REGULAR ARTICLE

Synthesis and structures of two cobalt compounds of 2-amino-2-methyl-1-propanol

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Abstract. The reactions of 2-amino-2-methyl-1-propanol (MepH) with $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in the presence of acetic acid gave $[\text{Co}_2(\text{Mep})_3(\text{OAc})(\text{MepH})](\text{ClO}_4)_2 \cdot \text{MepH}$ (**1**) and $[\text{Co}_4^{\text{III}}\text{Co}_2^{\text{II}}(\text{Mep})_8(\mu_3\text{-OH})_2(\text{OAc})_4](\text{ClO}_4)_2 \cdot 2\text{EtOH} \cdot 2\text{H}_2\text{O}$ (**2**). They were characterized by elemental analysis, IR and single crystal X-ray diffraction analysis. Compound **1** presents a dinuclear structure with its two Co atoms linked by two Mep[−] ligands and one acetate ligand. The two Co(II) and four Co(III) centers in **2** are held together by eight Mep[−] ligands, two $\mu_3\text{-OH}^-$ ions and four acetate ligands to form a hexanuclear skeleton which contains a defected face-shared dicubane core. Their discrete polynuclear units are further linked into double-layered and mono-layered two-dimensional H-bonded framework, respectively.

Keywords. Crystal structure; Cobalt; 2-amino-2-methyl-1-propanol.

1. Introduction

Polynuclear clusters are springing up in recent years due to their potential applications in various fields such as catalysis, magnetism and luminescence.^{1–7} One of the most fascinating challenges in this field is to design and construct some special aesthetic structures^{8–11} to satisfy aimed properties. As is well-known, the selection of appropriate ligands plays a vital role in the formation of targeted clusters. This includes two aspects.^{12,13} One aspect is to select the efficient linking groups which help to bridge metal ions, and the other one is to design applicable non-coordinating groups to control the growth of nuclearities in dimensionalities. As revealed in literature, the small and flexible polydentate ligands^{14–17} show much advantage in constructing targeted clusters. With the above-mentioned considerations in mind, we aimed to investigate the coordination chemistry of 2-amino-2-methyl-1-propanol (MepH), which has the alkoxide linking group and the simple non-coordinating group of methyl. We herein report one dinuclear compound $[\text{Co}_2(\text{Mep})_3(\text{OAc})(\text{MepH})](\text{ClO}_4)_2 \cdot \text{MepH}$ (**1**) and one hexanuclear compound $[\text{Co}_4^{\text{III}}\text{Co}_2^{\text{II}}(\text{Mep})_8(\mu_3\text{-OH})_2(\text{OAc})_4](\text{ClO}_4)_2 \cdot 2\text{EtOH} \cdot 2\text{H}_2\text{O}$ (**2**).

2. Experimental

2.1 Materials and instrumentation

CAUTION: Perchlorate salts are potentially explosive and should be prepared in small quantities and handled with great care.

The reagents and solvents were commercially available and used as received without further purification. Elemental analyses (C, H and N) were performed using a Perkin-Elmer 2400II elemental analyzer. FT-IR spectra were recorded in the range 400–4000 cm^{-1} on a Nicolet 360 spectrophotometer using KBr pellets. Magnetic susceptibility measurements were performed on a Quantum Design MPMSXL-5 SQUID magnetometer.

2.2 Synthesis of $[\text{Co}_2(\text{Mep})_3(\text{OAc})(\text{MepH})](\text{ClO}_4)_2 \cdot \text{MepH}$ (**1**) and $[\text{Co}_4^{\text{III}}\text{Co}_2^{\text{II}}(\text{Mep})_8(\mu_3\text{-OH})_2(\text{OAc})_4](\text{ClO}_4)_2 \cdot 2\text{EtOH} \cdot 2\text{H}_2\text{O}$ (**2**)

To a stirred solution of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.0366 g, 0.1 mmol) in absolute ethanol (10 mL) was added 2-amino-2-methyl-1-propanol (0.0178 g, 0.2 mmol) and acetic acid (0.0060 g, 0.1 mmol). The resulting solution was stirred for 24 h at room temperature. After filtration, the obtained solution was left at ambient temperature for solvent evaporation. After two weeks, pale blue block crystals of compound **1** and green needle-like crystals of compound **2** were obtained. The crystals were collected, washed with ethanol and dried, giving compounds **1** and **2** in a yield of 0.0061 g (10.6%

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based on $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 0.0086 g (15.0% based on $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$), respectively. They are stable in ambient condition. Anal. Calcd (%) for $\text{C}_{22}\text{H}_{55}\text{Cl}_2\text{Co}_2\text{N}_5\text{O}_{15}$ (**1**): C 32.26, H 6.72, N 8.55. Found (%): C 32.51, H 6.52, N 8.35. IR (KBr pellet, cm^{-1}): 3422w, 3297m, 3251m, 2968w, 2883w, 1563s, 1427m, 1238w, 1179m, 785w, 704w, 633m, 559m. Anal. Calcd (%) for $\text{C}_{44}\text{H}_{110}\text{Cl}_2\text{Co}_6\text{N}_8\text{O}_{30}$ (**2**): C 31.88, H 6.64, N 6.76. Found (%): C 32.02, H 6.34, N 6.58. IR (KBr pellet, cm^{-1}): 3423w, 3296m, 3252m, 2967w, 2873w, 1556s, 1448m, 1390w, 1374w, 1231w, 1179m, 1090s, 1053w, 982w, 784w, 702w, 623m, 560m.

2.3 X-ray Crystallography

Single-crystal X-ray diffraction data for compounds **1** and **2** were collected on a SuperNova CCD-based diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) by ω -scan at 298(2) K for compound **1** and for compound **2** at 153(2) K. Absorption correction were applied by using the multi-scan program SADABS.¹⁸ The structure was solved by direct methods using SHELXS-97 program and refined by the full-matrix least-squares method on F^2 with the SHELXL-97 program¹⁹ or the corresponding programs in the SHELXTL package.²⁰ All non-hydrogen atoms were refined with anisotropic thermal parameters. A summary of crystal data is presented in Table 1. The selected bond lengths and angles are shown in Table 2. Hydrogen bonds are listed in Table 3.

3. Results and Discussion

The reactions of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with 2-amino-2-methyl-1-propanol in absolute ethanol in the presence of acetic acid gave a dinuclear Co_2^{III} complex (**1**) and a mixed-valence hexanuclear $\text{Co}_4^{\text{III}}\text{Co}_2^{\text{II}}$ complex (**2**) as shown in Scheme 1. The oxidation states of the Co atoms in the two complexes were confirmed by the corresponding Co-O/N bond lengths, charge balance considerations and the bond valence sum (BVS) calculations.^{21,22}

3.1 Crystal structure of $[\text{Co}_2(\text{Mep})_3(\text{OAc})(\text{MepH})](\text{ClO}_4)_2 \cdot \text{MepH}$ (**1**)

The single crystal X-ray diffractational analysis reveals that compound **1** crystallizes in the triclinic space group $P\bar{1}$. The selected bond lengths and angles for **1** are given in Table 2. The asymmetric unit of **1** is composed of one $[\text{Co}_2(\text{Mep})_3(\text{OAc})(\text{MepH})]^{2+}$ cation, two ClO_4^- anions and one lattice MepH molecule (Figure 1). Three of the MepH molecules are deprotonated to serve as Mep^- ligands in **1**. As shown in Figure 1, both Co1 and Co2 in compound **1** adopt distorted octahedral geometries with a $[\text{N}_2\text{O}_4]$ environment^{23,24} due to the coordination of three Mep^- ligands and one OAc^- anion.

Table 1. Crystallographic data for compounds **1** and **2**.

Complex	1	2
Formula	$\text{C}_{22}\text{H}_{55}\text{Cl}_2\text{Co}_2\text{N}_5\text{O}_{15}$	$\text{C}_{44}\text{H}_{110}\text{Cl}_2\text{Co}_6\text{N}_8\text{O}_{30}$
FW	818.47	1655.88
T / K	298(2)	153(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/m$
$a / \text{\AA}$	10.3508(8)	22.8164(11)
$b / \text{\AA}$	10.6815(8)	13.3547(3)
$c / \text{\AA}$	17.8122(11)	16.4024(8)
$\alpha / ^\circ$	84.615(6)	90
$\beta / ^\circ$	76.113(6)	133.376(9)
$\gamma / ^\circ$	68.107(7)	90
$V / \text{\AA}^3$	1773.9(2)	3632.8(6)
Z	2	2
$D_c / \text{g cm}^{-3}$	1.532	1.514
μ / mm^{-1}	1.156	1.493
θ range for data / $^\circ$	2.99 to 26.00	3.05 to 25.01
Reflections collected	14450	11521
R_{int}	0.0388	0.0231
Data/restraints/parameters	6963 / 1 / 429	3357 / 8 / 244
$R_1^a (I > 2\sigma(I))$	0.0633	0.0311
$wR_2^b (I > 2\sigma(I))$	0.1557	0.0790
R_1^a (all data)	0.0887	0.0333
wR_2^b (all data)	0.1766	0.0807
Largest diff. Peak, hole / ($\text{e \AA}^{-3}$)	1.460 and -0.664	1.111 and -0.962

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1					
Co1–O3	1.861(3)	Co1–N1	1.947(4)	Co2–O1	1.922(3)
Co1–O1	1.892(3)	Co1–N3	1.949(4)	Co2–N4	1.940(4)
Co1–O2	1.923(3)	Co2–O4	1.876(3)	Co2–O6	1.945(3)
Co1–O5	1.935(3)	Co2–O2	1.912(3)	Co2–N2	1.953(4)
O3–Co1–O1	91.86(14)	O3–Co1–N3	85.92(15)	O1–Co2–N4	90.19(16)
O3–Co1–O2	91.82(15)	O1–Co1–N3	177.43(15)	O4–Co2–O6	87.02(14)
O1–Co1–O2	81.04(13)	O2–Co1–N3	97.73(16)	O2–Co2–O6	93.19(14)
O3–Co1–O5	173.54(14)	O5–Co1–N3	88.44(15)	O1–Co2–O6	91.71(14)
O1–Co1–O5	93.84(13)	N1–Co1–N3	95.88(17)	N4–Co2–O6	172.61(15)
O2–Co1–O5	92.06(14)	O4–Co2–O2	177.99(14)	O4–Co2–N2	96.63(16)
O3–Co1–N1	91.55(17)	O4–Co2–O1	97.47(14)	O2–Co2–N2	85.38(15)
O1–Co1–N1	85.45(15)	O2–Co2–O1	80.53(13)	O1–Co2–N2	165.62(15)
O2–Co1–N1	166.17(15)	O4–Co2–N4	85.65(16)	N4–Co2–N2	93.74(18)
O5–Co1–N1	85.88(16)	O2–Co2–N4	94.17(15)	O6–Co2–N2	86.16(17)
2					
Co1–O1	1.8833(16)	Co2–O1A	2.0258(17)	Co3–O5	1.8844(17)
Co1–O2	1.9273(14)	Co2–O3	2.055(3)	Co3–O4	1.926(3)
Co1–N1	1.945(2)	Co2–O5	2.0955(17)	Co3–O6	1.927(3)
		Co2–O2	2.169(2)	Co3–N2	1.940(2)
O1–Co1–O1A	176.73(11)	O1B–Co2–O1A	98.77(10)	O5–Co3–O5C	87.03(10)
O1–Co1–O2B	86.11(8)	O1A–Co2–O3	96.91(7)	O5–Co3–O4	94.52(8)
O1–Co1–O2	96.42(9)	O1B–Co2–O5	91.16(7)	O5–Co3–O6	89.69(8)
O2B–Co1–O2	79.29(10)	O1A–Co2–O5	163.78(7)	O4–Co3–O6	174.19(11)
O1–Co1–N1	85.41(8)	O3–Co2–O5	94.58(8)	O5–Co3–N2C	173.69(9)
O1A–Co1–N1	92.44(8)	O5C–Co2–O5	76.51(9)	O5–Co3–N2	86.79(8)
O2–Co1–N1	91.91(8)	O1A–Co2–O2	76.57(6)	O4–Co3–N2	84.71(9)
O2–Co1–N1A	167.01(9)	O3–Co2–O2	169.75(10)	O6–Co3–N2	91.54(8)
N1–Co1–N1A	98.26(13)	O5–Co2–O2	93.47(7)	N2C–Co3–N2	99.36(13)

Symmetry codes: A) $-x, y, -z$ B) $-x, -y, -z$ C) $x, -y, z$ **Table 3.** Hydrogen bonds for **1** and **2** (Å and °).

1				
D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
N1–H1D...O12	0.90	2.48	3.244(8)	142.6
N2–H2B...O11A	0.90	2.14	3.026(7)	166.2
N3–H3E...O15B	0.90	2.38	3.190(9)	148.9
O4–H4D...N5C	0.85	1.98	2.646(5)	134.9
N4–H4E...O7	0.90	2.10	2.969(6)	162.8
O7–H7...O3	0.849(10)	1.77(3)	2.582(5)	159(8)
N5–H5D...O9	0.89	2.05	2.937(7)	174.4
Symmetry codes: A) $x-1, y+1, z$; B) $-x+1, -y+1, -z+1$; C) $x, y+1, z$				
2				
N1–H1C...O8D	0.92	2.38	3.168(3)	143.9
N1–H1D...O5C	0.92	2.53	3.279(3)	138.5
O2–H2...O11	0.84	1.80	2.617(4)	164.4
N2–H2A...O7	0.92	2.22	2.955(3)	136.8
O11–H111...O12E	0.84	1.86	2.700(5)	171.5
O11–H112...O6	0.85	1.86	2.703(4)	178.2
O12–H12...O9	0.85	2.03	2.855(6)	163.5
Symmetry codes: C) $x, -y, z$; D) $x, -y+1, z$; E) $-x+1/2, -y+1/2, -z+1$				

Two of the Mep[−] ligands adopt chelating:bridging coordination modes using its N and O atoms to chelate to one Co(III) ion with the O atom bridging another Co(III) atom at the same time. However, the other Mep[−]

ligand and the MepH ligand behave as chelating coordination modes. The OAc[−] anion acts as a *syn:syn*-bridge. The oxidation states of the Co atoms in **1** are assumed to be +3 based on the Co–O/N bond lengths, charge

Scheme 1. Syntheses of **1** and **2**.

Figure 1. Molecular structure of **1** with selected atoms labeled and thermal ellipsoids drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

balance consideration, and bond valence sum calculations (3.34 and 3.28 for Co1 and Co2, respectively).²⁵ The Co-O bond lengths in **1** are in the range of 1.861(3)–1.945(3) Å (Table 2), which is similar to the reported Co(III)-O bond length in literature.²⁶ Co1 and Co2 in **1** are connected by two chelating:bridging Mep[−]

Figure 2. Pictures of the H-bonded chain (a), and the two-dimensional H-bonded sheet (b) of **1**. The dashed lines represent hydrogen bonds. The C-bonded H atoms are omitted for clarity.

ligands and one *syn:syn*-bridging OAc^- ligand, building the dinuclear skeleton of **1**.

The neighboring dinuclear units along the *b* axis are linked by free MepH molecules through hydrogen bonds $\text{O4} \cdots \text{N5}$ (symmetry code: $x, y+1, z$), $\text{O7} \cdots \text{O3}$, and $\text{N4} \cdots \text{O7}$ (Table 3), building one-dimensional H-bonded chains (Figure 2a). The free ClO_4^- ions interact with the adjacent one-dimensional chains through hydrogen bonds $\text{N5} \cdots \text{O9}$ and $\text{N2} \cdots \text{O11}$ ($x-1, y+1, z$) (Table 3), resulting in the formation of a two-dimensional H-bonded sheet in the *ab* plane (Figure 2b). Interestingly, two of such two-dimensional sheets are further connected by hydrogen bonds $\text{N3} \cdots \text{O15}$ ($-x+1, -y+14, -z+1$) to form a double-layered H-bonded structure as shown in Figure 3.

3.2 Crystal structure of $[\text{Co}_4^{\text{III}}\text{Co}_2^{\text{II}}(\text{Mep})_8(\mu_3\text{-OH})_2(\text{OAc})_4](\text{ClO}_4)_2 \cdot 2\text{EtOH} \cdot 2\text{H}_2\text{O}$ (**2**)

Compound **2** crystallizes in the monoclinic space group *C2/m* (Figure 4). The selected bond lengths and angles for **2** are given in Table 2. As seen in Figure 2, **2** has an inversion center and consists of one $[\text{Co}_4^{\text{III}}\text{Co}_2^{\text{II}}(\text{Mep})_8(\mu_2\text{-OH})_2(\text{OAc})_4]^{2+}$ cation, two ClO_4^- anions, two lattice EtOH molecules and two lattice water molecules per formula unit. The eight Mep[−] ligands bridge Co

centers in chelating:bridging modes. Two of the acetate ligands bridge two Co centers in a *syn-syn* bridging mode, while the other two acetate ligands behave as monodentate terminal ligands. Each Co ion is six-coordinated in a distorted octahedral geometry.²⁷ Co1 is coordinated by two hydroxyl O atoms (O1 and O1B) and two amino N atoms (N1 and N1A) from two Mep[−] ligands, and two O atoms (O2 and O2A) from two μ_3 -OH[−] ions with the Co1–N/O bond lengths varying in a range of 1.8833(16)–1.945(2) Å (Table 2). Co2 is coordinated by six O atoms from four Mep[−] ligands, one OH[−] anion and one OAc[−] anion. The Co2–O bond lengths are in the range of 2.0258(17)–2.169(2) Å.²⁸ The coordination atoms of Co3 are two O atoms (O5 and O5C) and two amino N atoms (N2 and N2C) from two Mep[−] ligands, and another two O atoms from two OAc[−] anions. The Co3–N/O bond lengths are in the

range of 1.8844(17)–1.940(2) Å. The bond valence sum calculations gave values of 3.33, 2.18 and 3.34 for Co1, Co2 and Co3 in complex **2**, respectively. These bond length information and the bond valence sum calculations reveal the oxidation state of +2 for Co2, and the oxidation state of +3 for Co1 and Co3, which are further confirmed by the charge balance.²⁹ Co1, Co1A, Co2 and Co2A are consolidated by two μ_3 -OH[−] ions and four alcoholic O atoms to form a face-sharing defected dicubane skeleton. Each unshared vertexes (Co2 and Co2B) are further connected to another Co atom (Co3 and Co3A), respectively, by two alcoholic oxygen atoms and one *syn:syn*-bridging OAc[−] anion. All of these connections lead to the construction of the hexanuclear structure of **2**.

Every two adjacent hexanuclear units along the b axis are connected by two free ClO₄[−] anions through electrostatic interactions, as well as through hydrogen bonds N1...O8 (*x*, −*y* + 1, *z*) (Table 3), leading to the formation of one-dimensional H-bonded chains (Figure 5). The neighboring one-dimensional H-bonded chains are linked by free ethanol and water molecules through H-bonds O2...O11, O11...O6, O11...O12 (−*x* + 1/2, −*y* + 1/2, −*z* + 1) and O12...O9 (Table 3), forming a two-dimensional H-bonded sheet as shown in Figure 5.

Figure 3. Double-layered H-bonded structure of **1**. The dashed lines represent hydrogen bonds. The C-bonded H atoms are omitted for clarity.

3.3 Magnetic Property of **2**

Solid-state variable-temperature dc magnetic susceptibility measurements for **2** were carried out in an applied magnetic field of 1000 Oe in the temperature range of

Figure 4. Molecular structure of **2** with selected atoms labeled. The thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry codes: A) −*x*, *y*, −*z*; B) −*x*, −*y*, −*z*; C) *x*, −*y*, *z*.

Figure 5. A picture of the two-dimensional H-bonded sheet of **2**. The dashed lines represent hydrogen bonds. The C-bonded H atoms are omitted for clarity.

Figure 6. Plots of χ_M and $\chi_M T$ vs. T of **2** at an applied field of 1000 Oe.

2–300 K. The plots of χ_m and $\chi_m T$ vs. T for **2** are shown in Figure 6. Its $\chi_m T$ value of $6.25 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K falls in the range ($4.2\text{--}6.8 \text{ cm}^3 \text{ K mol}^{-1}$) for experimentally observed two highly anisotropic high-spin Co(II) centers due to the largely unquenched orbital momentum of Co(II) ions.³⁰ Upon cooling, the $\chi_m T$ value decreases steadily to a minimum value of $3.0 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The profile of $\chi_m T$ vs. T curve for **2** is mainly due to the depopulation of crystal field splitting levels³¹ because the two Co(II) ions are well-separated.

4. Conclusions

An investigation of the coordination chemistry of 2-amino-2-methyl-1-propanol with Co(II) ions was carried out, which afforded one dinuclear cluster and one hexanuclear cluster. The hexanuclear cluster features a face-sharing defected dicubane skeleton with each of the two unshared vertexes further connected to another Co atom. The Mep^- ligands in the dinuclear compound present two types of coordination modes of chelating and chelating:bridging, however, all Mep^- ligands in the hexanuclear compound are in chelating:bridging coordination modes. The dinuclear units, free MepH and free ClO_4^- ions in **1** are further consolidated by hydrogen bonds to form a double-layered two-dimensional H-bonded framework. The hexanuclear units in **2** are connected by free ClO_4^- anions, free ethanol and water molecules through H-bonds to build a mono-layered two-dimensional H-bonded sheet.

Supplementary Information (SI)

Crystallographic data for the two structures in this paper have been deposited in the Cambridge Crystallographic Database Center, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge by quoting the depository number CCDC-1409594 for **1** and 1409595 for **2** (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

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