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ARTICLE

A Pentanuclear Cobalt Complex with two $[Co^{II}(CH_3O)_3]^-$ Units Wrapping a Triangular $[Co^{III}{}_3O]^{7+}$ Core: Synthesis, Structure, and Magnetic Properties

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Abstract. The reaction of Hppko (Hppko = phenyl 2-pyridyl ketone oxime) and $CoCl_2·6H_2O$ in the CH_3OH solvent with the presence of triethylamine (NEt_3) at room temperature and the exposure to air resulted in the formation of a new pentanuclear, mixed-valence cobalt complex with the molecular formula $[\{Co^{II}(CH_3O)_3\}_2\{Co^{III}{}_3(\mu_3\text{-}O)(ppko)_3\}Cl_2]$. X-ray single crystal analysis displays a trigonal bipyramid configuration with the terminal two Co^{II} ions wrapping an triangle $[Co^{III}{}_3O]^{7+}$ core. The intermolecular C–H···O and C–H···Cl interactions form a 2D network framework. The analysis of magnetic susceptibility revealed the dominant antiferromagnetic interactions and strong orbital contribution of Co^{II} ions.

Introduction

The construction of polynuclear transition metal complexes has attracted considerable attention in the coordination chemistry field due to their interesting topology structures and diverse magnetic properties, such as single molecule magnets (SMMs) and single chain magnets (SCMs).[1,2] In these reported polynuclear complexes, the involved bridging ligands consist of carboxylates, Schiff base derivatives, alkoxides, and oximes. However, the studies of such polynuclear complexes have revealed that the pentanuclear complexes with trigonal-bipyramidal topology have been less documented.[3,4]

In the syntheses of the trigonal-bipyramidal structural complexes, the pyrazole-based and triazole-based ligands were found to play important roles. These trigonal-bipyramidal complexes were also recognized as bis(triple-helical) cases, as well as exhibiting specific properties, such as chirality, magnetic properties, and multiredox.[3] Unexpectedly, the salicyladoxime (H_2salox) ligand also leaded to a trigonal bipyramid $Mn^{II}{}_2Mn^{III}{}_3$ structure with a large magnetic anisotropy.[4] But such complexes did not display bis(triple-helical) configuration. Therefore, to further investigate the pentanuclear trigonal-bipyramidal complexes, it is necessary to choose the suitable bridging ligands to prepare the target products.

Many oxime-metal complexes presented interesting metallic macrocyclic structural feature, and the corresponding complexes were named as metallacrowns (MCs),[5] which can be regarded as metal ions and nitrogen atoms replacing carbon atoms of methylene carbons in crown ethers to display M–N–O repeat units in MC rings. Following the different quantity of M–N–O repeat units in MC rings, MCs have diverse structural types, such as 9-MC-3, 12-MC-4, 15-MC-5, 24-MC-8 and so on. In the trigonal-bipyramidal structures, the triangle $[M_3O]$ units can act as 9-MC-3 structural type.[6] Meanwhile, we found that many transition metal ions (Mn, Cu, Zn) and 3d-4f heterometallic ions have been involved in the formation of MCs. However, it was limited for cobalt-oxime systems, only including two 9-MC-3[6f,7] and one 12-MC-4 MCs.[8]

In our studies, we also explored various oxime ligands, and reported several polynuclear complexes.[9] Recently, in view of the studies of high-spin Co^{II} ($S = 3/2$) complexes with charming magnetic properties, such as antiferromagnetic, ferromagnetic, spin frustration, SMMs and single ion magnets (SIMs),[10–14] we still devote our effort to discuss the syntheses of cobalt complexes with oxime ligands. Herein, we represent a pentanulear, mixed-valence cobalt complex $[\{Co^{II}(CH_3O)_3\}_2\{Co^{III}{}_3(\mu_3\text{-}O)(ppko)_3\}Cl_2]$ (**1**). This complex exhibits a trigonal-bipyramid structure with two $\{Co^{II}(CH_3O)_3\}_2^-$ units wrapping an triangle $[Co^{III}{}_3O]^{7+}$ core. Meantime, the magnetic properties were also investigated.

Result and Discussion

The structure of Hppko ligand and its coordination mode with central metal atoms are given in Scheme 1. Complex **1** crystallizes in triclinic space group $P\bar{1}$, and its crystal structure is shown in Figure 1. The molecule contains two Co^{II} ions, an triangle $[Co^{III}{}_3O]^{7+}$ core, three $ppko^-$ ligands, six CH_3O^- anions, and two coordinated Cl^-. The triangle $[Co^{III}{}_3O]^{7+}$ core consists of three cobalt ions (Co1, Co2, Co3) with a capping μ_3-O atom in the center. Two Co^{II} ions (Co4 and Co5) wrap the triangle $[Co^{III}{}_3O]^{7+}$ core with the help of six CH_3O^- anions linking three Co^{III} to form a trigonal bipyramid configuration. The Co4···Co5 distance is 4.945 Å. In the triangle core, the

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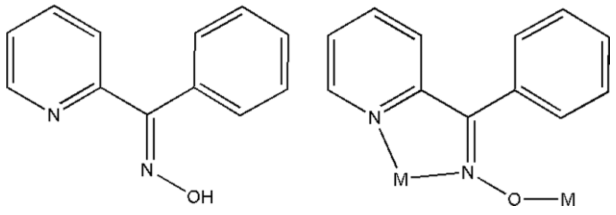
Co–Co distances are 3.232 Å (Co1–Co2), 3.211 Å (Co2–Co3) and 3.242 Å (Co1–Co3), and the Co–O–Co angles are 120.25° (Co1–O4–Co2), 118.92° (Co2–O4–Co3) and 120.59° (Co1–O4–Co3), respectively, approaching an equilateral triangle. Thus, the whole molecule possesses a pseudo-C_3 axis being perpendicular to the Co^{III}_3 plane and passing through the terminal Co^{II} ions and the central oxygen atom. The central O4 atom is displaced 0.054 Å out of the mean Co_3^{III} plane, which is in accordance with the reported distances (0.50 and 0.493 Å).[6f,15] More interetingly, the molecule structure is chiral, but the complex crystallized in the $P\bar{1}$ space group due to the presence of two molecules in one cell unit. The oxidation states of cobalt ions were determined through the bond lengths, charge balance, and bond-valence sum (Table S3, Supporting Information).[16]



Scheme 1. The structure of Hppko ligand and coordination mode of ppko⁻.

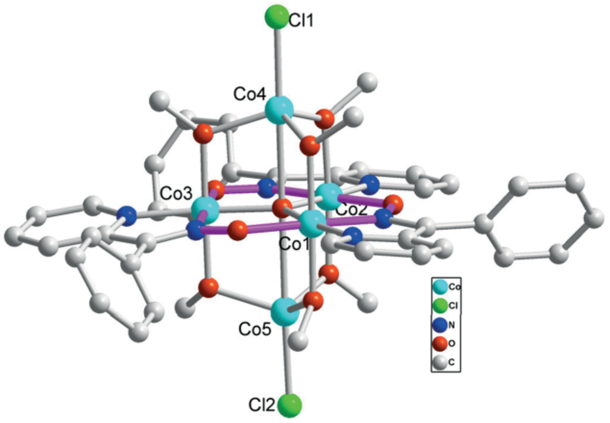


Figure 1. The asymmetric unit of complex **1**. The hydrogen atoms are omitted for clarity.

In the triangle core, three Co^{III} (Co1, Co2, and Co3) ions adopt six-coordination octahedral geometry with coordination atoms from two oximato N atoms and one oximato O atom of two adjacent ppko⁻ ligands, one μ_3-O atom and two CH_3O^- anions. Thus, three Co^{III} ions are bridged by three ppko⁻ groups along each edge of the triangle to display Co–N–O repeat unit. The Co–N–O-Co torsion angles are 6.3° (Co1–N2–O1–Co2), 6.2° (Co2–N4–O2–Co3), and 11.8° (Co3–N6–O3–Co1), respectively, indicating the smaller twisting for N–O bonds than that in the reported Co^{III} 9-MC-3 complexes.[6f,15] Each apical Co^{II} ions (Co4 and Co5) displays four-coordination, tetrahedral coordination arrangements with four coordination atoms supplied by three O atoms from three CH_3O^- and one Cl⁻. The Co^{II} complexes with tetrahedral coordination environment also have been reported.[17] The distances of Co–Cl are 2.302 Å (Co4–Cl1) and 2.298 Å (Co5–Cl2), respectively. For three ppko⁻ ligands, the benzene ring and pyridine ring of each ligand are not located in one plane with the twisting angles of 55.67, 67.99 and 57.21°, respectively. Furthermore, the inspection of the intermolecular interactions among complex **1** presents a 2D network arrangement via the weak supermolecular C–H···O [the distances of 2.633 Å (H2···O5), 3.485 Å (C2···O5)] and C–H···Cl [the distances of 3.730 Å (C11···Cl1), 3.602 Å (C22···Cl1) and 3.582 Å (C32···Cl2)] interactions (Figure 2a and b). The C–H···Cl interactions resulted in the formation of A and B chains, and the A and B chains were linked together through C–H···O interactions. Thus, ABAB frameworks are presented in 2D network following the arrangement of complexes **1** with the interactions of C–H···O and C–H···Cl (Figure 3).

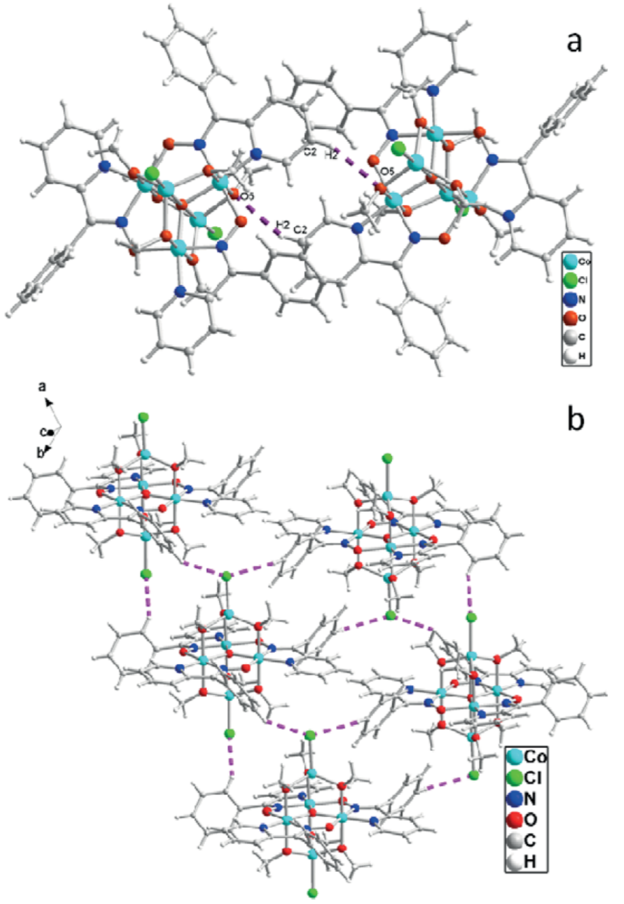


Figure 2. Intermolecular C–H···O (a) interactions with the distances 2.633 Å (H2···O5), 3.485 Å (C2···O5) and C–H···Cl (b) interactions with the distances 3.730 Å (C11–Cl1), 3.602 Å (C22–Cl1) and 3.582 Å (C32–Cl2).

Thermogravimetric analysis (TGA) reveals that **1** displays a weight loss of 12.2 % between 120–160 °C, corresponding to the release of two coordinated Cl⁻ anions. No further weight loss was observed below 400 °C, indicating good thermal stability of **1**. The powder X-ray diffraction (PXRD) demonstrates low purity for the samples obtained by evaporating solvent, compared with the simulated samples, which corresponds to the crystal samples.

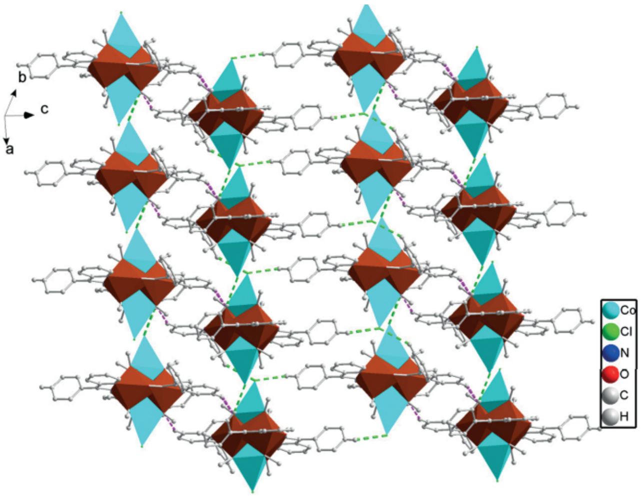


Figure 3. The polyhedral representation of the 2D network with ABAB frameworks.

The variable temperature DC magnetic susceptibility data were collected in the temperature range of 1.8–300 K for the powder samples. The plots of $\chi_M T$ vs. T and χ_M^{-1} vs. T are shown in Figure 4 (χ_M being the molar susceptibility). Because Co^{III} ion is low-spin (t_{2g}^6, $S = 0$), the magnetic properties only derive from two apical Co^{II} ions of the triangle bipyramidal mode. As seen from Figure 4, the $\chi_M T$ value at 300 K is 4.46 cm^3·K·mol^{-1}, significantly higher than the expected value of 3.75 cm^3·K·mol^{-1} for two non-interacting Co^{II} ions with $g = 2.0$. As decreasing temperature, the $\chi_M T$ values slightly decreased, then sharply dropped to 0.58 cm^3·K·mol^{-1} at 12 K before increasing to a maximum of 0.76 cm^3·K·mol^{-1}. Further cooling temperature, the value decreased to 0.38 cm^3·K·mol^{-1} at 1.8 K, confirming a relative small, non-zero ground state. This behavior of $\chi_M T$ clearly indicated the dominant antiferromagnetic interactions.[17] The decrease at low temperature was attributed to zero-field splitting/weak intermolecular interactions. Neglecting the effects of spin-orbit coupling, the presence of diamagnetic Co^{III} ions allows us to explore the Co–Co magnetic coupling interactions. The magnetic susceptibility equation is derived as:

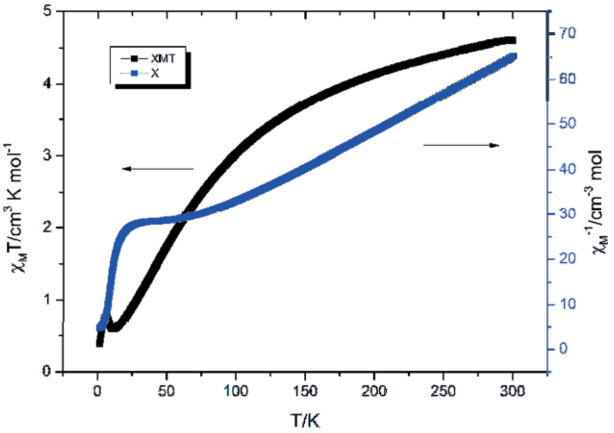


Figure 4. The $\chi_M T$ and χ_M^{-1} plots as functions of temperature (T) for complex **1** at 1000 Oe.

The fitting of magnetic susceptibility gives $J = -10.9$ cm^3·K·mol^{-1} and $g = 2.19$, suggesting the antiferromagnetic interactions and strong orbital contribution of the Co^{II} ions.

Conclusions

A novel pentanuclear, mixed-valence cobalt complex was successfully synthesized through $CoCl_2·6H_2O$ and Hppko in the presence of NEt_3. Five Co ions were held together to exhibit a trigonal bipyramid configuration with two Co^{II} occupying the apical positions and three Co^{III} ions residing in the equilateral triangular plane. The magnetic susceptibility measurements indicated the dominant antiferromagnetic coupling between two high-spin Co^{II} ions, and the fitting of magnetic susceptibility confirmed the strong orbital contribution of Co^{II} ions.

Experimental Section

Materials and Instrumentation: All chemicals used in the experimental process are commercially available and used as received without further purification. Elemental analyses on C, H, and N were carried out with an Elementar Vario EL analyzer. IR spectra were measured with a Perkin-Elmer Spectrometer. FT-IR spectra were recorded with a Perkin-Elmer Spectrum BX spectrometer in KBr pellets. The powder X-ray diffraction (PXRD) patterns were recorded with a Bruker D8 Advance diffractometer with Cu-K_α radiation ($\lambda = 1.5418$ Å) at room temperature. Thermogravimetric analyses (TGA) were performed in a nitrogen atmosphere with a heating rate of 10 K·min^{-1} with a Netzsch STA 449C thermal analyzer. The magnetic susceptibility measurements were obtained with a Quantum Design SQUID magnetometer MPMSXL in the temperature range of 1.8–300 K and an applied field of 1 kOe. The mass of sample in the magnetic measurement for complex **1** was 9.73 mg.

Single-crystal X-ray Diffraction: The crystal structure of complex **1** was determined through single-crystal X-ray diffraction. The corresponding data were collected with a Bruker Smart CCD area-detector diffractometer with Mo-K_α radiation ($\lambda = 0.71073$ Å) by ω-scan mode at room temperature. The program SAINT was used for integration of the diffraction profiles, and the semi-empirical absorption corrections were applied using SADABS.[18,19] All of the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL.[20] Metal ions were located from the E maps, and the other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. Generally, hydrogen atoms bonded to carbon atoms were determined theoretically and refined with isotropic thermal parameters binding on their parents. Hydrogen atoms of water and solvents were first located by difference Fourier E maps and then treated isotropically as riding.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-947001 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Synthesis of Hppko: Hppko ligand was synthesized following the reported procedure.[21] Phenyl-2-pyridone (17.2000 g, 0.10 mol) and hydroxylamine hydrochloride (8.0600 g, 0.116 mol) were mixed in 6 mL H_2O with the flask placed in ice water. Afterwards, NaOH (9.2000 g, 0.23 mol) was added into the above solution in batches. After stirring for 4 h in ice water, the solution was kept to stir for 40 h at room temperature until the massive light pink precipitate was separated out. The pH of the resulting precipitate in the ice water was changed to 5–6 through adding HCl. The sample was filtered and dried with the yield 78.69 % (31.0000 g). M.p. 154–156 °C. **IR** (KBr): $\tilde{\nu}$ = 3437 (s), 3056 (w),1667 (s), 1579 (m), 1465 (w), 1446 (m), 1435 (m), 1385 (m), 1322 (m), 1303 (m), 1283 (m), 1241 (w), 1155 (m), 1094 (w), 1074 (w), 993 (m), 943 (m), 927 (w), 882 (w), 818 (w), 779 (m), 749 (m), 731 (w), 706 (s), 651 (m), 616 (m), 543 (w) cm^{-1}. $C_{12}H_{10}N_2O$: calcd. C 72.73, H 5.05, N 10.03 %; found C 72.65, H 5.21, N 10.35 %.

Synthesis of [{Co^{II}(CH$_3$O)$_3$}$_2${Co^{III}$_3$(μ$_3$-O)(ppko)$_3$}Cl$_2$]: Hppko (0.0990 g, 0.5 mmol) and $CoCl_2·6H_2O$ (0.1190 g, 0.5 mmol) were mixed in MeOH (20 mL). NEt_3 (1 mmol) was added to the resulting mixture with stirring for 6 h. Afterwards, the mixture was filtered, and the filtering solution was left to stand out at air. The red crystals were obtained after six weeks. Yield: 53 % (based on Co). **IR** (KBr): $\tilde{\nu}$ = 3439 (mb), 3054 (w), 1640 (m), 1589 (w), 1556 (w), 1462 (s), 1432 (w), 1379 (m), 1365 (s), 1198 (s), 1097 (s), 1046 (m), 948 (w), 899 (m), 804 (m), 708 (s), 645 (s), 623 (w), 569 (s), 512 (m), 454 (m) cm^{-1}. $C_{42}H_{45}Cl_2Co_5N_6O_{10}$: calcd. C 43.51, H 3.91, N 7.25 %; found C 43.69, H 3.65, N 7.13 %.

Supporting Information (see footnote on the first page of this article): Tables showing Crystallographic data and structure refinement details, Selected bond distances and angels, as well as the oxygen state of Co ions (Tables S1-S3); Figures showing the TGA curve and PXRD patterns (Figures S1-S2).

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Keywords: Phenyl 2-pyridyl ketone oxime; Mixed-valence cobalt; Synthesis; Structure elucidation; Magnetic properties

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A Pentanuclear Cobalt Complex with two $[Co^{II}(CH_3O)_3]^-$ Units Wrapping a Triangular $[Co^{III}{}_3O]^{7+}$ Core: Synthesis, Structure, and Magnetic Properties