

A Hexanuclear Cobalt Cluster with Tetracubane-like Topology: Synthesis, Structure and Magnetic Properties^①

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ABSTRACT One hexanuclear cobalt cluster $[\text{Co}_2^{\text{III}}\text{Co}_4^{\text{II}}(\text{L})_4(\text{CH}_3\text{COO})_2(\text{MeO})_4] \text{MeOH}$ (**1**) was synthesized by the reaction of H_2L ($\text{H}_2\text{L} = 2-((2\text{-hydroxy-4-methoxy-benzylideneamino)methyl})\text{phenol}$) and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in MeOH under solvothermal conditions. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 14.397(3)$, $b = 16.625(3)$, $c = 18.992(4)$ Å, $\alpha = 109.47(3)^\circ$, $\beta = 99.24(3)^\circ$, $\gamma = 112.37(3)^\circ$, $D_c = 1.464 \text{ g/cm}^3$, $Z = 2$, $V = 3741.7(2) \text{ Å}^3$, the final $R = 0.0781$ and $wR = 0.1436$ for 13051 observed reflections with $I > 2\sigma(I)$. In the structure of **1**, two cobalt ions are in 3+ oxidation states and four cobalt ions are in 2+ valence states. The six cobalt atoms are held together by six phenolate oxygen atoms from four L^{2-} ligands, four oxygen atoms from two chelating acetates and four $\mu_3\text{-O}$ atoms from four MeO^- groups. The six cobalt atoms are located at six corners of four defective cubanes. Thus, complex **1** displays tetracubane-like topology. Solid-state dc magnetic susceptibilities were measured for **1** in the 2.0–300 K range. Antiferromagnetic interactions were determined for **1**.

Keywords: hexanuclear, cobalt, tetracubane, topology, magnetic property;

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1 INTRODUCTION

Polynuclear transition-metal clusters have attracted increasing interest due to their aesthetically pleasing architectures^[1-5] and diverse applications in magnetism^[6-8], luminescence^[9-11], and catalysis^[12, 13]. Particularly, polynuclear cobalt clusters have gathered tremendous attention in recent years especially for the following two important reasons: (i) some cobalt clusters behave as single-molecule magnets (SMMs)^[14-17], and could be potentially utilized in high-density information storage devices^[18, 19]; (ii) these clusters are also successfully used in many catalysis reactions, such as dioxygen reduction^[20-22] and epoxidation of alkenes^[23].

A fertile route for the preparation of polynuclear cobalt clusters involves employing polydentate ligands containing

several oxygen donors that could incorporate many cobalt ions into one molecular entity. In this work, we employed polydentate Schiff base H_2L ($\text{H}_2\text{L} = 2-((2\text{-hydroxy-4-methoxy-benzylideneamino)methyl})\text{phenol}$)^[24] as a ligand to assemble polynuclear cobalt compound. The existence of two -OH groups renders H_2L as a good ligand to generate polynuclear clusters. A hexanuclear cobalt compound with formula $[\text{Co}_2^{\text{III}}\text{Co}_4^{\text{II}}(\text{L})_4(\text{CH}_3\text{COO})_2(\text{MeO})_4] \text{MeOH}$ (**1**) was prepared. Herein, we report the synthesis, structure and magnetic properties of complex **1**.

2 EXPERIMENTAL

2.1 Materials and physical measurements

All manipulations were performed under aerobic and solvothermal conditions using reagents and solvents as

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received. The H₂L ligand (H₂L = 2-((2-hydroxy-4-methoxybenzylideneamino)methyl)phenol) was prepared according to the literature procedure^[24].

The C, H and N microanalyses were carried out with a Carlo-Erba EA1110 CHNO-S elemental analyser. FT-IR spectrum was recorded from KBr pellets in the range of 400~4000 cm⁻¹ on a Nicolet MagNa-IR 500 spectrometer. Variable-temperature dc magnetic susceptibility data were collected using a Quantum Design MPMS-7 SQUID magnetometer.

2.2 Synthesis of complex 1

A mixture of H₂L (0.0257 g, 0.1 mmol), Co(OAc)₂ 4H₂O (0.0249 g, 0.1 mmol) and MeOH (1.5 mL) was sealed in a Pyrex-tube (10 mL). The tube was heated at 80 °C for 2 days under autogenous pressure. Cooling of the resultant solution to room temperature gave dark-red needle-like crystals. The crystals were collected by filtration, washed with MeOH (2 mL) and dried in air. Yield: 0.019 g (45% based on cobalt).

Anal. Calcd. (%) for C₇₀H₇₈N₄O₂₂Co₆ (*M_r* = 1672.94): C, 50.02; H, 4.68; N, 3.33. Found (%): C, 49.97; H, 4.65; N, 3.49. Selected IR data for **1** (cm⁻¹): 1606 (s), 1529 (m), 1479 (m), 1446 (m), 1299 (w), 1251 (s), 1219 (s), 1165 (m), 1144 (m), 1122 (m), 1031 (m), 979 (m), 874 (w), 851 (w), 766 (w).

2.3 Structure determination

The data collection for **1** were carried out on a Bruker Smart ApexII diffractometer equipped with a graphite monochromator utilizing MoK α radiation (λ = 0.71073 Å); the ω -2 θ scan technique was applied. The crystal structure of complex **1** was solved with the Olex2 solve solution program^[25] using Intrinsic Phasing and refined by full-matrix least-squares minimization with the ShelXL refinement package^[26]. All non-hydrogen atoms were refined anisotropically. The collected crystal data for **1** are shown in Table S1. Selected bond lengths and bond angles of **1** are listed in Table 1 and Table S2.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for **1**

1					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Co(1)–O(2)	1.905(4)	Co(2)–O(2)	2.139(4)	Co(4)–O(19)	2.199(4)
Co(1)–O(13)	1.911(4)	Co(3)–O(4)	1.933(4)	Co(5)–O(9)	1.905(4)
Co(1)–O(1)	1.912(4)	Co(3)–O(5)	2.008(4)	Co(5)–O(8)	1.906(4)
Co(1)–N(4)	1.916(5)	Co(3)–N(1)	2.011(5)	Co(5)–N(3)	1.911(5)
Co(1)–O(19)	1.925(4)	Co(3)–O(1)	2.013(4)	Co(5)–O(20)	1.925(4)
Co(1)–O(17)	1.946(4)	Co(3)–O(19)	2.212(4)	Co(5)–O(16)	1.927(4)
Co(2)–O(15)	2.049(4)	Co(4)–O(10)	2.050(4)	Co(5)–O(18)	1.941(4)
Co(2)–O(14)	2.053(4)	Co(4)–O(5)	2.058(4)	Co(6)–O(11)	1.921(5)
Co(2)–O(18)	2.068(4)	Co(4)–O(18)	2.130(4)	Co(6)–O(10)	1.995(4)
Co(2)–O(17)	2.074(4)	Co(4)–O(17)	2.138(4)	Co(6)–N(2)	2.011(5)
Co(2)–O(8)	2.132(4)	Co(4)–O(20)	2.196(4)	Co(6)–O(9)	2.025(4)
Co(6)–O(20)	2.198(4)				
Angle	(°)	Angle	(°)	Angle	(°)
O(2)–Co(1)–O(13)	89.07(2)	O(15)–Co(2)–O(17)	171.08(2)	O(4)–Co(3)–O(19)	93.26(2)
O(2)–Co(1)–O(1)	174.59(2)	O(14)–Co(2)–O(17)	89.83(2)	O(5)–Co(3)–O(19)	81.65(2)
O(13)–Co(1)–O(1)	92.04(2)	O(18)–Co(2)–O(17)	82.06(2)	O(10)–Co(4)–O(5)	100.73(2)
O(2)–Co(1)–N(4)	93.94(2)	O(15)–Co(2)–O(8)	84.43(2)	O(10)–Co(4)–O(18)	91.02(2)
O(13)–Co(1)–N(4)	87.72(2)	O(14)–Co(2)–O(8)	108.12(2)	O(5)–Co(4)–O(18)	167.25(2)
O(1)–Co(1)–N(4)	91.40(2)	O(4)–Co(3)–O(5)	135.69(2)	O(10)–Co(4)–O(17)	168.70(2)
O(2)–Co(1)–O(19)	92.43(2)	O(4)–Co(3)–N(1)	92.2(2)	O(5)–Co(4)–O(17)	89.58(2)
O(13)–Co(1)–O(19)	176.07(2)	O(5)–Co(3)–N(1)	91.46(2)	O(18)–Co(4)–O(17)	79.16(2)
O(15)–Co(2)–O(14)	97.96(2)	O(4)–Co(3)–O(1)	115.95(2)	O(10)–Co(4)–O(20)	80.62(2)
O(15)–Co(2)–O(18)	90.58(2)	O(5)–Co(3)–O(1)	105.60(2)	O(5)–Co(4)–O(20)	104.88(2)
O(14)–Co(2)–O(18)	170.12(2)	N(1)–Co(3)–O(1)	104.95(2)	O(18)–Co(4)–O(20)	71.95(2)

3 RESULTS AND DISCUSSION

3.1 Synthesis and IR spectrum of 1

Complex **1** is prepared by mixing H₂L and

Co(OAc)₂ 4H₂O in 1:1 ratio in MeOH under solvothermal conditions. This solvothermal reaction mode allows to crystallize complex **1** directly from the reaction solution.

Several bands appear in the 1605~1445 cm⁻¹ range (Fig. S1).

Contributions from the carboxylic $\nu_{as}(\text{CO}_2)$ and $\nu_s(\text{CO}_2)$ vibrations would be expected in this region. The vibration of the C=N bonds is at 1445 cm^{-1} . Several bands appear in the $1299\sim 1121\text{ cm}^{-1}$ range, whilst the contributions from the vibrations of aromatic rings would be expected in this region. The overlap of the signals of aromatic rings with the vibrations of $-\text{CH}_3$ and $-\text{CH}_2$ groups makes assignments difficult. Several peaks in the $979\sim 766\text{ cm}^{-1}$ range are found. They can be ascribed to the vibrations of C-H bonds.

3.2 Structural description of 1

X-ray single-crystal analysis reveals that complex **1** crystallizes in the triclinic space group $P\bar{1}$. The structure consists of six cobalt atoms, four L^{2-} ligands, two acetate ions, two MeO^- ions and two solvent molecules (Fig. 1). Bond valence calculation^[27, 28] indicated that two cobalt atoms (Co(1), Co(5)) are in 3+ valence states while the other metal centers (Co(2), Co(3), Co(4) and Co(6)) are in 2+ oxidation states (Table 2). The presence of two Co^{III} ions is possibly due to the aerial oxidation of Co^{II} to Co^{III} . This phenomenon was observed in many polynuclear $\text{Co}^{\text{II/III}}$ clusters^[29, 30]. The six cobalt atoms are located at six corners of a defective tetracubane. Two cubanes share one face and

each misses one vertex (Fig. 1), and the Co(4) atom is shared by four cubanes. Thus, complex **1** looks like a butterfly (Fig. 1). In this hexanuclear compound, Co(1), Co(2), Co(4) and Co(5) atoms are hexa-coordinated, while Co(3) and Co(6) atoms are penta-coordinated. The six cobalt atoms are held together by six phenolate oxygen atoms from four L^{2-} ligands, four oxygen atoms from two chelating acetates and four $\mu_3\text{-O}$ atoms from four MeO^- groups. The coordination environments of Co(3) and Co(6) atoms are identical (NO_4), and they are coordinated by two oxygen atoms and one nitrogen atom from one L^{2-} ligand, one oxygen atom from a MeO^- unit and one phenolate oxygen atom from another L^{2-} ligand. The coordination environments of Co(1) and Co(5) atoms are the same (NO_5). The six coordination atoms are from one L^{2-} ligand ($\text{NO}(2)$), two MeO^- units and one acetate. The coordination spheres of Co(2) and Co(4) atoms are distinct. Co(4) atom is coordinated by four oxygen atoms of four MeO^- units and two oxygen atoms from two L^{2-} ligands. Co(2) atom is coordinated by two oxygen atoms of two acetates, two oxygen atoms of two MeO^- ions and two oxygen atoms from two L^{2-} ligands. The L^{2-} ligand displays $\mu_2:\eta^2, \eta^1, \eta^1, \eta^0$ and $\mu_3:\eta^0, \eta^2, \eta^1, \eta^2$ chelating modes.

Table 2. Oxidation States of Cobalt Atoms Obtained by Bond Valence Calculations^[27, 28]

Atom	Valence	Atom	Valence
Co(1)	3.57	Co(4)	1.88
Co(2)	2.06	Co(5)	3.29
Co(3)	2.24	Co(6)	2.28

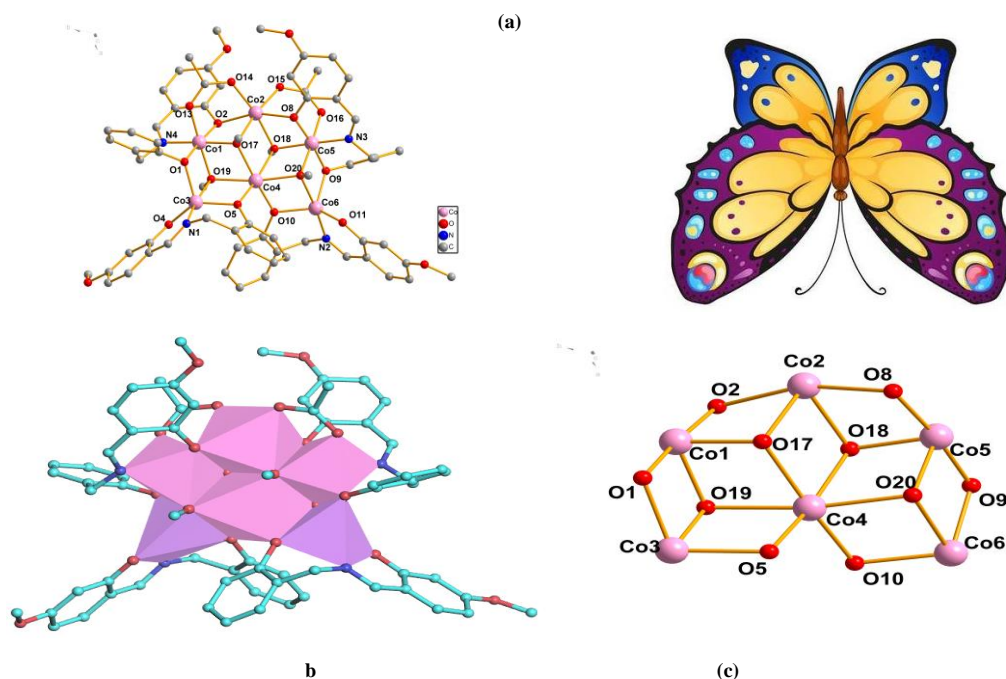


Fig. 1. (a) Molecular structure of **1** looking like a butterfly. (b) Coordination polyhedral of cobalt atoms. (c) Defect tetracubane structure of metal core. H atoms are omitted for clarity

Complex **1** is a member of a big family of hexanuclear cobalt clusters. These complexes display various structures including cage^[31], hexameric ring^[2, 21], and giant wheel^[22]. The examples of hexanuclear Co^{II/III} clusters which exhibit defect tetracubane core are very rare^[29].

There are many Co₇ clusters that show disc-like configuration, in which the seven cobalt centers are almost coplanar and occupy the vertexes of the six defect cubanes^[32-41]. Compared the structure of complex **1** with those of Co₇ clusters, complex **1** can be regarded as obtained by removing one of seven vertexes of the six cubanes.

3.3 Magnetic properties of **1**

Direct current (dc) magnetic susceptibilities for complex **1** were determined at an applied magnetic field of 1000 Oe in

the temperature range of 2~300 K. The $\chi_M T$ value of **1** at 300 K is 12.08 cm³ mol⁻¹ K (Fig. 2), which is much larger than the spin-only value of 7.50 cm³ mol⁻¹ K expected for four $S = 3/2$ uncoupled spins, probably due to the orbital contributions of the metal ions^[42, 43]. As the temperature is lowered, the $\chi_M T$ value decreases gradually to a minimum value of 4.53 cm³ mol⁻¹ K at 2 K. This behavior is indicative of the presence of antiferromagnetic exchange interactions between the metal ions. The relationship between $1/\chi_M$ and temperature of 2~300 K obeys the Curie-Weiss Law of $1/\chi_M = (T - \theta)/C$. The Curie constant $C = 14.28$ cm³ mol⁻¹ K and Weiss constant $\theta = -49.84$ K were obtained. The negative θ value confirms the antiferromagnetic exchange interactions.

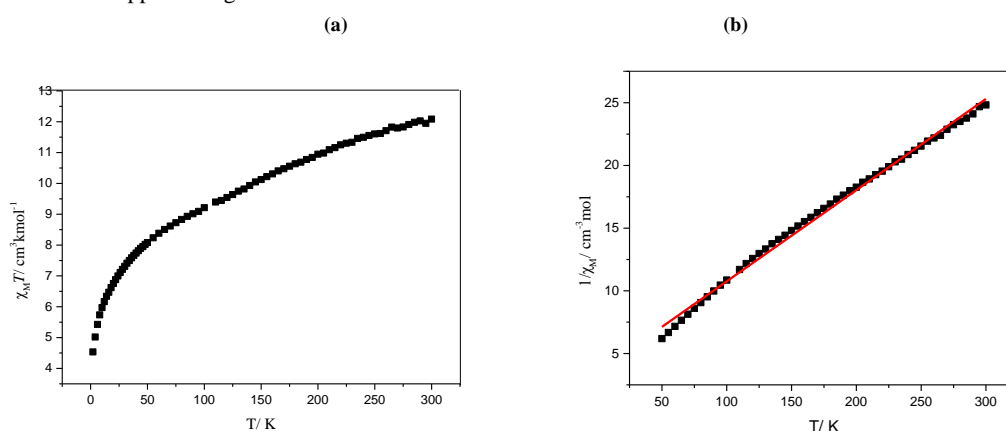


Fig. 2. Temperature dependence of magnetic susceptibilities in the forms of $\chi_M T$ vs. T (a) and $1/\chi_M$ vs. T (b) for **1** at 1 kOe. The red solid line corresponds to the best fit of the magnetic data

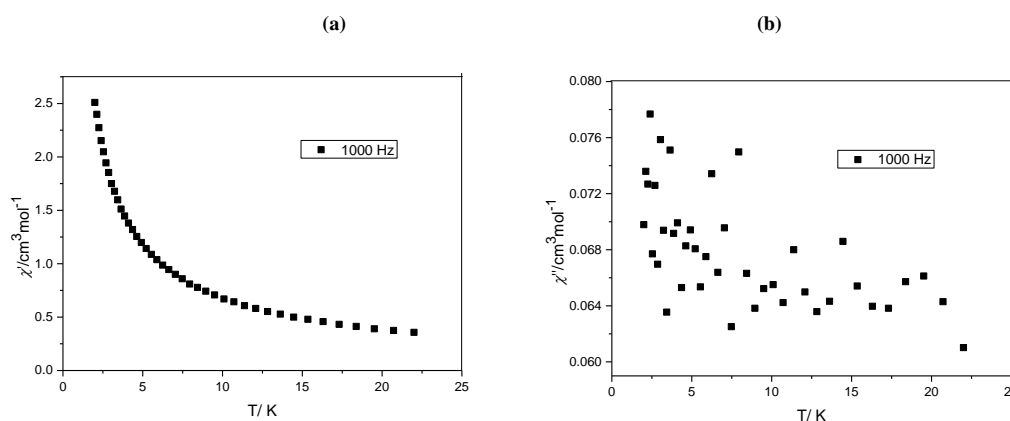


Fig. 3. Temperature dependence of the in-phase (χ') (a) and out-of-phase (χ'') (b) susceptibilities for **1** in the range of 2 to 25 K. The susceptibilities at 1000 Hz frequency under zero dc field

In order to study the magnetic dynamic behavior of **1**, the ac magnetic susceptibilities for complex **1** at 1000 Hz under a zero dc field were determined (Fig. 3). The χ'' susceptibilities do not increase with the decrease of temperature or no peaks were observed, which indicate that complex **1** is not a single-molecule magnet.

4 CONCLUSION

A mixed-valence hexanuclear cobalt complex [Co^{III}Co^{II}(L)₄(CH₃COO)₂(MeO)₄] 2MeOH (**1**) supported by a Schiff base ligand H₂L was synthesized. Complex **1** exhibits defect tetracubane-type architecture. Four cobalt

atoms are hexa-coordinated and two cobalt atoms are penta-coordinated. The dc magnetic property measurements reveal the existence of antiferromagnetic interactions.

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