

Synthesis, structure and magnetic property of cobalt(II) and manganese(II) complexes with mixed organic ligands



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ARTICLE INFO

Article history:

Received 1 October 2013

Accepted 13 November 2013

Available online 19 November 2013

Keywords:

Co(II) and Mn(II) complexes

Topologies

Crystal structure

Antiferromagnetic interactions

ABSTRACT

Two new metal complexes with mixed nitrogen-donor heterocyclic monocarboxylate and dicarboxylate ligands $\{[Co_2(L)_2(BDC)(H_2O)] \cdot 2H_2O \cdot 6DMF\}_n$ (1) and $[Mn(L)(OX)_{0.5}]_n$ (2) (HL = 3,5-di(pyridine-4-yl)benzoic acid, H_2BDC = 1,4-benzenedicarboxylic acid, H_2OX = oxalic acid) have been prepared and characterized by single crystal and powder X-ray diffractions, IR, and thermogravimetric analyses. Crystallographic and topological analyses identify that both complexes have new framework topologies. Complex 1 is a (3,8)-connected 2-nodal 3D net with a point (Schläfli) symbol of $(4^2.5)_2(4^4.5^{10}.6^7.7^6.8)$, while 2 is a (4,5)-connected binodal net with a point (Schläfli) symbol of $(4^2.6^3.8)(4^2.6^3.8^3)$. Furthermore, magnetic investigation shows that both complexes exhibit overall weak antiferromagnetic coupling between the adjacent metal centers.

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Metal-organic frameworks (MOFs) and coordination polymers (CPs) have been attracting extensive interest in recent years not only because of their intriguing varieties of architectures and topologies [1–3], but also due to their potential applications in magnetism, catalysis, non-linear optics, sorption and so on [4–9]. Thus, considerable efforts have been paid on design and synthesis of novel MOFs and CPs. An effective and facile approach for the synthesis of such complexes is still the appropriate choice of well-designed organic ligands together with metal salts with definite coordination number and geometry. Among the various ligands, N-donor-containing carboxylate ligands such as imidazole-4,5-dicarboxylic acid [10], pyridine-3,5-dicarboxylic acid [11], and pyrazine-2,3-dicarboxylic acid [12] have been proved to be good candidates for the construction of MOFs with diverse structures and interesting properties due to their excellent coordination capability and variable coordination patterns. In our previous studies, two-dimensional (2D) Co(II) and Zn(II) networks based on 3,5-di(pyridine-4-yl)benzoic acid (HL) were synthesized and structurally characterized [13], and it was found that there are counteranions or uncoordinated pyridine groups of L^- ligand in the resulted structures. For the systematic study, now we carried out the reactions of bivalent metal salts with HL as well as different rigid auxiliary carboxylic acids of 1,4-benzenedicarboxylic acid (H_2BDC) and oxalic acid (H_2OX). Herein, we report two new metal complexes $\{[Co_2(L)_2(BDC)(H_2O)] \cdot 2H_2O \cdot 6DMF\}_n$ (1) and $[Mn(L)(OX)_{0.5}]_n$ (2) (DMF = N,N-dimethylformamide) with new topologies [14]. The complexes were characterized by single crystal X-ray diffraction, elemental analyses, IR, powder X-ray diffraction (PXRD) and thermogravimetric analyses, and the magnetic properties have also been studied.

Single crystal X-ray structural analysis revealed that 1 crystallizes in trigonal space group $P3_121$ [15]. As depicted in Fig. 1a, each six-coordinated Co(II) atom adopts distorted octahedral geometry formed by two pyridine nitrogen atoms (N1, N2) and two carboxylate oxygen ones (O2, O1A) from four distinct L^- ligands, one carboxylate oxygen atom (O4) from BDC^{2-} and one ligated water molecule (O5). On the other hand, each L^- ligand acts as a μ_4 -bridge to link four Co(II) atoms: two pyridine nitrogen atoms link two Co(II), and the carboxylate group with $\mu_2-\eta^1:\eta^1$ mode connects the other two Co(II) atoms. Each BDC^{2-} ligand and the ligated water molecule act μ_2 -bridges, respectively, to connect two Co(II) atoms. Interestingly, two adjacent Co(II) atoms are connected by coordinated water molecule and two $\mu_2-\eta^1:\eta^1$ carboxylate groups to form a dimeric unit with the Co-Co distance of 3.641 Å. The dimeric Co(II) units are connected by L^- ligands to give a non-interpenetrating extended three-dimensional (3D) architecture (Fig. 1b), with large 1D channels along the *c*-axis. More interestingly, BDC^{2-} ligands link the dimeric Co(II) units to form a 1D homo right-handed helical chain circumgyrated along the *c*-axis (three-fold axial direction) with pitch length of 23.983 Å in the channels. The total solvent cavity volume in complex 1 is 3546.0 Å³, 61.8% per unit cell calculated by PLATON [19].

To further understand the structure of 1, topological analysis by reducing multidimensional structure to simple node-and-linker net was performed. Based on the simplification principle [20], each dimeric Co(II) unit connects six L^- ligands and two BDC^{2-} ligands, which can be viewed as a eight-connector. Each L^- or BDC^{2-} ligand in turn connects three or two dimeric Co(II) units, respectively, hence, they can be regarded as three- or two-connectors, respectively. Hence, the overall structure of 1 is a (3,8)-connected 2-nodal 3D net with stoichiometry $(3-c)_2(8-c)$, as shown in Fig. 1c. Topological analysis using TOPOS software [21,22] identified that the structure of 1 is a new topological net,

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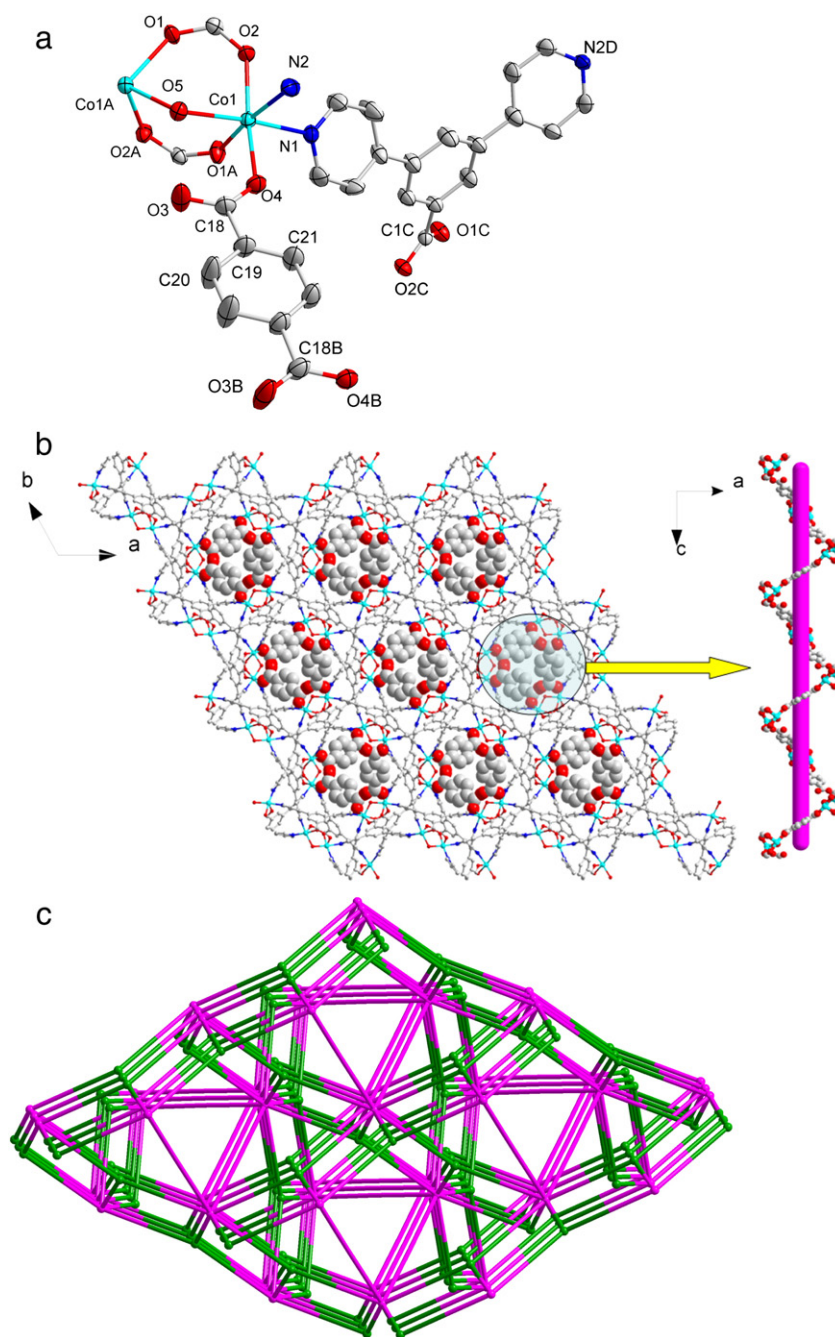


Fig. 1. (a) Coordination environment of Co(II) in 1 with the ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted for clarity. Symmetry codes: (A) $y, x, -z$; (B) $x - y, -y, -1/3 - z$; (C) $1 - x, -x + y, 1/3 - z$; (D) $y, -1 + x, -z$. (b) Schematic representation of 3D architecture of complex 1 (left) and the view of R-handed helical chain along the c -axis in 1 formed by BDC^{2-} ligands and dimeric Co(II) units (right); (c) Schematic representation of the (3,8)-connected 2-nodal 3D net of 1 with $(4^2.5)_2(4^4.5^{10}.6^7.7^6.8)$ topology: green, L⁻ ligand; pink, dimeric Co(II) unit.

which can be presented by a Schläfli symbol of $(4^2.5)_2(4^4.5^{10}.6^7.7^6.8)$ (td10 = 2410).

Complex 2 was readily synthesized by hydrothermal reaction of HL, H_2OX and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ [14]. Single-crystal X-ray structural analysis revealed that 2 crystallizes in monoclinic system space group $P2_1/n$ [15]. In the asymmetric unit of 2, there are one Mn(II) atom, one L⁻ ligand and half molecule of OX^{2-} . As shown in Fig. 2a, Mn1 atom in 2 is coordinated by two oxygen atoms (O1, O2C) and two nitrogen atoms (N2D, N1B) from four different L⁻ ligands, two oxygen atoms (O3, O4A) from one ligated OX^{2-} anion to form a distorted octahedral coordination geometry. In complex 2, the L⁻ ligand adopts the same coordination mode as that in 1. Interestingly, the adjacent Mn(II) atoms are connected

alternately by the $\mu_2\text{-}\eta^1\text{:}\eta^1$ carboxylate groups from L⁻ ligands and oxalate ligands with Mn \cdots Mn separations of 4.802 and 5.628 Å, respectively, resulting in formation of an infinite one-dimensional (1D) zigzag chain along a -axis with a Mn \cdots Mn \cdots Mn angle of 110.13° (Fig. 2b). Each 1D chain unit connects with other six adjacent ones through the L⁻ ligands in the b and c directions to give a non-interpenetrating extended 3D architecture (Fig. 2b).

Topologically, each L⁻ ligand links four Mn(II), and each OX^{2-} anion connects two Mn(II) atoms, so which can be regarded as four- and two-connectors, respectively. Meanwhile, each Mn(II) atom connects four L⁻ ligands and one OX^{2-} anion, thus, it can be considered as a five-connected node. The resulted structure of 2 is a (4,5)-connected binodal

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