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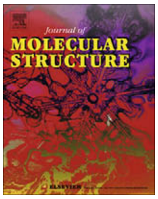

Shape recognition and cooperative magnetic behaviors observed in a chiral 3D coordination polymer containing mixed geometries cobalt(II) dimers linked by isonicotinate and D-(+)-camphorate

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ABSTRACT

A chiral cluster-based 3D coordination polymer $[Co_2(ca)(ina)_2(H_2O)]_n$ (**1**, ca = D-(+)-camphorate, ina = isonicotinate), containing mixed geometries cobalt(II) dimers as subunit, featuring unique rugate $[Co_2(ina)_2]_n^{2n+}$ 2D layers pillared by the ca ligands has been studied. The bridge modes and their intermolecular interactions of the mixed rigid planar ina and flexible bulky ca ligands display an interesting example of shape recognition in packing style of 3D frameworks. The bulky antiferromagnetic behavior of **1**, mainly arises from the cooperative magnetic effect of the interdimers arrangement in the chiral 3D network based on the nature of the exchange modes of mixed multi-carboxylate bridges within the mixed geometric Co(II) dimer.

1. Introduction

The research on cluster-based coordination polymers has attracted considerable attention for their intriguing variety of architectures and potential applications as functional materials [1–3]. Generally, different types of cluster units formed by the paramagnetic metals could display various magnetic behaviors and allow access to different types of nodes and bulky magnetic properties through space linkers in the extended lattices such as ferromagnetism, antiferromagnetism, metamagnetism, spin-canting, and spin glass, etc. [4,5]. Among a large number of above crystalline materials, the construction of multi-dimensional structures based on small clusters (smaller than five) are extremely interesting to understand the cooperative effects of magnetic clusters within the framework motif. In particular, the coordination polymers built from one of the smallest magnetic unit, metallic dimers, may be simple but typical case in the research on development of the magnetic theories [5,6]. In contrast with abundant homometallic dimmers, the dimers with mixed-geometries are limited in the cluster-based coordination networks, what is more, only a few studies have been devoted to their magnetic properties [5–9].

In our course of ongoing working on transitional metal small cluster-based coordination networks of the mixed carboxylate and aromatic amine ligands [5,10], it is advisable to choose rigid ina ligand, flexible D-(+)-ca ligand and paramagnetic Co(II) metal ion to create new chiral magnetic 3D frameworks [5c]. The various coordination modes adopted by the carboxylate groups can not only bind to metal clusters and transmit different magnetic exchanges, but also stretch the metal units into complicated frameworks [11]. Presented here is an interesting compound, $[Co_2(ca)(ina)_2(H_2O)]_n$ (**1**). During the course of preparation of this manuscript, the crystal structure of this compound was reported very recently in *Chem. Commun.* (2009, 206) [12], who emphasized on the absolute sense of helix made of chiral or achiral ligands. However, detailed spatial arrangement between mixed rigid planar ina and flexible bulky ca ligands, and elaborate magnetic measurements was unmentioned. Herein, we describe the intermolecular interactions and interesting shape recognition in packing style of 3D motif as well as the bulky magnetic properties of **1**. Our results reveal the relationship among intradimers exchange, interdimers arrangement, and the cooperative magnetic behaviors of **1**. These studies show the importance of correlation effect for a better understanding of the magnetic properties in cluster-based coordination polymers.

2. Experimental

2.1. General methods

The reagents and solvents employed were commercially available and used as received without further purification. The C, H,

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and N microanalyses were carried out with an PE Series 2400II CHNS Analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Bio-Rad FTS-7 spectrometer. Temperature and field-dependent magnetic measurements were carried out on a SQUID-MPMS-XL-7 magnetometer. Diamagnetic corrections were made with Pascal's constants.

*2.2. Synthesis of complex **1***

A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (1 mmol), H_2ca (0.5 mmol), Hina (1 mmol), triethylamine (0.3 mL) and water (10 mL) were sealed in a 23-mL teflon-lined, stainless-steel Parr bomb. The bomb was heated at 170 °C for 120 hours. Then red block crystals were obtained and picked out, washed with distilled water and dried in air. (yield: 30%, based on ca). Elemental analysis (%). Calcd (found) for **1** ($C_{22}H_{24}Co_2N_2O_9$): C, 45.69 (45.65); H, 4.18 (4.20); N, 4.84 (4.79). Selected IR data (KBr pellet, cm^{-1}): 3230*s*, 1604*s*, 1550*s*, 1385*vs*, 1231*m*, 1059*m*, 777*m*, 691*s*, 505*w*.

2.3. X-ray crystallography

Diffraction data were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-*K*α radiation (λ = 0.71073 Å). All intensity data were corrected for Lorentz and polarization effects, and empirical absorption corrections based on equivalent reflections were applied (SADABS). The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 with SHELXTL program package [13]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were generated geometrically. CCDC-703248 contains the supplementary crystallographic data for this paper. It can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The crystallographic details and selected bond lengths (Å) and bond angles (°) are provided in Tables S1 and S2. Also, the CIF file for **1** can be found in the Supporting Information.

3. Results and discussion

3.1. Crystal structures

For the completeness of this work and also for later description of the magnetic properties of compound **1**, we describe its structure here purposefully. As shown in Fig. 1, the asymmetric unit consists of two Co(II) ions, one ca ligand and two ina ligands. The dimeric SBU comprises one distorted CoN_2O_4 octahedral Co1 atoms (Co–N 2.104(4), 2.161(4) Å; Co–O 2.012(3)–2.200(3) Å) and another Co2 atom (Co–O 1.995(3)–2.137(3) Å) adopts grossly distorted five-coordination mode. For Co_2, the CoO_5 polyhedron exhibits an intermediate between a trigonal bipyramid (TBP) symmetry and a square pyramid (SP) symmetry. Analyzed with PLATON [14], the geometrical parameter τ calculated for the Co2 sites is 0.46 (τ = 0 infers a perfect SP, τ = 1, a perfect TBP). Two metal atoms are linked via three different kinds of carboxylate-bridges (Fig. 5 up): μ_2-3-carboxylate-ca-O,O′ (I), μ_2-1-carboxylate-ca-O bridge (II, Co–O–Co 105.0(1)°) and μ_2-carboxylate-ina-O,O′ bridges (III), respectively, the mixed dimeric unit feature moderate intradimer distance of Co1···Co2 3.344(1) Å. There have only a few cases of 3D framework featuring mixed geometries Co(II) introduced by mixed carboxylates systems [5a].

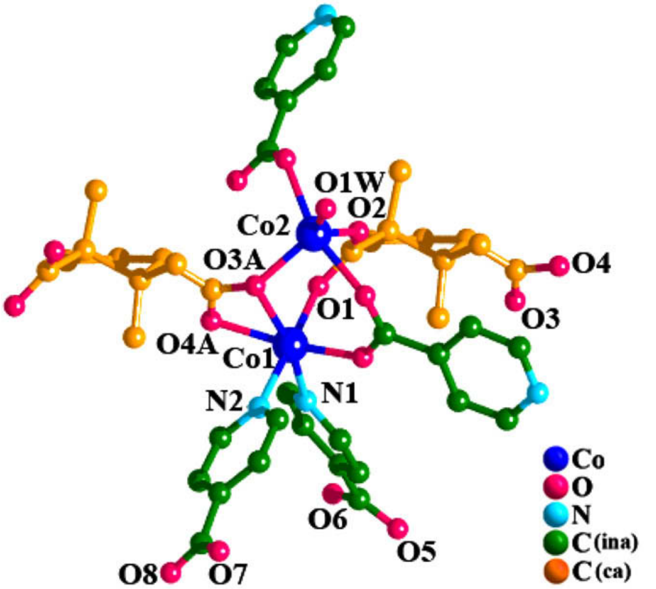
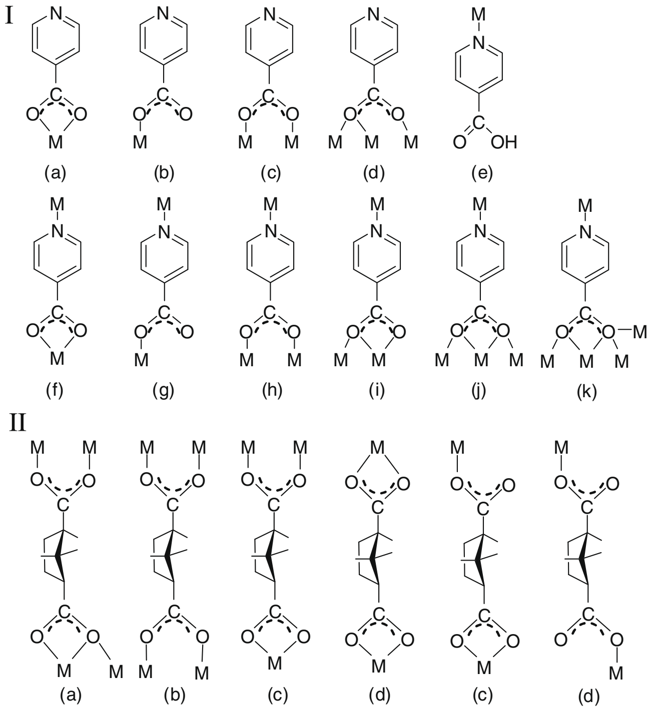


Fig. 1. The Co(II) coordination environments in the dimer SBU of **1**. Hydrogen atoms have been omitted for clarity.

It is worthy of note that compared with the ina [5b,6,15] and ca [5c,12] ligand coordination modes reported (Scheme 1), in **1**, two kinds of coordination modes: $\mu_2{:}\eta_1{:}\eta_1$ and $\mu_3{:}\eta_1{:}\eta_1{:}\eta_1$ type (Scheme 1I, g, h) adopt by the different ina ligands, which alternatively linked by the two kinds of Co(II) ions to build a rugate $[Co_2(ina)_2]_n^{2n+}$ 2D layer of thickness *ca.* ~12 Å in the *bc* plane (Fig. 2a). More interestingly, the layer can be regarded as combination of infinite helical chains, the central axis of each helical chain is a twofold screw axes (with a pitch of *ca.* 13.3 Å) running along the *a* axis, neighboring two of which are further intertwisted by sharing Co1 atoms (Fig. 2a). The crystal packing shows that the adjacent layers are in an AA parallel array. The convex surface of one layer is exclusively perched on the concave surface of the adjacent layer and the shortest separation between them is *ca.* 3.51 Å. As a flexible dicarboxylate spacer, ca provides the prevalent $\mu_4{:}\eta_1{:}\eta_1{:}\eta_1{:}\eta_2$ coordination mode with Co(II) centers (Scheme



Scheme 1. The coordination modes exhibited by ina and ca ligand.