

Self assembly of a novel mixed-ligand hydrogen bonding three dimensional supramolecular network [Co(Phmal)(Him)₄]

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Abstract

A novel supramolecular mixed ligand complex of formula [Co(Phmal)(Him)₄] (Phmal = phenylmalonate, Him = imidazole) has been synthesized and characterized by FT-IR spectroscopy, thermogravimetric analysis (TG), UV-Vis spectra. X-ray crystallographic studies of the complex reveal that the cobalt atom exhibits a distorted octahedral geometry being coordinated by four nitrogen atoms of Him ligands, two oxygen atoms from the phenylmalonate ligand. The intramolecular C–H... π interaction exists in the title complex. The three dimensional supramolecular network is constructed from the strong intermolecular N–H...O hydrogen bonds.

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1. Introduction

Recently, the design and synthesis of supramolecular networks that provide new shapes, sizes and chemical environments as well as the searches for new functional materials causes an incessant interest in supramolecular chemistry [1–10]. This is not only due to their complicated structural diversity, but also they are fundamental steps to discover and fabricate various fundamental supramolecular devices or technologically useful materials [11–15]. The use of noncovalent interactions (such as the hydrogen bonds and aromatic π – π stacking interactions) to arrange molecular building blocks has evolved into one of the most useful and flexible strategies for the crystal engineering design of extended supramolecular networks that have versatile functions [16–20]. The current interest is focused on the controlled assembly of donor and acceptor building blocks in order to generate an entirely supramolecular polymer. In this context, the rational design of organic ligands and judicious selection of coordination geometry of metal ions have

great effect on the formation of desirable networks. [10,21,22]. Use of flexible ligands may offer a greater degree of structural diversity and often be regarded as an effective strategy for the design and synthesis of new functional materials. Recently, we have started a systematic study on metal(II) coordination with phenylmalonate ligand (dianion of phenylmalonic acid, H₂Phmal) in the presence of other N-containing ligands. One of the aims of this project is to analyze the influence that factors such as the rigidity and the possibility of specific attractive interactions between phenyl rings can exert on the structure and functional properties of phenylmalonate – containing metal(II) complexes. Phmal is a suitable candidate for assembling such complexes due to its two interesting structural features. At first, it can adopt several kinds of coordination modes in metal complexes, which may provide abundant structural motifs [23,24]. Second, it can act as hydrogen-bond acceptors and provide the pyridyl ring which may cause the aromatic π – π stacking interactions. To the best of our knowledge, the supramolecular complexes with Phmal ligand have not been extensively studied so far [23,24]. Furthermore, the introduction of Him ligand may induce new structural evolution. The Him ligand is important in

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maintaining the desired low dimensional coordination polymer and may provide potential supramolecular recognition sites for π – π aromatic stacking and hydrogen bonding interactions. So, we assumed that Phmal ligand could be useful in the formation of supramolecular networks with some important features in the presence of Him ligand. In the present paper, we report a novel supramolecular coordination polymer [Co(Phmal)(Him)₄] based on the mixed Phmal and Him ligand. The complex exhibits a 3D supramolecular network which is constructed from the intense intermolecular N–H...O hydrogen bonds.

2. Experimental

2.1. Materials and characterization

All reagents were reagent grade and used without further purification. Elemental analyses (C, H and N) were carried out on a 240 C Elemental analyzer. FT-IR spectrum (400–4000 cm⁻¹) was recorded from KBr pellet in Magna 750 FT-IR spectrophotometer and UV-Vis spectra on a Shimadzu UV-3100 spectrophotometer. Thermogravimetric analysis (TG) was taken on NETZSCH STA 409 PG/PC instrument.

2.2. Synthesis

Imidazole (0.339 g, 0.555 mmol) was dissolved in methanol (10 ml) and then an aqueous solution of Co(NO₃)₂·6H₂O (0.485 g, 1.65 mmol) in water (5 ml) was added whilst stirring. To this solution a mixture of phenylmalonic acid (0.300 g, 1.65 mmol) and NaOH (0.120 g, 3.30 mmol) in water (10 ml) was added and stirred for 10 min and then filtered. The filtrate was kept at ambient temperature for several days and block red crystals were formed. They were filtered and washed thoroughly with methanol and dried in vacuum (yield: 42.0% based on phenylmalonic acid). Anal. Calcd for C₂₁H₂₂CoN₈O₄: C, 49.51; H, 4.35; N, 21.99. Found: C, 49.58%; H, 4.62%; N, 21.85%.

2.3. X-ray crystallography study

A red crystal having approximated dimensions 0.22 × 0.20 × 0.14 mm was used for data collection. Diffraction data were collected at 293(2) K with a Siemens SMART CCD diffractometer using graphite-monochromated (Mo–K α) radiation ($\lambda = 0.71073$ Å), ψ and ω scans mode. The cell constants were determined from the Full-matrix least-squares fit of 2597 reflections with θ in the range 2.48° and 21.57°. The structure was solved by direct methods and refined by Full-matrix least-squares on F^2 method. Intensity data were corrected for Lorenz and polarization effects and an empirical absorption correction was performed. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added geometrically and allowed to ride on their respective parent atoms.

Table 1

Crystallographic data and structure refinement for the title complex

Empirical formula	C ₂₁ H ₂₂ CoN ₈ O ₄
Formula weight	509.39
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>P</i> 2(1)2(1)2(1)
<i>a</i> (Å)	8.569(6)
<i>b</i> (Å)	13.411(10)
<i>c</i> (Å)	20.795(16)
α (°)	90
β (°)	90
γ (°)	90
Volume	2389.5(3) Å ³
<i>Z</i>	2
Calculated density	1.405 Mg/m ³
Absorption coefficient	0.762 mm ⁻¹
<i>F</i> (000)	1036
Theta range for data collection (°)	1.81–25.02
Limiting indices	$-10 \leq h \leq 9$, $-15 \leq k \leq 15$, $-19 \leq l \leq 24$
Reflections collected/unique	13112/4216 [<i>R</i> (int) = 0.0382]
Completeness to $\theta = 25.06^\circ$	100%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.5469
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4216/0/307
Goodness-of-fit on F^2	1.091
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0378$, $wR_2 = 0.0936$
<i>R</i> indices (all data)	$R_1 = 0.0500$, $wR_2 = 0.0989$
Largest diff. peak and hole (e Å ⁻³)	0.395 and -0.202

The contribution of these hydrogen atoms was included in the structure factor calculations. All calculations were carried out on a PC computer using SHELXL-97 program [25]. Details of crystal data, collection and refinement are listed in Table 1.

3. Results and discussion

3.1. Structural description

Determination of the structure of [Co(Phmal)(Him)₄] by X-ray crystallography reveals that the complex consists of

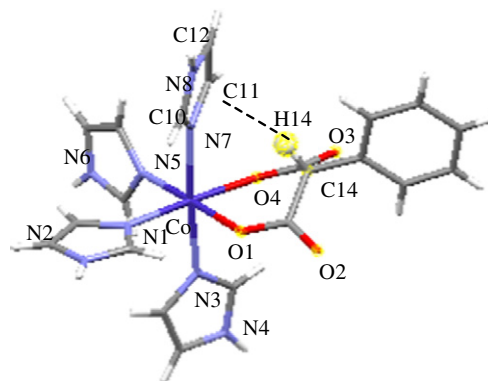


Fig. 1. Molecular structure of the title complex. The dashed line indicates the intramolecular C–H... π interaction. Hydrogen atom participating in C–H... π interactions is indicated as ball.

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