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A novel 3D coordination polymer containing pentacoordinate cobalt(II) dimers with antiferromagnetic ordering

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Abstract

A novel three dimensional (3D) polymer, $[Co_2(hypa)_2(4,4'-bipy)]$ (1) (H₂hypa = hydroxy-phenyl-acetic acid, 4,4'-bipy = 4,4'-bipyridine), featuring pentacoordinate, dimeric cobalt(II) as subunits have been prepared, which shows low-dimensional antiferromagnetic ordering blow 15.2 K (T_N).

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Judicious choice of appropriate molecular building blocks provides the means to create a rich variety of new materials with interesting structural and magnetic properties [1]. Typically, these compounds consist of paramagnetic transition metal ions interlinked together by bridging ligands into polymeric arrays. The magnetism of high-spin (HS) cobalt(II) complexes is a challenging topic because the orbital angular momentum causes difficulties in the magnetic analysis [2]. In general, the orbital angular momentum is totally or partially quenched in a ligand field of a certain symmetry [3]; the effect of the orbital angular momentum is highly dependent on the symmetry around the metal ion. Although abundant cases of the magnetic properties of the HS cobalt(II) coordination polymers under an octahedral symmetry (O_h) or a tetrahedral symmetry (T_d) have been investigated [1c,1e,4], to our knowledge, there are only few cases of one- or two dimensional (2D) coordination polymers with HS cobalt(II) under trigonalbipyramidal symmetry (TBP) or a square-pyramidal symmetry (SP) [5], but no three dimensional (3D) framework structure featuring uniquely pentacoordinate cobalt(II). The magnetism of HS cobalt(II) complexes of a TBP or SP symmetry can be classified into two categories: (1) in a normal (or slightly distorted) SP or TBP symmetry, the ground term does not have an orbital angular momentum, thus a spin-only treatment is valid for them; (2) in a highly distorted lower symmetrical case, the ground term possesses an orbital angular momentum due to the admixture with higher states, thus a spin-orbit coupling treatment is valid for them [2,3]. In this communication, we report the synthesis, crystal structure and magnetic properties of a 3D coordination polymer comprising u-alkoxo-bridged, penta-coordinate Co^{II} dimeric subunits, namely $[Co_2(hypa)_2(4,4'-bipy)]$ (1) (H₂hypa = hydroxy-phenyl-acetic acid, 4.4'-bipy = 4,4'-bipyridine), which was generated through hydrothermal treatment using cobalt(II) ions and chiral H₂hypa (D- or L-isomers, or the racemate) as the reac-

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Fig. 1. Perspective view of the dimeric cobalt(II) subunit in 1.

tants. Obviously, the chiral H_2 hypa becomes racematic during the hydrothermal procedure.¹

X-ray crystallography ² shows that **1** has a centrosymmetrical dimeric Co₂(hypa)₂ subunit (Fig. 1). The Co(1) ion is coordinated by one 4,4'-bipy nitrogen atom (Co(1)–N(1) 2.075(2) Å), two hypa carboxy oxygen atoms (Co(1)–O(2b) 1.982(2) Å and Co(1)–O(1) 2.192(1) Å), and two µ-alkoxo groups (Co(1)–O(3a) 2.000(1) Å, Co(1)–O(3) 1.947(1) Å). The bond angles around the Co^{II} ion are in the range of 77.65(5)° to 156.30(5)°, which have been analyzed with PLATON [6] to be an intermediate between a TBP symmetry and an SP symmetry with a τ value of 0.51 ($\tau = 0.00$ for SP and 1.00 for TBP).

It should be noted the chiral hypa ligands are racematic, each acts in a tridentate-O, O', O'' mode. The $Co_2(hypa)_2$ dimer with a very short $Co \cdot \cdot Co$ distance of 3.021(1) Å is sustained by a pair of μ -alkoxo groups, which is further interconnected by the syn-anti carboxylate bridges into neutral 2D layers about the (100) planes (Fig. 2), with the adjacent interdimer $Co \cdot \cdot \cdot Co$ distance of 5.206(1) Å. The 4,4'-bipy ligands act as

² Crystal data for C₁₃H₁₀CoNO₃ **1**: M_r = 287.16, monoclinic, space group C2/c (No. 15); a = 27.077(1), b = 9.887(1), c = 9.217(1) Å, $\beta = 108.85(1)^\circ$, V = 2335.1(4) Å³ and Z = 8, $\rho_{calcd.} = 1.645$ g cm⁻³, $\mu = 1.474$ mm⁻¹. The data collections were carried out on a Siemens R3m diffractometer using Mo Kα radiation ($\theta = 0.71073$ Å) at 293(2) K. Final R_1 value of 0.0294 for 164 parameters and 2289 unique reflections with $I \ge 2\sigma(I)$ and wR_2 of 0.0816 for all 2338 reflections. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC-211373.



Fig. 2. Perspective view of the layer constructed by the metal ions and μ_3 -hypa-O, O', O'' ligands in **1**. Hydrogen atoms and phenyl groups are omitted for clarity.

bridges (Co···Co 11.191(1) Å) to connect the Co^{II} ions in the adjacent layers into a 3D pillared-layer structure (Fig. 3), in which the pyridyl groups of each 4,4'-bipy is significantly twisted with a dihedral angle of ca. 50°. It should be pointed out that there exist different types of aromatic π - π stacking interactions, providing extra intramolecular forces for 1, namely very strong face-toface π - π stacking between vicinity phenyl groups of hypa and pyridyl groups of 4,4'-bipy (3.27 Å) and strong edge-to-face interactions between vicinity bipy pyridyl groups of (3.59 Å), as well as weak edge-to-face interactions between hypa phenyl groups (3.72–3.97 Å) [7]. In words, 1 represents a new 3D framework structure featuring uniquely pentacoordinate cobalt(II) centers.

The magnetic susceptibility of 1 from 1.89 to 300 K was measured at 10 kOe (Fig. 4). The $\chi_M T$ value is 5.630 K mol⁻¹ per Co^{II} dimer at 300 K, corresponding to a moment of 4.745 μ_B per Co^{II} ion, which is in the range of the value of an HS pentacoordinate Co^{II} ion (4.3–4.8 μ_B) under the strong influence of the spin–orbital coupling [8]. The $\chi_M T$ decreases continuously with decreasing temperature and reaches a minimum of 0.14 cm³ mol⁻¹ K near 1.89 K. The magnetic susceptibility above 50 K obeys the Curie–Weiss law with a Weiss constant θ of



Fig. 3. Perspective view of the 3D framework of 1.

¹ In a typical experiment, H₂hypa (0.152 g, 1 mmol) in an aqueous solution (6 mL) of NaOH (0.080 g, 2 mmol) was mixed with 4,4'-bipy in EtOH (2 mL). The resulting solution was then added to an aqueous solution (2 mL) of $Co(NO_3)_2 \cdot 6H_2O$ (0.291 g, 1 mmol). The mixture was placed in a 23-mL Teflon-lined autoclave and heated at 160 °C for 160 h. The autoclave was cooled over a period of 12 h at a rate of 5 °Ch⁻¹, and 1 as dark-purple crystals was collected by filtration, washed with water, and dried in air. Pure product was obtained by manual separation (Final yield: 106 mg, 37% based on Co). Elemental analysis (%) Calc. for 1 (C₁₃H₁₀CoNO₃): C, 54.37, H, 3.51, N, 4.88; Found: C, 54.34, H, 3.52, N, 4.86%. IR data (ν , cm⁻¹) for 1: 3431.5 m, 3048.4 w, 3021.2 w, 1609.9 m, 1553.0 vs, 1416.1 vs, 1104.5 s, 1065.9 m, 806.0 m, 753.3 m, 699.7 m, 538.8 m, 498.3 w, 432.0 w.



Fig. 4. Temperature dependence of χ_M (\blacksquare) and $\chi_M T$ (Δ) values per Co_2^{II} for 1.

-25.01 K and a Curie constant C of 5.94 cm³ mol⁻¹ K, suggesting a strong antiferromagnetic interaction among the Co^{II} ions. As the temperature is decreased from 50 K, the magnetic susceptibility slowly increases up to a local maximum of 0.114 cm³ mol⁻¹ at 19.9 K, then the $\chi_{\rm M}$ quickly decreases and tends to a constant value of 0.076 cm³ mol⁻¹ below ca. 5 K, which is 2/3 of the χ_M value $(0.114 \text{ cm}^3 \text{ mol}^{-1})$ at T_{max} . This behavior is expected for a polycrystalline two-sublattice collinear antiferromagnet [2b,9]. and is in agreement with the equation $(\chi_{powder} = \langle \chi \rangle = (\chi_{||} + 2\chi_{\perp})/3$ and so $\langle \chi \rangle$ at 0 K is 2/3 of the value at T_N) in molecular field theory of antiferromagnetism [2b]. The critical temperature $T_{\rm N} = 15.2$ K is determined by the peak of $d(\chi T)/dT$. The field dependence of the magnetization for 1 at different temperatures below and around T_N (15.2 K) all shows a highly linear slow increase, as shown in Fig. 5, and no spin flop state was observed. The magnetization under 70 kOe at 1.8 K is only 0.92 $N\beta$ per dimeric Co^{II}, also far from the saturation value of ca. 2.5 $N\beta$ expected for a Co^{II} with $S_{\rm eff} = 1/2$, and g = 5.0 [10]. This being further evidence supporting the antiferromagnetic ordering of 1.



Fig. 5. Field dependence of magnetization at different temperatures for 1 per Co^{II}.

The magnetic properties of molecules, whether they interact with one another or not, depend on the local geometry and the chemical links between them. Compared with the structures of other Co^{II} coordination polymers [1c,1e,4,11] the orderly magnetic behavior in **1** may be attributed mainly to the unusual Co^{II} coordination geometry and the connection between Co ions, which has an implication of a two-sublattice collinear structure by the offset arrangement of the 2D nets into a 3D framework (Fig. 3).

The antiferromagnetism observed for 1 can be attributed to the contribution of the orbital angular momentum due to the spin-orbit coupling as well as the magnetic couplings between the Co^{ÎÎ} ions within the 3D framework. According to the superexchange mechanism [12] and structural parameters, three possible magnetic exchange pathways can be defined in 1. The first and strongest is the exchange between Co^{II} ions in the dimeric subunits featuring the shortest metal-ligand bond distance with the exchange angle Co(1)-O(3)-Co(1B) at 99.89(6)°. Such a larger (compared with 90°) superexchange angle usually leads to strong antiferromagnetic interaction [11a], consistent with the observed negative Weiss temperature ($\theta = -25.01$ K) and the moderate Neel constant $(T_N = 15.2 \text{ K})$ in **1**. The second in the hierarchy is the exchange between the binuclear subunits via the syn-anti O-C-O bridges at a Co^{II}...Co^{II} distance of 5.206(1) Å, which is weak and could be antiferromagnetic [4b,13]. The last is that between the layers involving the non-coplanar 4,4'-bipy pillars with the longest Co^{II}...Co^{II} distances (11.19 Å), which should therefore be much weaker. Therefore, the antiferromagnet possess obviously 2D characteristics, as the ratio of $T_{\rm N}/T_{\rm max}$ 0.76, is quite low.

In summary, we have successfully constructed a new 3D polymer featuring pentacoordinate cobalt(II) dimeric subunits, which is a low-dimensional antiferromagnet.

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