

Short communication

Two cobalt complexes derived from 1*H*-1,2,3-triazole-4,5-dicarboxylic acid: Syntheses, structures and magnetic properties

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ABSTRACT

Two cobalt(II) homometallic complexes, [Co₂(HTDA)₂(H₂O)₆·2H₂O] (**1**) and {[Co₃(TDA)₂(H₂O)₈]·H₂O}_n (**2**) (H₃TDA = 1*H*-1,2,3-triazole-4,5-dicarboxylic acid) have been synthesized and structurally characterized in detail. Single-crystal X-ray crystallographic study reveals that they crystallize in trigonal space group *R*-3 and orthorhombic space group *Pna*2₁, respectively. In **1**, two Co²⁺ cations are bonded by two HTDA²⁻ ligands to generate a binuclear Co^{II} unit, which can further be extended to a 3D supermolecular structure via the hydrogen bonds. At variance with **1**, the nearest Co²⁺ cations of **2** are connected via TDA³⁻ ligands to form a 1D coordination polymer and can be further linked to each other to result in a 3D supermolecular framework through the hydrogen bonding interactions as well. The magnetic properties of them were studied in detail.

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Crystalline molecular magnetic materials have attracted considerable attention of the academic community in recent years because of their impressive properties and potential applications in high-density data storage devices and nanosized electronics [1]. These materials could be realized by incorporating metal ions or metal clusters and organic ligands into one system via metal-ligand coordinate bonds, resulting in a variety of interesting structures [2]. As a result, much work has been devoted to preparing such multifunctionalized crystalline molecular magnetic materials by employing pure 3*d* or 4*f* or mixed 3*d*–4*f* spin carriers to construct magnetic moments [3–5]. Among them, the exchange coupled molecular magnetic complexes containing cobalt(II) ions are extraordinary interesting as the systems exhibiting strong orbital contributions to the magnetic moments and thus strong magnetic anisotropy [6]. This orbital magnetism arises from the ground orbital triplet ⁴T₁ of each cobalt(II) ion in a surrounding cubic crystal. However, it is still a challenge for the interpretation of magnetic data for the coordination complexes with octahedral cobalt(II) centers due to the first order orbital contribution, leading to the difficulties in both syntheses and magneto-structural correlation analyses. And consequently, the precise nature of the magnetic superexchange, the orientation of the local zero-field splitting tensors and how these contribute to the anisotropy of octahedral cobalt(II) centers are undoubtedly critical questions that should be further investigated.

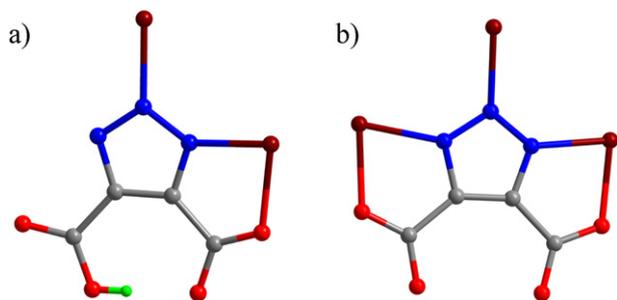
Significantly, one of the essential prerequisites in the construction of crystalline molecular magnetic materials is the magnetic exchange

pathways, which are confirmed to be a required factor of the influence on the magnetic coupling effect. An appropriate magnetic exchange media should be arranged in a special topological motif via the spin carries and more readily to communicate magnetic information. 1*H*-1,2,3-triazole-4,5-dicarboxylic acid (H₃TDA) has been proved to be a promising magnetic exchange medium to communicate magnetic information and has been extensively studied as an effective magnetic exchange pathways, but it still deserved to be further investigated [3*b*, *c*, 7]. In this contribution, two cobalt(II) homometallic complexes, [Co₂(HTDA)₂(H₂O)₆·2H₂O] (**1**) and {[Co₃(TDA)₂(H₂O)₈]·H₂O}_n (**2**) have been obtained and structurally characterized by infrared spectra, thermogravimetric analysis, elemental analysis, powder X-ray diffraction and single-crystal X-ray diffraction. The magnetic properties were studied in detail to determine the following magnetic parameters: *g* = 2.47, *D* = 36.85 cm⁻¹, *zJ* = -0.61 cm⁻¹, and *R* = 0.9979 for **1**; *A* + *B* = 9.79 cm³ K mol⁻¹, *E*₁ = -31.27 K, *E*₂ = -1.55 K and *R* = 0.9998 for **2**, respectively, suggesting dominant antiferromagnetic interaction between Co²⁺ ions.

Reaction of CoCl₂·6H₂O and H₃TDA in the presence of 1*H*-1,2,4-triazole (HTZ) in the mixture of water and C₂H₅OH at room temperature, gives the crystals of **1** in ca. 58% yield, where HTZ was absent in the final product and H₃TDA was partially deprotonated, forming HTDA²⁻ ligand (Scheme 1*a*). This structure was isomorphous with the known structure [Co₂(HTDA)₂(H₂O)₆·5H₂O] [8], which crystallizes in trigonal space group *R*-3 and consists of two Co(II) ions, two HTDA²⁻ ligands, six coordinated water molecules and five free water molecules, generating a binuclear Co^{II} unit (Fig. 1*a*). Co1 adopts a slightly distorted octahedral {CoO₄N₂} coordination geometry with one oxygen atom(O1A), two nitrogen atoms(N1A and N2) from two HTDA²⁻ ligands

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Scheme 1. Coordination modes of H_3TDA in **1** and **2**.

and three oxygen atoms (O5, O6 and O7) from three water molecules. The binuclear Co^{II} units can be linked each other to a 3D supermolecular structure via the hydrogen bonds, which further consolidate the structure of **1** (Fig. 1b). The differences between them are the number of free water molecules. Therefore, the detailed structure of **1** is accordingly ignored here.

While hydrothermal reaction of $CoCl_2 \cdot 6H_2O$ and H_3TDA in the presence of benzotriazole (HBTZ) in water at $150^\circ C$, gives the crystals of **2** in ca. 35% yield, where HBTZ was absent in the final product as well but H_3TDA was completely deprotonated, forming TDA^{3-} ligand (Scheme 1b). Single-crystal X-ray diffraction analysis reveals that **2** crystallizes in orthorhombic space group $Pna2_1$. Each unit cell contains

crystallographically independent three $Co(II)$ ions, two TDA^{3-} ligands, eight coordinated water molecules and one free water molecule (Fig. 2a). $Co1$ adopts a slightly distorted octahedral $\{CoO_4N_2\}$ coordination geometry with one oxygen atom (O5), two nitrogen atoms (N2 and N4) from two TDA^{3-} ligands and three oxygen atoms (O12, O13 and O14) from three water molecules. Similar to $Co1$, $Co2$ is hexacoordinated by one oxygen atom (O4), two nitrogen atoms (N3 and N5) from two TDA^{3-} ligands and three oxygen atoms (O9, O10 and O11) from three water molecules as well, forming a slightly distorted octahedral $\{CoN_2O_4\}$ coordination geometry. Different from the coordination environments of $Co1$ and $Co2$, $Co3$ is coordinated by two oxygen atoms (O1A and O8), two nitrogen atoms (N1A and N6) from two TDA^{3-} ligands and two oxygen atoms (O15 and O16) from two water molecules forming an octahedral $\{CoO_4N_2\}$ coordination geometry. The bond lengths of $Co-N$ are in the range of $2.081(9)$ – $2.154(9)$ Å and those of $Co-O$ are in the range of $2.050(7)$ – $2.195(7)$ Å, respectively. Obviously, the bond lengths of $Co-N$ and $Co-O$ fall in the normal values of the previously reported Co -based complexes [6,9]. There are two different types of TDA^{3-} ligands: one chelates two Co^{II} ions ($Co1$ and $Co2$) through the carboxylate oxygen atom (O4) and the triazole nitrogen atoms (N2 and N3), one crystallographically equivalent $Co3A$ ion through the same carboxylate oxygen atom O1 and triazole nitrogen atom N1 neighboring to N2 atom. Interestingly, the other one chelates

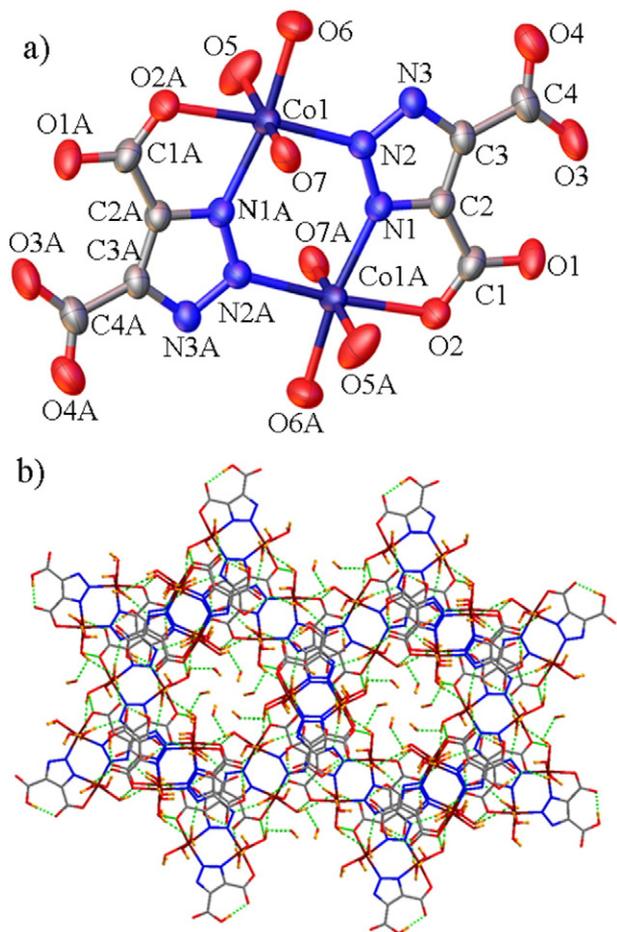


Fig. 1. (a) The coordination environments of $Co(II)$ ions in **1** (thermal ellipsoids are drawn at the 30% probability level). All hydrogen atoms and uncoordinated water molecules were omitted for clarity. [Symmetry code: (A) $-x, -y + 1, -z$]; (b) The 3D supermolecular structure via the hydrogen bonds of **1**. purple: Co; red: O; blue: N; black: C, yellow: H. The green dashed lines stand for the hydrogen bonds.

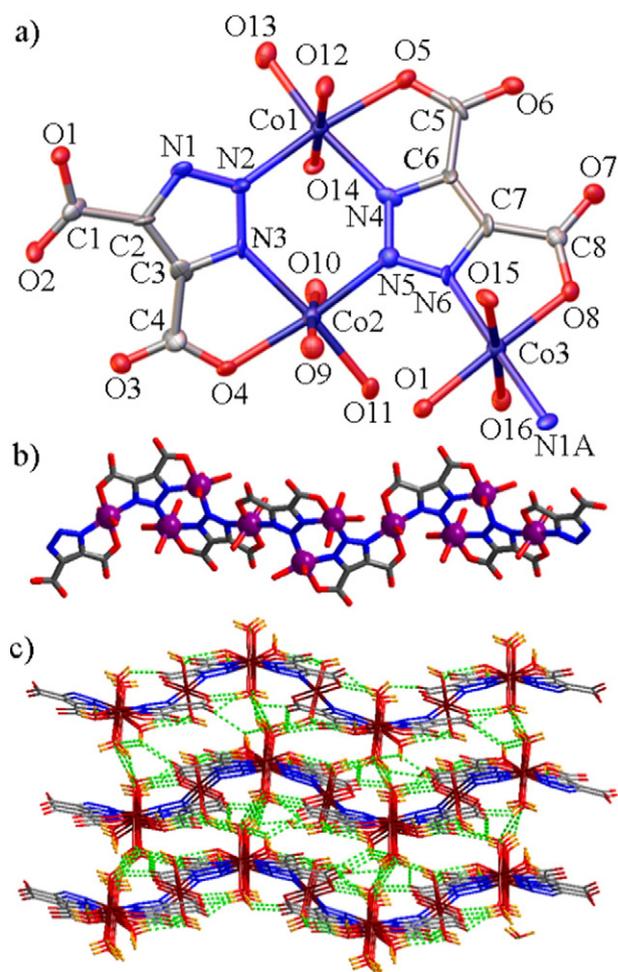


Fig. 2. (a) The coordination environments of $Co(II)$ ions in **2** (thermal ellipsoids are drawn at the 30% probability level). All hydrogen atoms and uncoordinated water molecules were omitted for clarity. [Symmetry code: (A) $-x + 3/2, y - 1/2, z + 1/2$]; (b) The 1D coordination polymer of **2**; (c) The 3D supermolecular structure via the hydrogen bonds of **2**. purple: Co; red: O; blue: N; black: C, yellow: H. The green dashed lines stand for the hydrogen bonds.

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