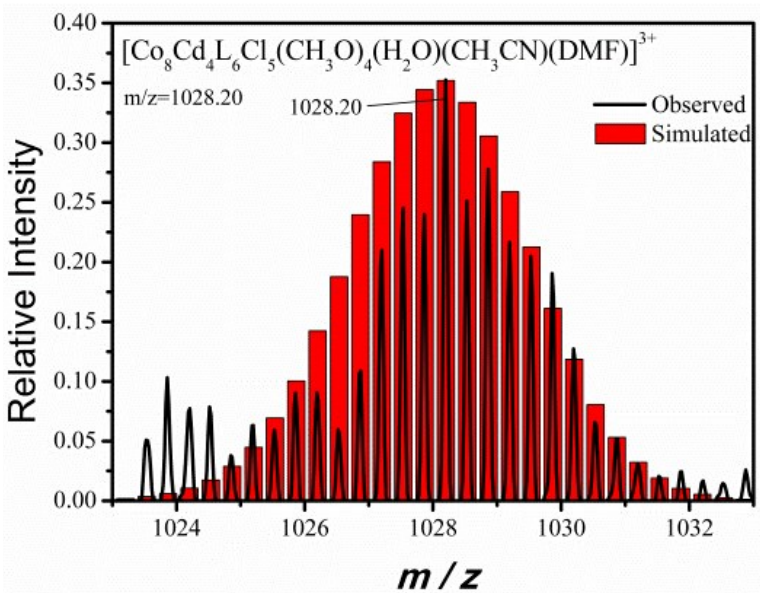

[Co8Cd5L6Cl7(CH3O)4(H2O)(CH3CN)]3+
m/z=1064.79
1064.80
Observed
Simulated
Relative Intensity
m / z

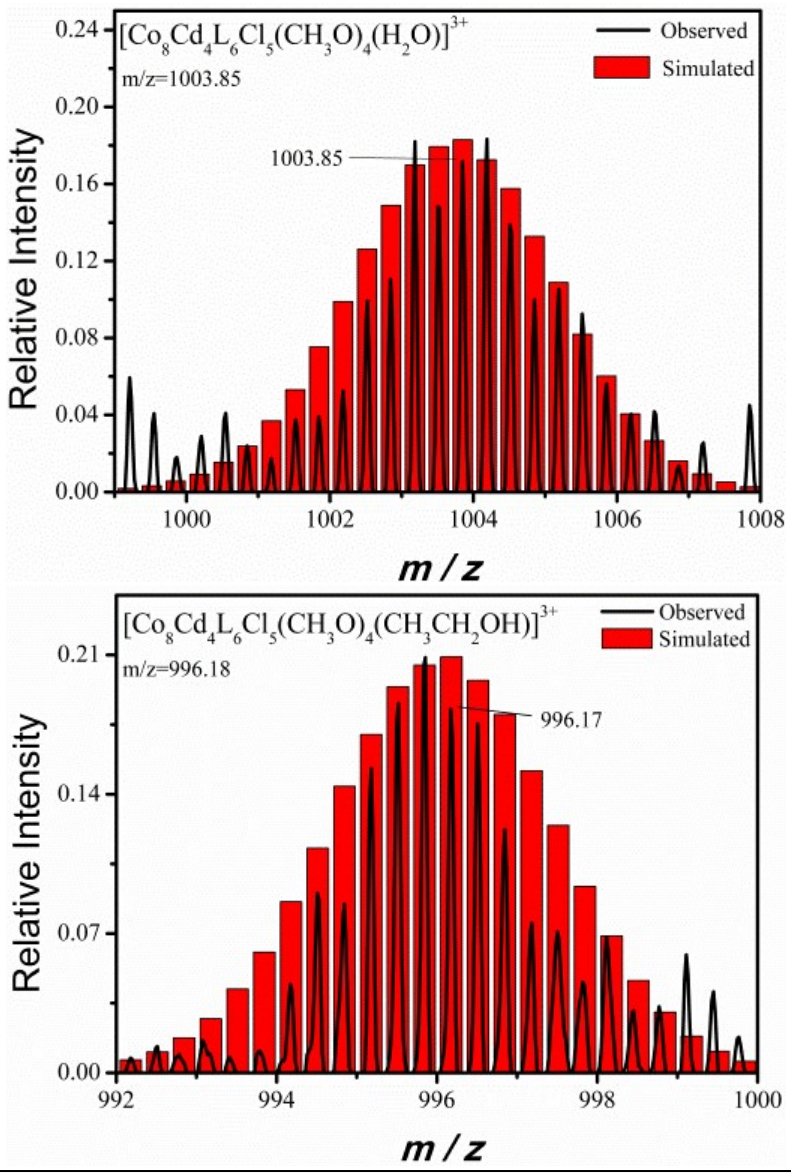

[Co8Cd5L6Cl7(CH3O)4(H2O)2]3+
m/z=1057.22
1057.21
Observed
Simulated
Relative Intensity
m / z

Peaks of cation fragment {Co_8Cd_4}

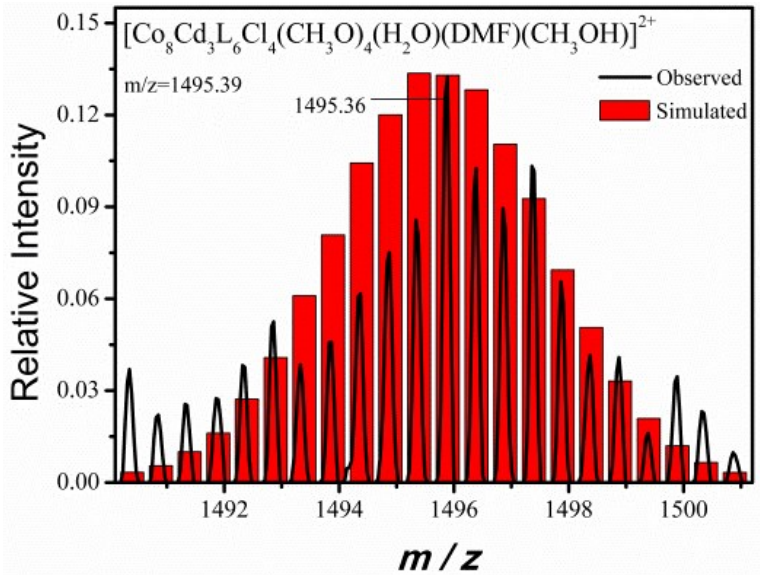


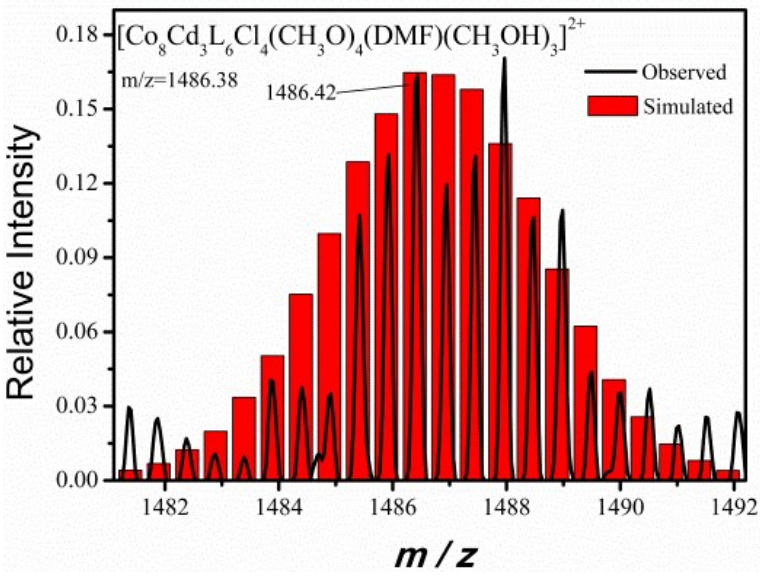


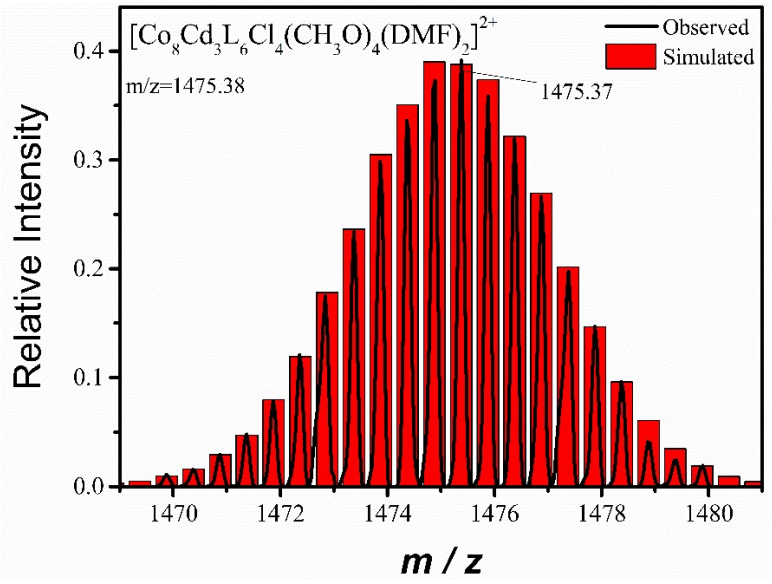


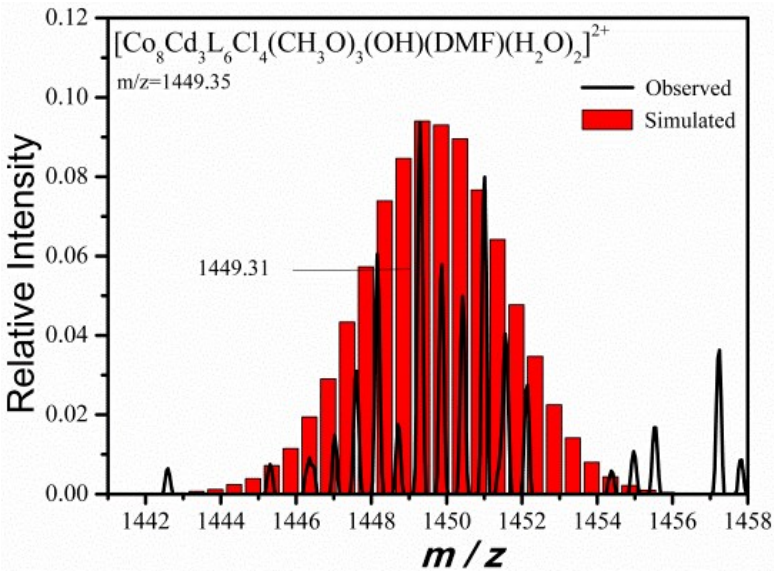


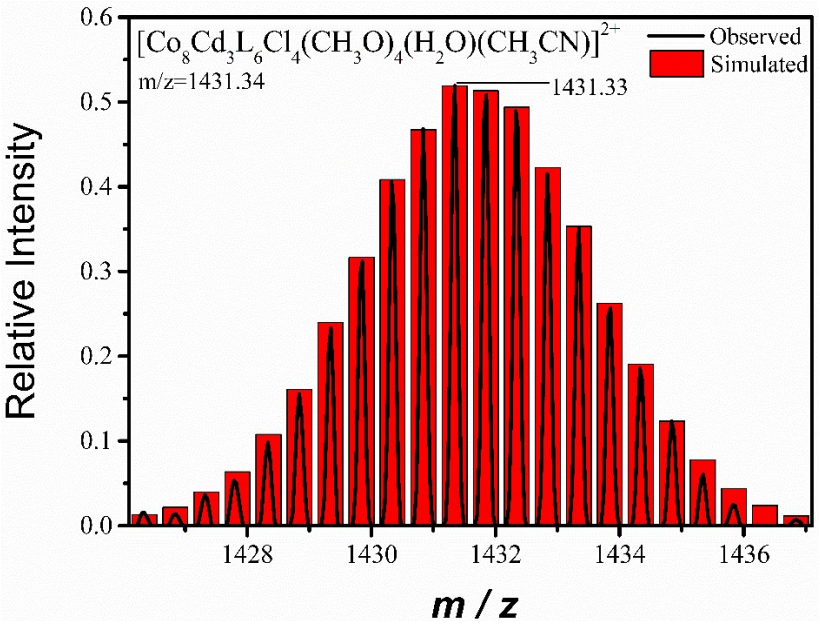
Peaks of cation fragment $\{Co_8Cd_3\}$

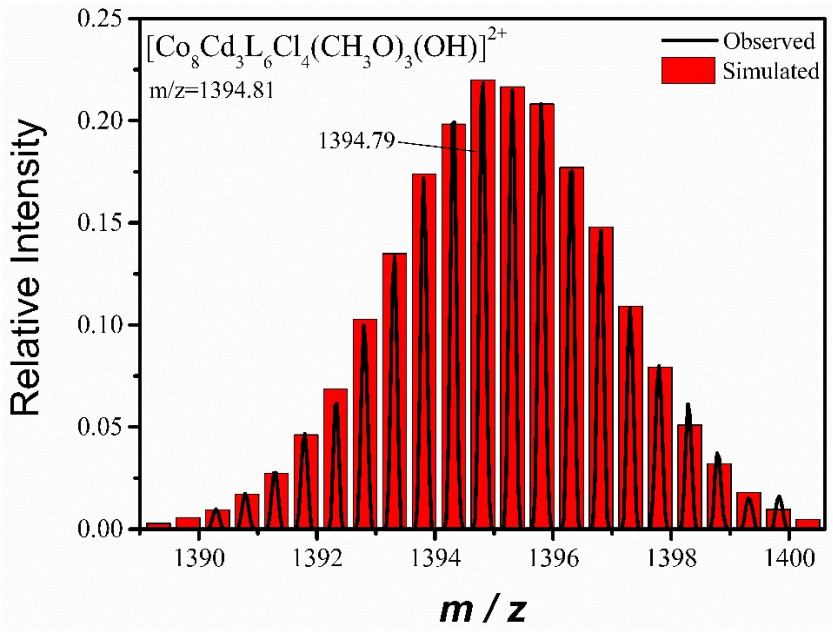

[Co8Cd3L6Cl4(CH3O)4(H2O)(DMF)(CH3OH)]2+
m/z=1495.39
1495.36
Observed
Simulated
Relative Intensity
0.15
0.12
0.09
0.06
0.03
0.00
1492
1494
1496
1498
1500
m / z


[Co8Cd3L6Cl4(CH3O)4(DMF)(CH3OH)3]2+
m/z=1486.38
1486.42
Observed
Simulated
Relative Intensity
0.18
0.15
0.12
0.09
0.06
0.03
0.00
1482
1484
1486
1488
1490
1492
m / z

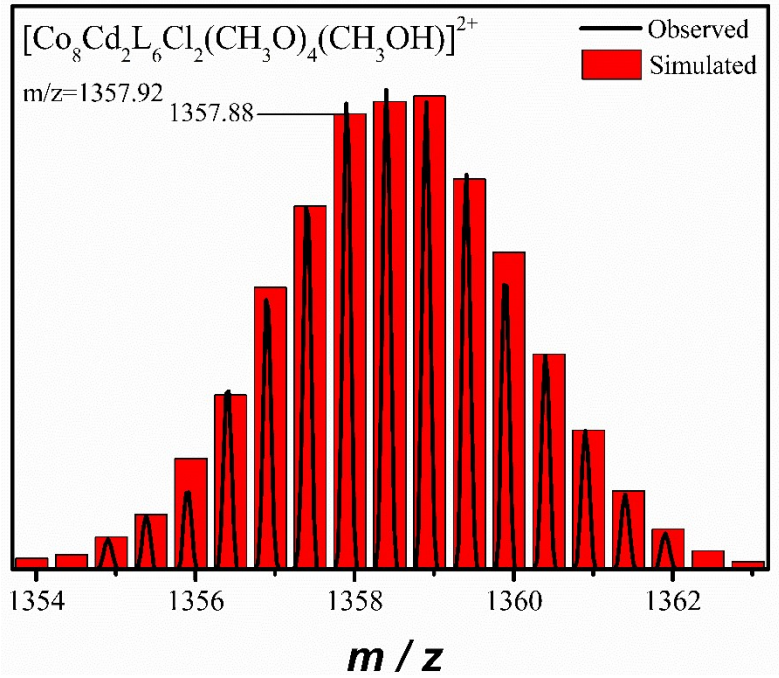

[Co8Cd3L6Cl4(CH3O)4(DMF)2]2+
m/z=1475.38
1475.37
Observed
Simulated
Relative Intensity
0.4
0.3
0.2
0.1
0.0
1470
1472
1474
1476
1478
1480
m / z


[Co8Cd3L6Cl4(CH3O)3(OH)(DMF)(H2O)2]2+
m/z=1449.35
Observed
Simulated
1449.31
Relative Intensity
m / z


[Co8Cd3L6Cl4(CH3O)4(H2O)(CH3CN)]2+
m/z=1431.34
Observed
Simulated
1431.33
Relative Intensity
m / z



Peaks of cation fragment $\{Co_8Cd_2\}$



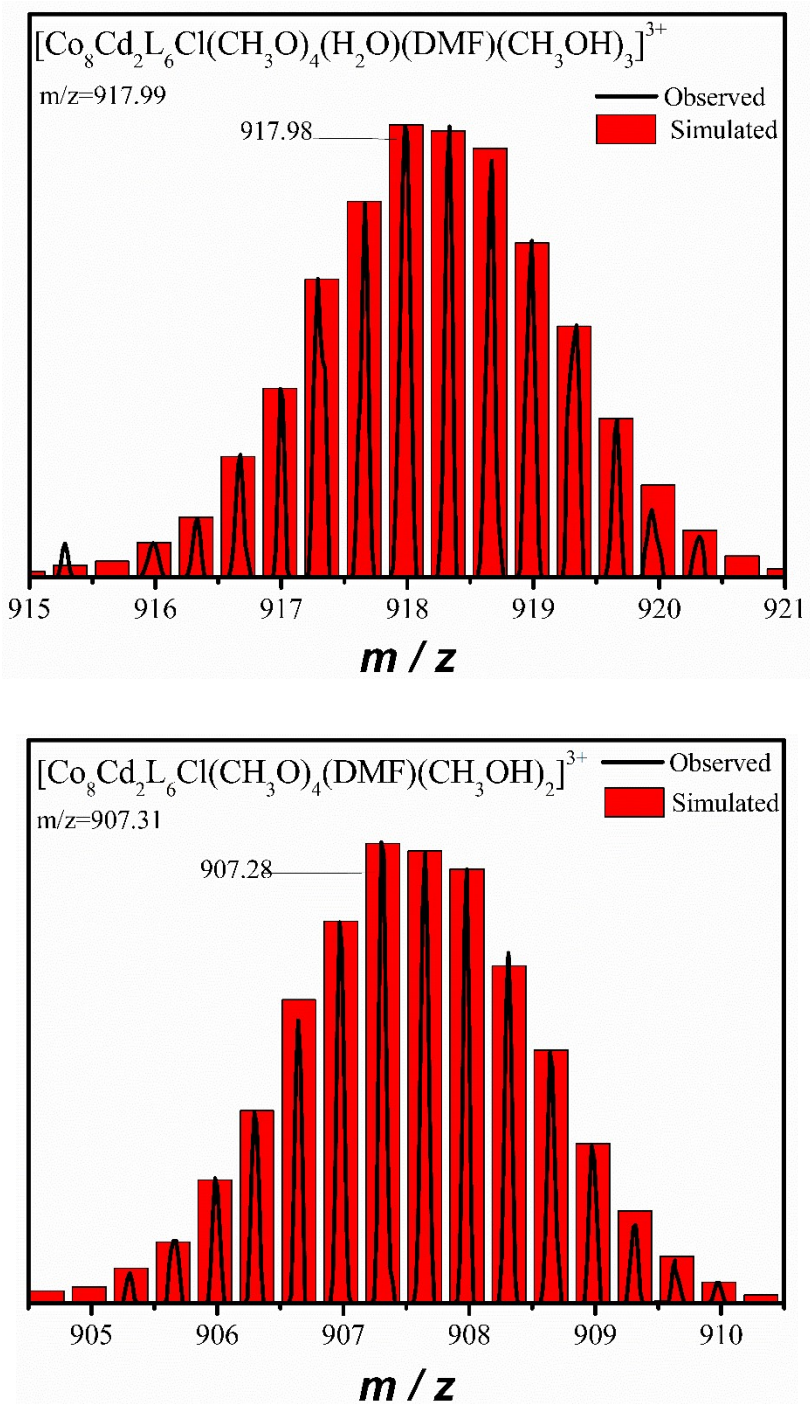


Figure S12. The superposed simulated and observed spectra of several species with different composite ion fragments for compound **2**.

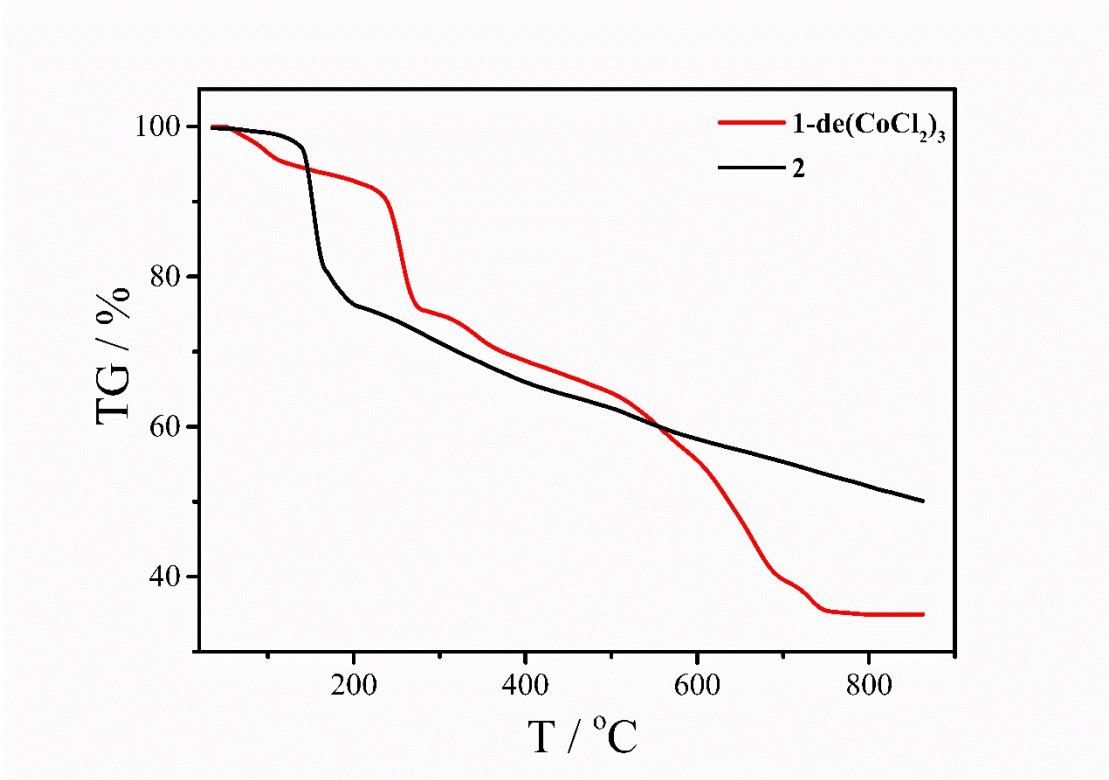


Figure S13. The TG curves of compound **1** and **2**.

Reference

[1] SHELXTL, version 6.10; Bruker Analytical Instrumentation: Madison, WI, 2000.

[2] (a) Sheldrick, G. M. *SADABS 2.05*; University of Göttingen; Göttingen, Germany. (b) Sheldrick, G. M. A short history of SHELXL. *Acta Crystallogr., Sect. A: Found. Crystallogr*. 2008, **64**, 112-122. (c)

[3] Sheldrick, G. M. A short history of SHELXL. *Acta Crystallogr., Sect. A: Found. Crystallogr*. 2008, **64**, 112-122.

[4] Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem*. 2015, **71**, 3-8.

[5] (a) Spek, A. L. J. *Appl. Crystallogr*. 2003, **36**, 7; (b) Vander Sluis, P.; Spek. A. L. *Acta Cryst*. 1990. **A46**, 194.