

Feature article

Two unique cobalt-organic frameworks based on substituted imidazole-dicarboxylate and dipyridyl-type ancillary ligands: Crystal structures and magnetic properties



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ABSTRACT

Two three dimensional (3D) Co(II) coordination polymers incorporating similar substituted imidazole-dicarboxylate and dipyridyl-type ancillary ligands pillared layer, namely, $\{\text{Co}_3(\text{mimda}^{3-})_2(\text{bpe})_3 \cdot 3\text{H}_2\text{O}\}_n$ (**1**) and $\{\text{Co}_3(\text{eimda}^{3-})_2(\text{bipy})_3 \cdot 8\text{H}_2\text{O}\}_n$ (**2**) ($\text{H}_3\text{mimda} = 1\text{H-2-methyl-4,5-imidazole-dicarboxylic acid}$, while $\text{H}_3\text{eimda} = 1\text{H-2-ethyl-4,5-imidazole-dicarboxylic acid}$, $\text{bpe} = 1,2\text{-di(4-pyridyl) ethylene}$ and $\text{bipy} = 4, 4'\text{-bipyridine}$) have been successfully synthesized. Both polymers **1** and **2** have been characterized by elemental analysis, IR spectroscopy, single-crystal X-ray diffraction, and thermogravimetric analysis (TGA). X-ray structural analysis reveals that they are nearly isostructural, possessing similar symmetry units based on trinuclear clusters, and further is propagated into a Kagomé-like lattice. The lattice consists of corner-sharing triangles of spins with magnetic coupling between the nearest neighboring Co(II) ions. Magnetic measurements revealed spin-canting-like antiferromagnetism behaviors for compounds **1** and **2** at lower temperature. The interaction in **1** is slightly stronger than that of **2**, which can be explained by the discrepancy of organic linker between the adjacent Co(II) centers.

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In the past several decades, the design and synthesis of metal-organic frameworks (MOFs) bridged by nitrogen-heterocyclic ligands have attracted considerable attention in materials chemistry and inorganic chemistry [1–3]. The motive comes not only from the intriguing structural diversity, but also from the demand for applications of functional materials in field of catalysis, porosity, magnetism, luminescence, conductivity and sensing properties [4–10]. Among the reported studies, multifunctional ligands containing N- and O-donors are especially interesting because they can adopt a variety of coordination modes and induce diversity in the coordination modes and interesting properties [11–15]. A variety of nitrogen-heterocyclic and aliphatic carboxylate

mixed ligands, such as multicarboxylate triazine/imidazoline/pyridine-based ligands, has been always selected as multifunctional ligands, because they are multidentate and semi-flexible ligands with multi-proton donor-acceptor sites, giving rise to a variety of coordination fashions, such as monodentate bridging, chelating, and bidentate bridging [16,17]. However, to the best of our knowledge, the complexes containing combination modified multicarboxylate-imidazoline/pyridine-based ligands have been seldom documented [18]. On the other hand, rod-like N,N' -donor building blocks have been employed as auxiliary ligands, which was modification by introducing spacers between two 4-pyridyl groups, can result in distinct spatial effects to produce unexpected architectures and new properties. Cobalt compounds are magnetically interesting due to its high spin quantum number anisotropic nature of an octahedral coordinated Co(II) centre arising from spin-

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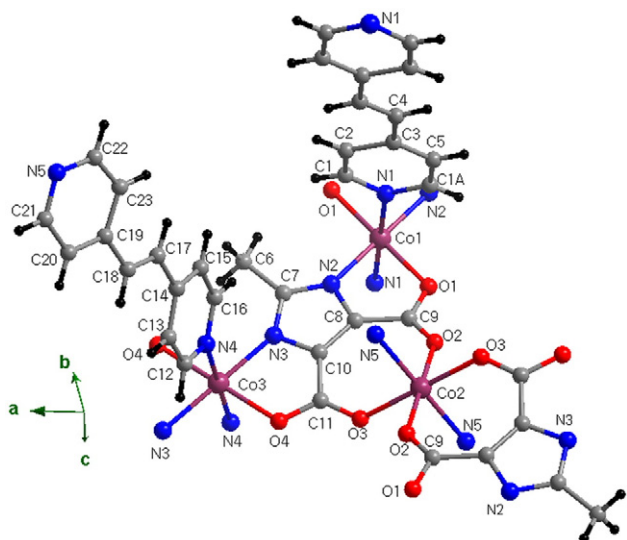


Fig. 1. Illustration of the trinuclear cobalt cluster in **1** (The hydrogen atoms and free water molecules have been omitted for clarity).

orbit coupling [19]. Compared with small magnetic couplers such as azide and cyano ligands, polycarboxylate's aroma has rarely been used as linkers to build coordination polymers exhibiting long-range magnetic ordering, as the connection between magnetic moment carriers (metal nodes) within the interacting range required. However, reports on the metamagnetism with spin canting in 3D cobalt (II) materials are still rare till now [20] as a continuation of our previous investigation [18] and influence exerted by the second ligand on the structures and the magnetic property. In this contribution, a mixed ligands approach is used to show a promising way to construct new molecular magnetic materials. H_3mimda and H_3eimda were chosen as the major ligand to synthesis two new cobalt polymers under hydro-thermal conditions [21]. The presence of the different electron-donating ($-CH_3$ or $-CH_2CH_3$) uncoordination groups in dicarboxylate ligands may change their electronic and steric properties, which generate complexes with different structures, and novel properties are also investigated.

In IR spectrum, the observed absorption signals at about 3450 and 33,200 cm^{-1} of both polymer **1** and **2** are attributed to the O–H and N–H stretching vibration. The broad and intense spectra at 1606, 1445 cm^{-1} are attributed to the asymmetric and symmetric stretching vibrations of carboxylic groups, respectively [22]. The strong peaks at about 1620 cm^{-1} are assigned to the C=C stretching vibration in bpe coligand of polymer **1** [23]. Strong absorption peaks at about 2940 cm^{-1} are corresponding to stretching vibrations of CH_3 or C_2H_5 in main ligands.

The X-ray diffraction analysis [24] reveals that polymers **1** and **2** exhibit very similar molecular structure except the distinction of second ligands and different numbers of water molecules in the crystal lattice. As

depicted in Fig. 1, the centrosymmetric unit of **1** consists of three independent Co(II) ions, two symmetry $mimda^{3-}$ ligands and one bpe auxiliary ligand, as well as three free water molecules. In the complex **1**, the Co(II) ion adopts two types of coordination modes, both of which can be portrayed as a slightly distorted octahedral geometry [27].

The first type of coordination mode around the Co(II) ion is being bound by two carboxylate oxygen atoms ($Co_3-O_4 = 2.104 \text{ \AA}$) and two imidazole N atoms from two $mimda^{3-}$ ligands ($Co_3-N_3 = 2.0417 \text{ \AA}$), as well as two pyridine nitrogen atoms from two bpe ligands ($Co_3-N_4 = 2.1004 \text{ \AA}$). The Co center is in a distorted octahedral N_2O_4 environment with two bpe located at the *trans* positions, in which each $mimda^{3-}$ binds to the first Co(II) site with five-membered chelation rings in the equatorial plane. The second kind donor set around Co(II) is defined by an N_4O_2 , among which two oxygen atoms are from two $mimda^{3-}$ ligands, two nitrogen atoms are from two $mimda^{3-}$ ligands, while another two pyridine nitrogen atoms derived from two bpe complete the distorted octahedral geometry. The bond lengths of Co–O vary from 2.036 to 2.052 \AA , while Co–N bond lengths are 2.144 \AA , which are well matched to those observed in Co(II) complexes with similar ligands [28]. Interestingly, both two bpe ligands present slightly distortion “S” type, and the dihedral angle between two pyridine rings is about 20.78°, demonstrating the large deviation from the plane defined by linker C=C group, as described in Fig. 2. In both complexes, each imidazole-dicarboxylate ligand features a hexadentate ligand linking adjacent three Co(II) ions by adopting bis-(bridging) and chelate modes in an anti-anti conformation. This results in the six-membered chelation of $mimda^{3-}$ around central ion, as illustrated in Scheme 1 (a).

In trinuclear Co_3 clusters, two $mimda^{3-}$ ligands linked three Co(II) ions into a homometallic $[Co_3(mimda^{3-})_2(bpe)_3]$ aggregate as the secondary building unit (SBU), in which the three Co(II) ions are coplanar completely. Two bpe molecules located at *trans* positions and two $mimda^{3-}$ molecules are in equatorial plane, in which the Co_2 center is located in the crystallographic inversion center. These trinuclear clusters act as the secondary building unit (SBU), being further extended through the carboxylic oxygen into zigzag 1D chain subsequently, as displayed in Fig. 2. The coordination sites of Co_1 and Co_3 are almost equivalent, which make the spin (Co_1, Co_2, Co_3) alignments arrange in triangular motifs as well and subsequently generate a Kagomé-like lattice (Fig. 3b), in which the shortest separation of $Co...Co$ is 5.7915 \AA . The lattice consists of corner-sharing triangles of spins with antiferromagnetic coupling between the nearest neighbors.

Finally, bpe auxiliary ligand interlinks the adjacent $[Co_3(mimda)_2]$ layers into double-layer arrays using the terminal N atoms (N4, N5), which further stack parallel to each other along the *c* direction and are extended into a pillared-layer 3D framework, as described in Fig. 4.

As shown in Fig. 5, Co(II) ions in polymer **2** adopt the similar coordination modes as those in polymer **1**. The *eimda* ligand connects the adjacent three Co(II) ions employing N and O atoms into triangular array, as illustrated in Scheme 1 (b), giving rise to an alternate 1-D chain. These chains are interlinked by *eimda* to form 2D Kagomé-like lattice, followed by formation the final bipy pillared 3D framework. We briefly

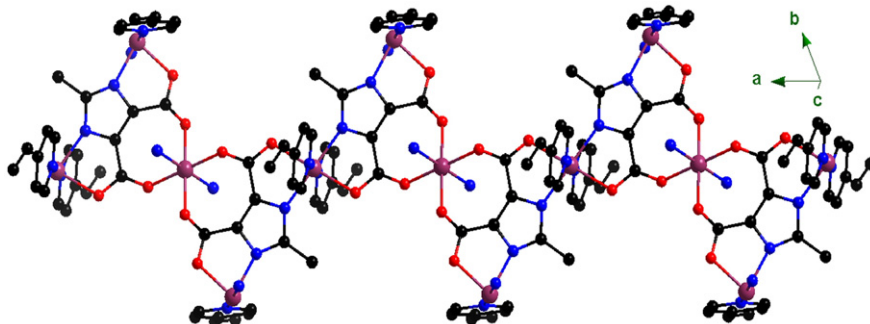


Fig. 2. View of alternate 1-D zigzag chain in polymer **1**.

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