



## Self-assembly, electrochemistry and magnetic behaviors of cobalt complexes with featuring imidazole–tripodal ligand



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### ABSTRACT

The coordination chemistry of imidazole–tripodal ligand *N,N*-bis(2-(1-methylimidazolyl)methyl)glycine (HL) has been studied with cobalt (II). Single-crystal X-ray analysis showed that the mononuclear complex [CoLCl] (1) could further act as the charge-negative metalloligand to assemble a heptanuclear complex of Co[CoLCl]<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub> (2) through the bridge linking of carboxylato O of L and the cooperation of the central metal ions. The electrochemical and magnetic properties were explored.

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Imidazole and its derivatives are often employed as key coordination ligands in the construction of functional complexes not only for their variable coordination modes but also for their inherent electronic effect. For example, imidazole containing Fe(II) and Fe(III) complexes (Scheme 1a) offer a rich variety of spin crossover behaviors arising from the multi-*N* coordination environment [1] whereas the planar conjugated systems provide opportunities for higher-efficient luminescent materials (Scheme 1b) [2]. According to previous experiences of imidazole-based metal complexes [3–13], the unsymmetrical tripodal ligands which possess the N<sub>2</sub>O, N<sub>2</sub>O<sub>2</sub>, or N<sub>3</sub>O donor atoms would possibly be favorable for (i) imposing a fixed geometry upon the transition metal ions and (ii) possessing a negative charge which should greatly enhance the stability and inertness of the coordination complexes. Interestingly, these effects are also valid to similar ligands such as 3-[bis(2-pyridylmethyl)amino]propionic acid (Scheme 1c) which include two neutral nitrogen donors and one anionic oxygen donor (from carboxylate or phenolate) [14]. The resulting metal–organic coordination complexes are well known as carboxypeptidase, superoxide dismutase [15] or alkaline phosphatase [16], and L-fucose 1-phosphate aldolase [17] or the peptidase astacin [18]. In this work, an analogous tripodal ligand *N,N*-bis(2-(1-methylimidazolyl)methyl)glycine (HL, Scheme 1d) was employed to test these effects.

Under pH 6.5–7.5, the addition of equimolar CoSO<sub>4</sub>·7H<sub>2</sub>O and NaCl to the methanol solution of HL leads to the mononuclear [CoLCl] (1) which crystallizes in the monoclinic space group *P*2<sub>1</sub>/*n*. The coordination polyhedron around cobalt (II) atom is trigonal bipyramid geometry. The cobalt (II) atom deviates from the trigonal plane defined by three basal ligating atoms [0.4691(1) Å]. Two imidazole rings in ligand are not perpendicular to each other with a dihedral angle of 57.4(9)°. The adjacent [CoLCl] units form a chain (Fig. 1b) through the non-classic hydrogen bond between the C atom and the coordinated chloride atom with the distance of Cl...C being 3.660(3) Å. These chains were further assembled by non-classic hydrogen bonds into an infinite 2-D supramolecular sheet (Fig. 1c).

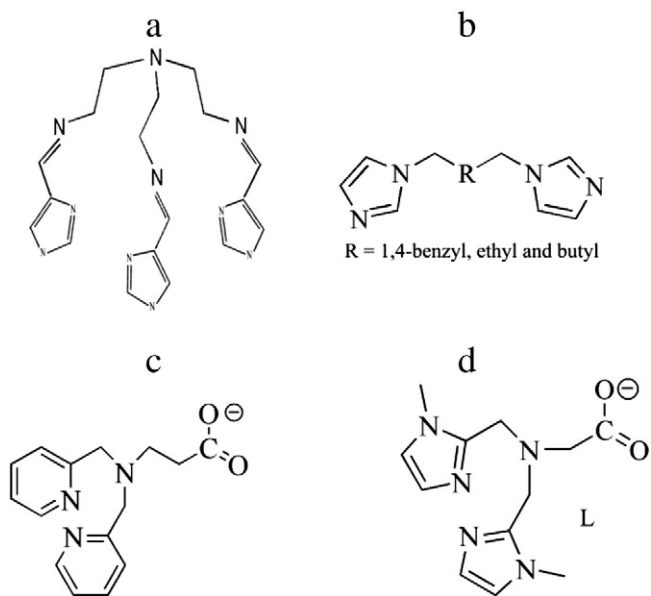
Under the same condition, the addition of equimolar Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and NaCl to the methanol solution of HL leads to the heptanuclear Co[CoLCl]<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub> (2) which crystallizes in the Rhombohedral space group *R*-3. The X-ray diffraction analysis shows that the molecule consists a heptanuclear Co[CoLCl]<sub>6</sub><sup>2+</sup> cations, two nitrate anions and two acetonitrile molecules (Fig. 2a, b). The Co[CoLCl]<sub>6</sub><sup>2+</sup> cation is composed of the six mononuclear ([CoLCl]) units and a cobalt (II) cation. Each ([CoLCl]) unit is the same as the complex 1 but with different bond lengths and bond angles. The ligand also acts as a tetradentate chelate for the cobalt (II) atom, utilizing two nitrogen atoms from imidazole groups and one carboxy oxygen atom to bind the metal atom at the equatorial positions [Co–O(2) = 2.006(3), Co–N(4) = 2.033(4) and Co–N(2) = 2.032(4) Å]. At the same time, a chloride atom and an imino nitrogen atom from ligand ligate the cobalt (II) atom at the axial positions with much longer bond distances [Co–N(1) = 2.336(4) and Co–Cl = 2.2833(15)], resulting in an elongated trigonal bipyramid

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Scheme 1. Imidazole derivatives.

geometry. The cobalt (II) atom deviates from the trigonal plane defined by the basal three ligating atoms [0.4603(0) Å], which is nearly equal to that of **1**. The two imidazole rings in ligand are not perpendicular to each other with a dihedral angle of 66.9(2)°, which is different from that of the complex **1**. Best interestingly, the central cobalt cation is coordinated

by six O atoms from carboxy groups of the ligand in [Co(L)] unit with the same bond length Co–O [Co2–O(1) = 2.312(3) Å] in an octahedral geometry fashion, which results in a octahedral heptanuclear cluster compound. The heptanuclear Co[Co(L)]<sub>6</sub><sup>2+</sup> cations were further assembled by non-classic hydrogen bonds into 3-D (Fig. 2c, d) supramolecular networks.

The electrochemical properties of metal complexes have been characterized by cyclic voltammetric measurements. The CVs of complexes **1** and **2** show very similar features. As illustrated in Fig. 3a and b, a group of redox couples can be observed with the oxidation peaks at the potential near +0.20 V (for **1**) and +0.12 V (for **2**), the corresponding reduction peaks at +0.06 V (for **1**) and +0.014 V (for **2**), which can be assigned to the reaction [Co<sup>III</sup>(L)] + e → [Co<sup>II</sup>(L)] [19]. The peak currents were increasing with multi cycles, suggesting the deposition of poly-Co(L) film on the glassy carbon electrode.

The plots of  $\chi_M^{-1}$  and  $\chi_M T$  vs  $T$  in **1** are represented in Fig. 4. When cooling from 300 K to 40 K, the  $\chi_M T$  decreases slowly from 1.643 to 1.616 cm<sup>3</sup>·K·mol<sup>-1</sup>. Then it decreases slowly to a value of 1.61 cm<sup>3</sup>·K·mol<sup>-1</sup> at 13 K before it declines abruptly to a minimum value of 0.941 cm<sup>3</sup>·K·mol<sup>-1</sup> at 2 K. The susceptibility data between 12.0 and 300 K follows the Curie–Weiss law with a Weiss constant  $\theta = 1.07$  K and Curie constant  $C = 0.066$  cm<sup>3</sup>·K·mol<sup>-1</sup>. The room-temperature effective magnetic moment (3.97 B.M.) is higher than that of the expected spin-only value of Co(II) cations (low spin, 3.87 B.M.).

For the complex **2**, we can see that when cooling from 300 K to 13 K, the  $\chi_M T$  basically decreases slowly from 15.454 to 14.457 cm<sup>3</sup>·K·mol<sup>-1</sup>. Then it declines sharply to a minimum of 10.84 cm<sup>3</sup>·K·mol<sup>-1</sup> at 2 K. The susceptibility data between 20.0 and 300 K follows the Curie–Weiss law with a Weiss constant  $\theta = -1.48$  K and Curie constant  $C = 15.45$  cm<sup>3</sup>·K·mol<sup>-1</sup>, indicating that there is very weak antiferromagnetic interaction among Co(II) ions ( $S = 3/2$ ). The room-temperature effective magnetic moment (11.11 B.M.) is higher than that of the expected spin-only value of Co(II) (low spin, 10.25 B.M.).

By comparing the structures of the two complexes, we can know that the ligand can form mononuclear and heptanuclear complexes with Co(II) under the participation of different anions. Particularly for compounds **2**, the central metal is also bridged to the surrounding metals through another oxygen atom from the carboxylate group. In addition, some unique accumulate effects were resulted from different coordinated anions and hydrogen bonds. The cyclic voltammetry tells us that the oligonuclear compound changes to the mononuclear compound when dissolved in solvent. The magnetic studies show that, the magnetic properties of the complexes change following the variation of the coordination structures. The mononuclear complexes show single-ion behavior down to 2 K. The heptanuclear **2** shows very weak anti-ferromagnetic interactions between the cobalt(II) centers.

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## Appendix A. Supplementary material

CCDC 876436–876437 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found online at <http://dx.doi.org/10.1016/j.inoche.2013.12.004>.

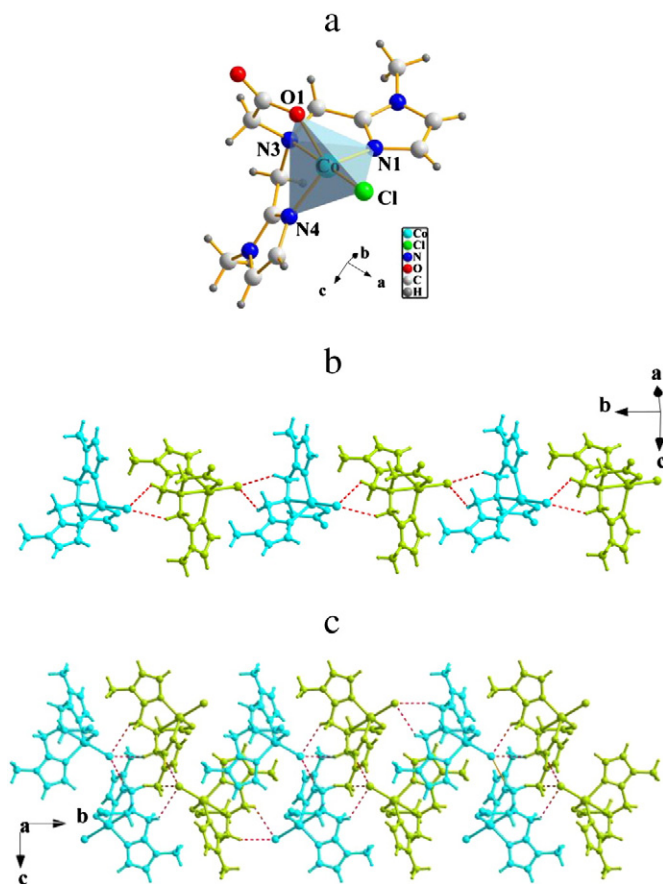


Fig. 1. (a) The coordination environment of the Co<sup>II</sup> atom, (b) Helical chain and (c) 2-D structure linked via C–H···O hydrogen bonds of **1**.

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