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## Ferromagnetic interactions in a bis( $\mu$ -end-on azido)cobalt(II) linear trimer

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### ABSTRACT

A linear trinuclear Co(II) compound,  $[\text{Co}_3(\mu_{1,1}\text{-N}_3)_4(\text{N}_3)_2(\text{H}_2\text{O})_2(\text{bpbp})_2] \cdot 2\text{H}_2\text{O}$  (**1**, bpbp = 3,3'-bis-Dimethylamino-1,1'-pyridine-2,6-diyl-bispropenone), is reported. The central Co(II) ion is bridged to Co(II) ions on both sides by four end-on azide ( $\mu_{1,1}\text{-N}_3^-$ ) ligands resulting in a centrosymmetric trimer with adjacent Co···Co distance of 3.233 Å. Each Co(II) ion possesses distorted octahedral geometry, the central one is coordinated by two aqua ligands and four  $\mu_{1,1}\text{-N}_3^-$  nitrogen atoms and each terminal Co(II) is coordinated by two  $\mu_{1,1}\text{-N}_3^-$  nitrogen atoms, one terminal  $\text{N}_3^-$  nitrogen atom and capped by terminal tridentate bpbp ligand. Variable temperature magnetic studies indicate ferromagnetic coupling between adjacent Co(II) ions within the trimer.

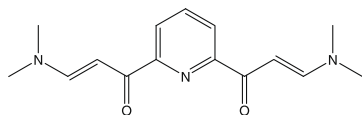
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The synthesis and study of polynuclear paramagnetic clusters (PMCs) has long been hot topic in the field of molecular magnetism, because they not only help to improve our understanding of the mechanism involved in magnetic coupling but also function as building blocks applicable in molecular-based materials [1]. In order to obtain discrete PMCs, small bridging ligands such as oxo, chloride, hydroxide, alkoxo, phenolate, carboxylate or azide are often used to react with transition metal ions with the help of blocking terminal ligands that prevent the growth of clusters into infinite networks. Among these, the azide ligand has been shown to exhibit a wide variety of coordination modes [2] and propagate established magnetic interactions. Normally, for example, the end-on azide ligand mediates ferromagnetic interactions [2]. In our attempt to pursuit PMCs, we focus our attention on the cobalt clusters [3] because of their interesting and complicated magnetic properties. Here we report a new linear trinuclear Co(II) compound,  $[\text{Co}_3(\mu_{1,1}\text{-N}_3)_4(\text{N}_3)_2(\text{H}_2\text{O})_2(\text{bpbp})_2] \cdot 2\text{H}_2\text{O}$  (**1**), with only end-on azide ions as bridging ligands and bpbp (bpbp = 3,3'-bis-dimethylamino-1,1'-pyridine-2,6-diyl-bispropenone) as capped molecules. Linear Co(II) trimers have been reported by several groups that can be classified as two series according to the bridging ligands, one is those with dipyridylamine bridging ligands [4] that show Co(II)···Co(II) bonding and another is those with carboxylate bridging ligands [5]. To our knowledge, compound **1** is the first linear Co(II) trimers with azide bridging ligands. In a recent paper, a mixed-valence linear azide-bridged Co(III)–Co(II)–Co(III) compound was reported [6].

The ligand bpbp (Scheme 1) is the intermediate for the synthesis of 2,6-bis(pyrazol-3-yl)pyridine and was synthesized according Ref. [7] and recrystallized in ethanol. The synthesis of compound **1** was carried out by reaction of  $\text{Co}(\text{OAc})_2$ , bpbp and  $\text{NaN}_3$  in a ratio of 2:1:4 in methanol–water solution [8]. Red block-like crystals in about 50% yield were obtained by evaporation of the filtrate in three days.

Compound **1** consists of linear trinuclear unit of Co(II) atoms, where the central Co(II) atom lies on a crystallographic inversion center and is linked by double end-on azide anions to the terminal Co(II) atoms [9]. The structure of **1** is shown in Fig. 1. The central Co(II) atom in the  $\text{CoN}_4\text{O}_2$  coordination environment has slightly distorted octahedral geometry with four end-on azide nitrogen atoms forming the equatorial plane and two aqua molecules occupying two apical positions. The Co2–N bond distances are 2.129(2) and 2.138(2) Å and Co2–O1 W distance is 2.067(2) Å. The terminal Co(II) atoms are coordinated with two end-on azide ligands and one terminal azide ligand, the other three positions are occupied by a tridentate chelating bpbp ligand. The three azide nitrogen atoms and one bpbp pyridyl nitrogen atom occupy the in-plane positions with Co1–N bond distances varying from 2.063(2) to 2.185(2) Å, the two carbonyl oxygen atoms (O1 and O2) from bpbp occupy the apical positions with Co1–O distances of 2.149(2) and 2.182(2) Å. The angles around the terminal Co(II) atom are 74.50(8)–106.12(9)°, which indicates that the octahedral environment of the terminal Co(II) atom is more distorted than that of the central one (78.85(10)–101.15(10)°). The distance between the neighboring Co(II) atoms is 3.23 Å, similar to that of a pyridazine- and hydroxide-bridged Co(II) trimer [5d] and much shorter than those of carboxylate-bridged Co(II) trimers [5a–c].

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3,3'-bis-Dimethylamino-1,1'-pyridine-2,6-diyl-bispropenone

(bpbp)

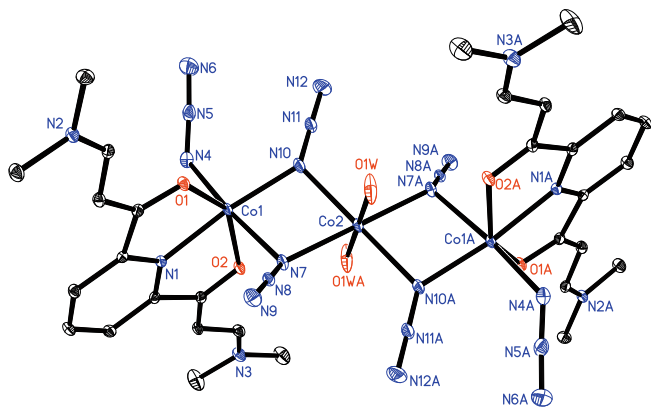
**Scheme 1.** 3,3'-bis-dimethylamino-1,1'-pyridine-2,6-diyl-bispropenone (bpbp).

The temperature-dependent magnetic susceptibility for microcrystalline **1** was measured in the temperature range 1.8–300 K with an applied field of 1000 G. As shown in Fig. 2, the  $\chi_M T$  value per trimer at room temperature is  $9.19 \text{ cm}^3 \text{ K mol}^{-1}$ , which is large than that for three noninteracting cobalt ions of  $S = 3/2$  because of the orbital contribution. Upon cooling, this value steadily increases to  $12.48 \text{ cm}^3 \text{ K mol}^{-1}$  at 9 K, followed by a rapid decrease to  $10.38 \text{ cm}^3 \text{ K mol}^{-1}$  at 1.8 K. The  $1/\chi_M$  value above 100 K fitted with the Curie–Weiss law gave  $C = 10.67 \text{ cm}^3 \text{ K mol}^{-1}$  and  $\theta = 8.84 \text{ K}$ , which shows an intramolecular ferromagnetic coupling of the adjacent cobalt atoms.

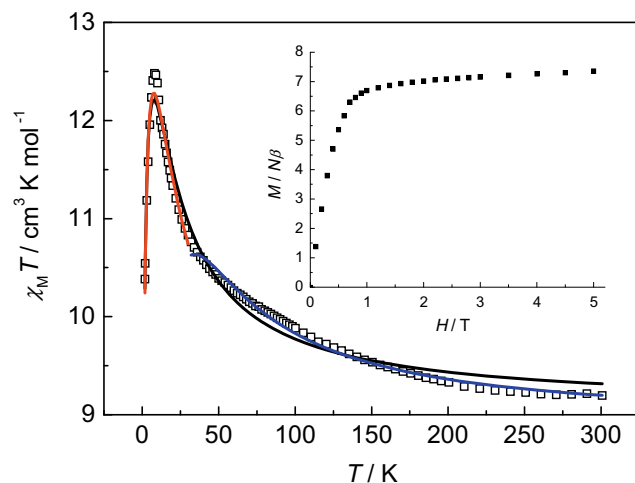
In order to simulate the experimental magnetic data, we tried the modified Lines's model [5c] and the linear trinuclear model [5d] with two different  $g$  tensors, which however did not give reasonable results. So we tried to analyze the magnetic susceptibility by the corresponding expression derived through the spin Hamiltonian which included the effect of the zero-field splitting parameter ( $D$ ) and the intermolecular exchange interaction ( $zJ'$ ) in the molecular-field approximation:

$$\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_{1A} \cdot \hat{S}_2) + D\hat{S}^2/3 \quad \text{and} \quad \chi = \frac{\chi_{\text{trimer}}}{1 - \frac{2zJ'}{Ng^2\beta^2} \chi_{\text{trimer}}} \quad (1)$$

where  $S_1 = S_{1A} = S_2 = 3/2$ . The best fit for the temperatures greater than 5 K gives  $g = 2.54$ ,  $J = 4.30 \text{ cm}^{-1}$ ,  $D = 5.01 \text{ cm}^{-1}$  and  $zJ' = -0.028 \text{ cm}^{-1}$  with  $R = 1.26 \times 10^{-4}$  ( $R = \sum (\chi_{\text{obs}} - \chi_{\text{cal}})^2 / \sum \chi_{\text{obs}}^2$ ), the calculated fit is however slightly off at temperature greater than



**Fig. 1.** ORTEP drawing of the structure of **1** at the 35% probability level. Hydrogen atoms are omitted for clarity. Symmetry code: (A)  $-x, -y, -z$ . Selected bond lengths (Å) and angles (°): Co1–N1 2.063(2), Co1–N4 2.098(3), Co1–N7 2.185(2), Co1–N10 2.063(2), Co1–O1 2.1496(19), Co1–O2 2.1818(18), Co2–N7 2.129(2), Co2–N10 2.138(2), Co2–O1W 2.067(2); N1–Co1–N4 91.38(9), N10–Co1–N4 94.75(10), N1–Co1–O1 75.52(8), N10–Co1–O1 106.12(9), N4–Co1–O1 97.03(8), N1–Co1–O2 74.50(8), N10–Co1–O2 102.84(9), N4–Co1–O2 91.15(8), O1–Co1–O2 149.07(7), N1–Co1–N7 94.46(9), N10–Co1–N7 79.23(10), O1–Co1–N7 89.08(8), O2–Co1–N7 85.81(8), O1W–Co2–O1WA 180.000(1), O1W–Co2–N7 89.04(9), O1WA–Co2–N7 90.96(9), O1W–Co2–N10 87.17(10), N7–Co2–N10 78.85(10), N7–Co2–N10A 101.15(10), Co2–N7–Co1 97.09(10), Co1–N10–Co2 100.64(11).



**Fig. 2.** Thermal variation of  $\chi_M T$  for **1** at a magnetic field of 1000 G (empty square), the solid lines are the best fit using the Eq. (1) (black), the best fit with  $S_{\text{eff}}(\text{Co}) = 1/2$  at temperature below 30 K (red) and the best fit with  $S_i(\text{Co}) = 3/2$  above 30 K (blue). The inset is the magnetic field dependent of magnetization at 1.8 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

25 K. On the other hand, the Co(II) ion is usually treated as an effective spin  $S'_{\text{Co}} = 1/2$  at low temperature [10], thus a symmetric trimer model through Kambe's method [11] may be used with  $S'_1 = S'_{1A} = S'_2 = 1/2$ . Fitting of the magnetic susceptibility data in the temperature range of 1.8–30 K gives  $g = 5.39$ ,  $J = 13.67 \text{ cm}^{-1}$ , and  $zJ' = -0.16 \text{ cm}^{-1}$  with  $R = 9.4 \times 10^{-5}$  ( $R = \sum (\chi_{\text{obs}} - \chi_{\text{cal}})^2 / \sum \chi_{\text{obs}}^2$ ). Using the same method to fit the data above 30 K with  $S_1 = S_{1A} = S_2 = 3/2$  gives  $g = 2.57$ ,  $J = 1.08 \text{ cm}^{-1}$ , and  $zJ' = -0.69 \text{ cm}^{-1}$  with  $R = 1.7 \times 10^{-5}$ . All fittings give positive  $J$  values that exclusively indicate ferromagnetic coupling within the trimer. It should be noted that the above calculations by considering  $J$  and  $g$  as isotropic are quite rough, because they are often anisotropic.

The measured magnetization as a function of field at 1.8 K gives a saturation magnetization value of  $7.35 N\beta$  (Fig. 2, inset) at 5 T, which suggests a ground state of  $S'_T = 3/2$  with  $g = 5.26$  (each  $S'_{\text{Co}} = 1/2$ , which is also well consistent with the estimation from the low-temperature  $\chi_M T - T$  data, where the maximum of  $12.48 \text{ cm}^3 \text{ K mol}^{-1}$  corresponds to  $S'_T = 3/2$  with  $g = 5.16$ ).

In compound **1**, the magnetic interaction of the adjacent cobalt atoms comes from the magnetic coupling through end-on azide ligands, which in the end-on coordination mode is an effective bridging ligand that quasi-systematically affords ferromagnetic coupling between two, three, and four metal ions for a large range of M–N–M bond angles [2]. In the case of compound **1**, Co(II)–N(azide)–Co(II) angles are  $97.09^\circ$  and  $100.64^\circ$ , similar to those of ferromagnetic Co(II)–end-on azide compounds [12].

In conclusion, a new linear trinuclear Co(II) compound containing end-on azide bridging ligands was structurally characterized, variable temperature magnetic susceptibility studies indicated ferromagnetic interactions between adjacent Co(II) atoms.

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## Appendix A. Supplementary material

CCDC 703759 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article

can be found, in the online version, at [doi:10.1016/j.inoche.2008.12.004](https://doi.org/10.1016/j.inoche.2008.12.004).

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- [8] Synthesis: A methanol solution (15 mL) containing bpbp (0.2 mmol), Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.4 mmol) and NaN<sub>3</sub> (0.8 mmol) were stirred for 10 min at 50 °C, then 3 mL water was added and the solution was stirred for further 5 min. The reaction mixture was filtered and the filtrate was left for slow evaporation to give red blocks of compound **1** in a yield of 50%.
- [9] Diffraction data were collected at 150 K on a Rigaku SATURN70 CCD diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Crystallographic data for **1**: C<sub>15</sub>H<sub>23</sub>Co<sub>1.5</sub>N<sub>12</sub>O<sub>4</sub>, Mr = 523.85, Triclinic, *P*-1, *a* = 9.320(2) Å, *b* = 11.464(2) Å, *c* = 11.814(2) Å,  $\alpha = 61.01(3)^\circ$ ,  $\beta = 80.16(3)^\circ$ ,  $\gamma = 81.69(3)^\circ$ , *V* = 1085.1(4) Å<sup>3</sup>, *Z* = 2. 8847 measured reflections, 4762 independent reflections. *R*<sub>1</sub> = 0.0389, *wR*<sub>2</sub> (all data) = 0.1088, GOF = 1.073.
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