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A unique mixed-bridged trinuclear Co (II) complex and its extended system: Structural and magnetic studies

Yu-Ting Yang, Fang-Hua Zhao, Yun-Xia Che, Ji-Min Zheng*

Department of Chemistry, Nankai University, Tianjin 300071, PR China

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ABSTRACT

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Polynuclear-based magnetic complexes have attracted great attention in the field of molecular magnetism for decades, because they not only help to improve our understanding of mechanism of magnetic coupling but also function as building blocks applicable in molecular-based materials [1-3]. The most popular and effective strategy to design such materials is connecting paramagnetic centers by short bridging ligands such as oxo, hydroxide, alkoxo, phenolate, carboxylate, or azide, in combination with different organic coligands to adjust the structure and dimensionality [4–6]. Among these, azide and carboxylate are the most extensively studied short bridges because of their multiple bridging modes and the diversity in the propagation of magnetic behavior [7]. It is well-known that azide anion can link metal ions in *u*-1.1 (end-on, EO), *u*-1.3 (end-to-end, EE), μ -1.1.3. or still other modes, generating discrete, one-, two- and three-dimensional species with various topologies [8]. In general, the EO mode transmits ferromagnetic (FM) exchange interaction, while the EE mode affords antiferromagnetic (AFM) exchange between the paramagnetic centers [9] and other mixed azide bridging modes also give interesting magnetic properties [10]. An effective synthetic approach for obtaining complexes with novel structures and magnetic properties is to incorporate a second short bridge that provides different pathways for magnetic exchange. Considering that the carboxylate can also efficiently transmit magnetic interactions, we pay particular attention to combining azide and carboxylate into one system. However, turning the assumption into reality is still a challenge in coordination chemistry, perhaps because of the

Two novel complexes, $[Co_3(N_3)_2(bca)_4(phen)_2]$ (1, bca = benzenecarboxylic acid, phen = 1,10-Phenanthroline) and $[Co_3(N_3)_2(bdc)_2(phen)_2]_n$ (2, bdc = terephthalic acid), have been synthesized hydrothermally and characterized by single crystal X-ray diffraction (XRD), infrared spectra (IR) and element analysis (EA). Complex 1 features unprecedented discrete linear Co₃ clusters that formed by mixed (μ -EO-N₃)(μ -COO)₂ (EO = end-on) triple bridges whereas 2 presents an extended (2D) network based on the similar trinuclear units as 1. Magnetic studies of 1 and 2 reveal that the mixed (μ -EO-N₃)(μ -COO)₂ triple bridges transmit ferromagnetic behavior.

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mismatch between azide and carboxylic oxygen ligand in the competition to bind metal ions [11]. In contrast to the extensive structural and magnetic studies on compounds with azide or carboxylate bridges, so far, only very few examples containing mixed azide and carboxylate bridges have been reported, and magnetic studies exhibit that mixed bridges usually transmit FM interactions between neighboring metal ions [11,12]. Herein, we report the synthesis, structure, and magnetic properties of two cobalt complexes, namely $[Co_3(N_3)_2$ $(bca)_4(phen)_2]$ (1) and $[Co_3(N_3)_2(bdc)_2(phen)_2]_n$ (2), which contain rare $[Co_3(\mu-EO-N_3)_2(\mu-COO)_4]$ molecular building blocks. To the best of our knowledge, this is the first Co_3 clusters bridged by mixed $(\mu-EO-N_3)(\mu-COO)_2$ triple bridges [13].

Single crystal X-ray diffraction reveals that complex **1** crystallizes in the triclinic space group P-1 [14]. The asymmetric unit consists of two crystallographically independent Co (II) atoms (Co1 and Co2), one azide anion, two bca ligands and one phen molecule. Complex 1 consists of linear trinuclear unit of Co (II) atoms, where the central Co1 atom lies on a crystallographic inversion center and is linked by double carboxyl groups of bca ligands and one end-on azide anion to the terminal Co(2) atoms (Fig. 1.). The central Co1 atom in the CoO₄N₂ coordination environment has slightly distorted octahedral geometry with four carboxylic oxygen atoms from four different bca ligands forming the equatorial plane and two end-on azide nitrogen atoms occupying two apical positions. The angles around the Co1 atom are 87.96(18) - 92.04(18) °. The Co1-O distances are 2.070(4) and 2.121(5) Å and Co1–N3 distance is 2.186(5) Å. The terminal Co2 atom is coordinated by two carboxylic oxygen atoms from two bca ligands, one azide nitrogen atom and two phen nitrogen atoms, resulting the five-coordinate CoO2N3 coordination environment with distorted trigonal-bipyramidal geometry. The Co2-O bond

^{*} Corresponding author. Tel.: + 86 22 23507950; fax: + 86 22 23508056. *E-mail address*: jmzheng@nankai.edu.cn (J.-M. Zheng).

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Fig. 1. View of the local coordination environment for Co atoms in 1 (symmetry codes A: -x + 2, -y, -z + 1). Hydrogen atoms are omitted for clarity.





Fig. 2. (a) 2D layer structure in 2. (b) Schematic description of the 4-connected (4,4) net.



Fig. 3. Temperature dependence of $\chi_M T$ vs. *T* plot for **1** (a) and **2** (b) at 1000 Oe. Inset: χ_M vs. *T* plot, and the red solid line represent the simulation results.

distances fall in the range between 2.022(5) and 2.111(5) Å, and Co2–N distances range from 2.089(6) to 2.128(5) Å. The angles around the terminal Co2 atom are $78.9(2) - 139.90(19)^{\circ}$. The Co–O/N bond lengths and angles are all consistent with corresponding ones found in other Co-based complexes [15].

The completely deprotonated bca anion acts as a bidentate bridging spacer linking two Co (II) atoms, and the carboxyl group show the μ_2 : η^1 , η^1 coordinated mode. While the azide anion shows the EO (end-on) bridging mode, acts as a bidentate bridging spacer linking two Co (II) atoms. Each Co1 atom connects to two Co2 atoms through mixed (μ -EO-N₃)(μ -COO)₂ triple bridges, generating a linear trimeric Co₃ cluster along the *a*-axis direction [Co1–N3–Co2 = 94.0(2)°]. To our knowledge, such a mixed bridging mode for Co₃ is unprecedented in the literature. The Co1…Co2 distance spanned by the ($\mu_{1,1}$ -N₃) (μ -COO)₂ triple bridges is 3.12 Å, and the Co1–N3–Co2 angle is 94.0 (2)°, comparable to the reported (μ -EO-N₃)(μ -COO)₂-bridged Co (II) complexes [12].

Furthermore, we chose bdc that contains two carboxylate groups in opposite position to replace bca in **1**, and isolated a 2D layer framework. Complex **2** crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit consists of two crystallographically independent Co (II) atoms (Co1 and Co2), one azide anion, two bdc ligands and one phen molecule. The azide anion adopts μ -1,1 (EO) coordination mode, while bdc ligand shows the μ_4 : η^1 , η^1 , η^1 , η^1 coordination mode. The basic building block of **2** is linear trinuclear $[Co_3(\mu-EO-N_3)_2 (\mu-COO)_4]$ unit which is bridged by two nitrogen atoms of azide anion and four carboxyl oxygen atoms of bdc ligands [Co1-O=2.0027(16)-2.0466(16) Å, Co1-N=2.080(2)-2.0297(19) Å, Co1-N3-Co2=103.07 (8)°]. This unit is similar to complex**1**. It should be noted that the bond angle Co1-N3-Co2 (103.07(8)°) in**2**is larger than the corresponding one (94.0(2)°) in**1** $, which suggests that it may affect the magnetic properties of molecules [12]. The adjacent Co1...Co2 and Co1...Co1 distances are 3.230 Å and 6.460 Å in Co₃ unit. Each trimer is connected to four adjacent ones by four bdc ligands to a 2D layer structure (Fig. 2a). The nearest interlayer Co...Co distance is 10.616 Å. Besides, a (4, 4) 2D net is constructed by making the <math>[Co_3(\mu-EO-N_3)_2(\mu-COO)_4]$ unit as 4-connected node (Fig. 2b).

Further analysis of the crystal packing reveals that the phen planes of the neighboring layers are obviously parallel with each other, and the phenyl_{phen}-phenyl_{phen} rings stack in an offset face-to-face orientation (π - π stacking offset distance is 3.310 Å), connecting neighboring layers into 3D supramolecular network (Fig. S1).

Temperature-dependent magnetic susceptibility measurements of complexes **1** and **2** were performed under a field of 1000 Oe in the temperature range of 2–300 K. **1** and **2** show similar magnetic behaviors (Fig. 3). The $\chi_M T$ values of **1** and **2** are 7.94 and 7.64 cm³ K mol⁻¹ at 300 K, respectively. These two values are larger than the sum of the expected value (5.62 cm³ mol⁻¹ K, g=2.0, S=3/2 [1]) for three uncoupled high-spin Co (II) ions, because of the significant contribution from the unquenched orbital momentum in the octahedral field (the ${}^{4}T_{1g}$ state). As the temperature is lowered, the $\chi_M T$ values first increase smoothly and then rise abruptly to the maxima values of 13.33 cm³ mol⁻¹ K at 7.5 K for **1**, and 14.65 cm³ mol⁻¹ K at 5.0 K for **2**. Upon further cooling, $\chi_M T$ curves sharply decrease to minimum values of 10.68 cm³ mol⁻¹ K and 13.09 cm³ mol⁻¹ K at 2 K for **1** and **2**, respectively.

Temperature-dependent magnetic susceptibilities of complexes **1** and **2** indicate significant ferromagnetic (FM) behavior. This is consistent with that observed in other Co-based complexes with the mixed (μ -EO-N₃)(μ -COO)₂ triple bridges motif [12]. The decrease of $\chi_M T$ is possibly due to ZFS (zero field splitting) and/or inter-trimer antiferromagnetic interaction [1].

Magnetic susceptibility data per Co₃ unit for **1** and **2** can be fitted to the Curie–Weiss law ($\chi_M = C/(T - \theta)$), giving a Curie constant C = 7.96 cm³ mol⁻¹ K, and Weiss constant $\theta = +6.0$ K at 2–300 K for **1**, C = 7.37 cm³ mol⁻¹ K, and $\theta = +11.79$ K at 90–300 K for **2**, respectively. The positive θ values indicate the domination of FM interaction between the adjacent Co1 and Co2 atoms through the mixed (μ -EO-N₃)(μ -COO)₂ triple bridges.



Fig. 4. Field dependence of magnetization for 1 and 2 at 2 K.



Fig. 5. Hysteresis loop at 2 K for 1 and 2. The insets give a blown-up view of the hysteresis loop below 200 Oe.

According to the structural data, both **1** and **2** can magnetically be treated as trinuclear complexes in which magnetic coupling is mediated through the triple bridge $(\mu$ -EO-N₃) $(\mu$ -COO)₂. To simulate the experimental magnetic behavior, the data of **1** and **2** are approximately fitted by the isotropic linear trinuclear model that is based on spin Hamiltonian:

$$\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_{1A} \cdot \hat{S}_2)$$
 and $\chi = \frac{\chi_{trimer}}{1 - \frac{2}{Ne^2 G^2} \chi_{trimer}}$

where $S_1 = S_{1A} = S_2 = 3/2$. The best fit gives the J=4.15 cm⁻¹, g=2.4 for **1** (Fig. 3a) and J=7.85 cm⁻¹, g=2.25 for **2** (Fig. 3b). These results are also consistent with the experimental research.

The *M* vs. *H* measurement at 2 K among 0–50 kOe is given in Fig. 4. The curves raise first sharply till saturation and then gradually to 8.46 $N\beta$ for **1** and 7.86 $N\beta$ for **2** at 50 kOe. These findings are close to the expected value ($Ms = 9 N\beta$) for g=2 and S=3/2, confirming the expected FM coupling in **1** and **2**. Isothermal magnetization experiments performed at 2 K exhibit a hysteresis with small coercive field (*Hc*) and remnant magnetization (Mr) of 12 Oe and 0.014 $N\beta$ for **1**, 15 Oe and 0.015 $N\beta$ for **2** (Fig. 5), typical of soft ferromagnetic behavior.

To gain insight into the FM ordering, ac magnetic susceptibility measurements were performed on **1** and **2** under a zero dc field and a 3 Oe ac field oscillating at different frequencies. The ac response of both crystals was weak, no peak was found for χ' or χ'' data. Feeble frequency-dependent phenomena of the out-of-phase were observed at low temperature for **1** and **2** (Fig. S2). More evidence is required to determine if they belong to molecular magnet.

In conclusion, we have described two novel complexes: **1** is linear trinuclear Co_3 cluster structure in which Co (II) atoms linked each other by mixed (μ -EO-N₃)(μ -COO)₂ triple bridges. **2** is a 2D network composed of linear trinuclear Co_3 units which are similar to **1**. It is worth noting that the mixed (μ -EO-N₃)(μ -COO)₂ triple bridges induced ferromagnetic coupling in linear Co_3 units, and this work provides a new approach toward materials with ferromagnetic properties. Continued structure and property investigations of polynuclear paramagnetic clusters containing mixed bridges are underway in our laboratory.

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Appendix A. Supplementary data

CCDC-820575 (1) and CCDC-820576 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. or e-mail: deposit@ccdc.cam. ac.uk. Additional figures, selected bond lengths and angles are available as electronic supplementary information in the online version, at doi:10.1016/j.inoche.2011.08.014.

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- [13] CAUTION! Although not encountered in our experiments, azide compounds of metal ions are potentially explosive. The materials should be handled in small amounts and with care. Synthesis of 1: A mixture of CoCl2·6H2O (0.36 g, 1.5 mmol), NaN₃ (0.065 g, 1.0 mmol), bca (0.24 g, 2.0 mmol), and phen (0.20 g, 1.0 mmol) in the molar ratio of 1.5:1:2:1 was added into 7 ml of water. Consequently, the resulting solution was transferred and sealed in a 25 ml Teflonlined stainless steel vessel, which was heated at 160 °C for 4 days. After the reactor was slowly cooled to room temperature at a rate of 5 °C/h, pure deep red block-shaped crystals were filtered off, and dried in air. Yield: 67% based on Co. Elemental analysis (%) calcd for 1 (C₅₂ H₃₆ Co₃ N₁₀O₈), C, 56.48; H, 3.28; N, 12.67. Found: C, 56.52; H, 3.31; N, 12.72. IR (KBr): ν (cm⁻¹) = 3062 (m), 2071 (vs), 1598 (vs), 1553 (vs), 1403 (vs), 1345 (m), 1059 (s), 1283 (m), 852 (s), 727 (vs), 673 (m), 466 (m). Synthesis of 2: A mixture of CoCl₂·6H₂O (0.36 g, 1.5 mmol), NaN $_3$ (0.065 g, 1.0 mmol), bdc (0.16 g, 1.0 mmol), and phen (0.20 g, 1.0 mmol) in the molar ratio of 1.5:1:1:1 was added into 7 ml of water. Consequently, the resulting solution was transferred and sealed in a 25 ml Teflonlined stainless steel vessel, which was heated at 170 °C for 4 days. After the reactor was slowly cooled to room temperature at a rate of 5 °C/h, pure purple blockshaped crystals were filtered off, and dried in air. Yield: 58% based on Co. Elemental analysis (%) calcd for **2** (C_{40} H₂₄ Co₃ N₁₀O₈), C, 50.60; H, 2.55; N, 14.75. Found: C, 50.64; H, 2.61; N, 14.79. IR (KBr): ν (cm⁻¹) = 3427 (s), 2075 (vs), 1577 (vs), 1428 (m), 1387 (vs), 1366 (s), 835(s), 814 (m), 752(s), 715(s), 524 (m).
- [14] Suitable single crystals of 1 and 2 were selected and mounted in air onto thin glass fibres. Accurate unit cell parameters were determined by a least-squares fit of 20 values, and intensity data were measured on a Bruker Smart CCD or Rigaku Raxis Rapid IP diffractiometer with Mo-K α radiation (λ = 0.71073 Å) at room temperature. The intensities were corrected for Lorentz and polarization effects as well as for empirical absorption based on a multi-scan technique; all structures were solved by direct methods and refined by full-matrix leastsquares fitting on F² by SHELX-97. All non-hydrogen atoms were refined with anisotropic thermal parameters. Aromatic hydrogen atoms were assigned to calculated positions with isotropic thermal parameters, and hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by the use of geometrical restraints. Crystal data for 1: Triclinic, space group P-1, a = 9.6393(19) Å, b = 11.573(2) Å, c = 11.987(2) Å, $\alpha = 114.95(3)^{\circ}$ $\beta = 95.71(3)^\circ$, $\gamma = 96.57(3)^\circ$, V = 1882.3(7) Å³, Z = 1, GOF = 0.977, final R1 = 0.0909, $\omega R2 = 0.1688$. Crystal data for **2**: Monoclinic, space group $P2_1/n$, a = 10.409(2) Å, b=15.419(3) Å, c=11.375(2) Å, β =90°, V=1793.1(6) Å³, Z=2, GOF=1.000, final $R1 = 0.0384, \omega R2 = 0.0974.$
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