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Inorganic Chemistry Communications 6 (2003) 1347-1349



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Hydrothermal synthesis and crystal structure of a metal–organic coordination polymer with double-helical structure: $[Fe(phen)(ipt)]_n$ (ipt = isophthalate, phen = 1,10-phenanthroline)

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Received 4 June 2003; accepted 21 August 2003 Published online: 11 September 2003

Abstract

A novel metal-organic coordination polymer $[Fe(phen)(ipt)]_n$ 1 has been hydrothermally synthesized and structurally characterized. Compound 1 exhibits a novel neutral cross double-helical structure composed of left-handed and right-handed helical chains.

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Keywords: Coordination polymer; Helical structure; Hydrothermal synthesis; Crystal structure

Over the past decade, helical metal complexes have been extensively concerned not only in coordination chemistry but also in materials chemistry because of their similarities to nucleic acids and proteins and their potential applications in asymmetric catalysis and nonlinear optical materials [1]. Since the early pioneering work of Lehn and co-workers [2-12] on double-helical Cu(I) complexes, a lot of helicates have been synthesized using different ligands and metal cations through selfassembly process. These helicates have been assembled by coordinate-covalent bonding, hydrogen bonding, $\pi - \pi$ aromatic stacking interaction or the combination of the two [13,14]. Usually, exo-bidentate ligands composed of 2, 2'-bipyridine and 2, 2':6', 2"-terpyridine, combined with metal ions that adopt appropriate coordination geometry, tetrahedron or octahedron, are used to synthesize double-stranded helicates [15]. But doublestranded helicates constructed from asymmetrically dicarboxylate ligands have far been unexplored.

Recently, a good strategy in synthesizing metal complex with helical structure is to adopt two kinds of ligands such as asymmetrically dicarboxylate bridging ligands and aromatic bidentate chelate ligands [16]. This is because the nonlinear flexible or V-shaped dicarboxylate ligands can produce the helicity or flexuosity of the polymeric chains and aromatic bidentate chelate ligands can prevent the forming of high dimensional expanded structure [16,17] and provide potential supramolecular recognition for intermolecular π - π stacking interaction [18,19]. Based on the above synthesis strategy, we choose V-shaped dicarboxylate ligand ipt, bidentate chelate ligand phen and metal ion with appropriate geometry as the study system to explore potential charming helical structures. In this communication, we report the hydrothermal synthesis and structural characterization of 1, to our knowledge, 1 is a novel neutral cross double-helical compound composed of two single helical chains, left-handed and right-handed, that are covalently interlinked by metal dimers and induced by the supramolecular aromatic stacking interactions.

Compound 1 was prepared from a mixture of $FeCl_2 \cdot 4H_2O$ (0.198 g), isophthalic acid (0.166 g), phen (0.198 g), NaOH (0.08 g) and H_2O (8.0 ml) in an 18 ml

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Teflon-lined autoclave under autogenous pressure at 180 °C for six days [21].

The X-ray diffraction analysis [22] reveals that compound 1 is a 3D supramolecular metal-organic coordination polymer with double-helical structure. The fundamental unit, as shown in Fig. 1, consists of one Fe(II) atom, one ipt ligand, and one chelating phen ligand. Each Fe(II) center displays a distorted octahedral coordination geometry, being coordinated by two nitrogen atoms of one phen ligand and four oxygen atoms from three different carboxylate groups of three ipt ligands. The average Fe–N bond length is 2.1891(19) Å, and the Fe-O bond lengths vary from 2.0469(15) to 2.3182(14) A. The ipt ligand exhibits an interesting connection mode with metal ions. Two carboxyl groups display two different kinds of coordination modes, that is, the bidentate chelating and monodentate bridging mode. Based on these connection modes, one carboxyl group adopts the bidentate chelating mode to coordinate to the Fe(II) center, and the other carboxyl group from the same ipt ligand acts as a bridge to link other two Fe(II) centers to form a dimer unit. Hence each ipt ligand coordinates to three Fe(II) centers and each Fe(II) center links to three ipt ligands. Every two dimers are linked by two ipt ligands along two different directions alternatively to form a double-helical chain along the c axis direction with a long pitch of 18.574 Å, as shown in Fig. S2. The two helical chains, left-handed and right-handed, are interlinked together by the metal dimer that functions as a knot (see Fig. 2).

There are two kinds of π - π interactions in compound 1, namely, within the same chain and between the adjacent chains. The close contact distance between adjacent aromatic rings is 3.397 Å within the same chain and 3.338, 3.318 and 3.365 Å between adjacent chains. These supramolecular interactions together with the coordinate-covalent interactions between metal and organic ligand strengthen the stability of the double-helical chain. Therefore, we can infer that the aromatic bidentate chelate ligands are crucial to the formation of he-



Fig. 1. ORTEP drawing of 1 showing the local coordination environment of Fe(II) with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.



Fig. 2. Seeing the *bc* plane, phen ligands project above and below into the interlamellar region and there exist strong π - π stacking interactions between adjacent chains.

lical structure. The bond valence calculation [20] (Fe 1.95) suggests all Fe atoms are in the +2 oxidation state.

In this communication, we report a novel doublehelical metal-organic coordination polymer [Fe(phen) (ipt)]_n **1** which exhibits a double-helical structure consisted of two helical chains which are linked together by metal dimmers.

Supplementary materials

Crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and the IR spectrum of compound **1** were available from the authors on request.

CCDC reference number: 208497.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (20171010).

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- [21] Elem. anal. found: C: 59.7; H:3.2; N: 6.8; Fe: 16.1, calcd. For $C_{20}H_{12}$ Fe N₂ O₄ C: 60; H: 3.0; N: 7.0; Fe: 14 (%). Selected FT/IR data (cm⁻¹): 3050(w), 1610(s), 1580(m), 1540(s), 1490(w), 1480(m), 1440(s), 1430(s), 1390(s), 1100(m), 1080(m), 976(m), 912(m), 864(m), 868(m), 847(s), 827(m), 773(s), 744(s), 725(w), 717(s), 640(m), 582(m), 513(m), 422(s).
- [22] Crystal data for 1: $C_{20}H_{12}FeN_2O_4$, Monoclinic, space group P2/c, a = 8.3261(7) Å, b = 10.3192(14) Å, c = 18.5739(12) Å, $\beta = 99.819(3)$, V = 1572.5(3) Å³, Z = 4, $D_c = 1.690$ mg/m³, $\mu = 0.991$ mm⁻¹, F(000) = 816, T = 293 K. 6732 reflections measured ($2.23^{\circ} < \theta < 27.48^{\circ}$, $\lambda = 0.71073$ Å), 3599 unique ($R_{int} = 0.0433$). Structure solution and refinement based on 3599 independent reflections with $I > 2\sigma$ (I) and 244 parameters gave $R_1(wR_2) = 0.0352$ (0.0649) and S = 1.007.