

# Crystal structure of a binuclear polymeric self-assembled Cobalt complex; $[\text{Co}(\text{Pht})(1\text{-MeIm})_2]_n$

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**Abstract:** Reaction of phthalic acid with 1-methylimidazole and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in aqueous solution give rise to a three-dimensional complex  $[\text{Co}(\text{Pht})(1\text{-MeIm})_2]_n$  (Pht-2 = dianion of o-phthalic acid; 1-MeIm = 1-methylimidazole). The product has been characterized by infrared spectroscopy (IR), and single crystal X-ray diffraction. The complex crystallizes in the Pccn space group with  $a = 17.2402(19) \text{ \AA}$ ,  $b = 25.712(3) \text{ \AA}$ ,  $c = 16.1672(18) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 7166.6(14) \text{ \AA}^3$ ,  $Z = 8$ . In this three-dimensional complex two independent metal atoms are tetrahedrally ( $\text{N}_2\text{O}_2$ ) coordinated to a pair of Pht ligands and a pair of 1-MeIm molecules.

**Keywords:** Phthalic acid; Cobalt complex; Crystal structures

## Introduction

In recent years, the crystal engineering of supramolecular architectures based on metal and organic building blocks has rapidly emerged as an exciting area of supramolecular chemistry because of their novel and diverse topologies and potential applications in host-guest chemistry, high thermal stability linear optical behavior, catalysis, microporosity, electrical conductivity, and molecular magnetism. The creation of metal-organic coordination networks based on complexes of transition metals and multi-functional bridging ligands has proven to be a fertile field due to the intriguing network topologies and potential functions as new classes of materials. These metal-containing supramolecular frameworks can be

constructed through two different types of interaction: (I) coordinate covalent bonds linking metal centers and organic ligands [1-4], and (II) noncovalent intermolecular forces such as hydrogen bonding,  $\pi$ - $\pi$  stacking, and coulombic interactions.

Currently, the rational design and synthesis of new extended supramolecular networks by means of both coordinative covalent and hydrogen-bonding interactions are of great interest and have brought forth a great variety of such frameworks with fascinating structural motifs [5-6].

In general, extended networks possessing higher dimensionalities can be obtained by the assembly of coordination polymers, polymers with lower dimensionalities via hydrogen bonding interactions and  $p$ - $p$  stacking [7-8]. However, it is still a challenge when

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we hope to control the final products. The studies in this respect are limited because the assembly of molecules through weak interactions requires incorporation of many factors which cannot be completely controlled until now. For this, proper selection of metal ions and ligands are the key issues in designing self-assembly [9-11].

Recently, using phthalate and several N-donor ligands like pyridine, imidazole and their derivatives scientist have successfully constructed novel coordination polymers [12-20].

We recently prepared a three-dimensional supramolecular Co(II) coordination polymer based on Phthalic acid and 1-methylimidazole. We report herein the preparation and crystal structure, of the compound  $[\text{Co}(\text{Pht})(1\text{-MeIm})_2]_n$ .

## Experimental

### General procedures

All reagents were commercially available from Merck and were used as received. Doubly distilled deionized water was used in the procedures when needed. The FT-IR spectra were recorded as KBr pellets in the 4000 – 400  $\text{cm}^{-1}$  range on a Perkin Elmer FT/IR spectrometer. X-ray crystallography of the product was done by X-Ray Structural Centre Institute of Organoelement Compounds in Russia (X-RAY STRUCTURAL CENTER (XRSC) General and Technical Chemistry Division Academy of Sciences of Russia.) The condition of X-ray crystallography is explained below.

### Synthesis of $[\text{Co}(\text{Pht})(1\text{-MeIm})_2]_n$

Phthalic acid (0.836 g, 5 mmol) was added to a solution of (0.788 ml) 1-methylimidazole and then during string of this solution aqueous solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1.455 g, 5 mmol) added to this solution. The resulting solution was heated at 50 °C for 1 hour and then filtered and kept in room temperature. After a month dark red crystals of  $[\text{Co}(\text{Pht})(1\text{-MeIm})_2]_n$  that were suitable for X-ray diffraction studies. The product was yielded and washed with MeOH and dried in air.

The IR spectrum of obtained sample is indicated in figure 1 and spectral data are listed as follows (KBr,  $\text{cm}^{-1}$ ): 3490(m), 3380(m), 3113(s), 1540(m), 1385(s), 1097(s), 936(w), 826(m), 756(m), 660(w), 619(w), 494(w)  $\text{cm}^{-1}$ .

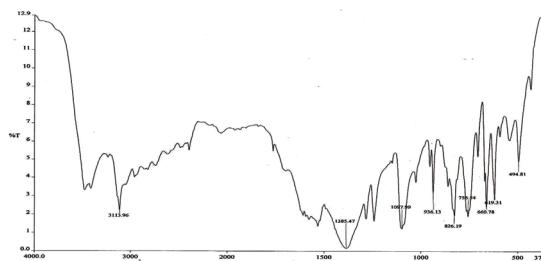


Figure 1 IR spectra of  $[\text{Co}(\text{Pht})(1\text{-MeIm})_2]_n$

The IR spectrum of the prepared complex presents two distinguishable regions. In high energy bands, ranging from 3500 to 3000  $\text{cm}^{-1}$ , there are three absorption peaks at 3490, 3380 and 3113  $\text{cm}^{-1}$ , due to N-H stretching vibrations (3490, 3380  $\text{cm}^{-1}$ ) and aromatic C-H (3113  $\text{cm}^{-1}$ ).

In the low energy region, a series of absorption peaks are observed. Weak absorption of asymmetric stretching vibrations of carboxylic acid are observed in the region of 1550 to 1700  $\text{cm}^{-1}$ . Also, stretching vibrations of C=C aromatics are found in about 1500  $\text{cm}^{-1}$ . Absorption peak at 1385  $\text{cm}^{-1}$  is related to symmetric stretching vibrations of carboxylic acid and stretching vibration of C-N.

### X-ray crystallography

Structure measurements of  $[\text{Co}(\text{Pht})(1\text{-MeIm})_2]_n$  was performed at 293 K on a Bruker SMART APEX2 CCD area detector with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and the  $\theta$  scan mode in the range of 1.42 to 27.16°. Cell parameters were obtained by the global refinement of the positions of all collected reflections. It is isostructural to compound  $[\text{Co}(\text{Pht})(1\text{-MeIm})_2]_n$  with cell parameters  $a = 17.2402(19)$  Å,  $b = 25.712(3)$  Å,  $c = 16.1672(18)$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 7166.6(14)$  Å<sup>3</sup>,  $Z = 8$ , and space group Pccn. An empirical absorption correction was applied. The structures were solved by direct methods and refined by a full-ma-

trix least-squares technique based on F2 using the SHELXL-97 program. All of the nonhydrogen atoms were refined anisotropically. Crystallographic details for the structure of  $[\text{Co}(\text{Pht})(1\text{-MeIm})_2]_n$  are summarized in Table 1. Selected bond lengths and angles for  $[\text{Co}(\text{Pht})(1\text{-MeIm})_2]_n$  are given in Table 2.

Table 1 Crystallographic data, details of structural determination

Empirical formula	$\text{C}_{32}\text{H}_{32}\text{Co}_2\text{N}_8\text{O}_8$
Formula weight	774.52
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P c c n
Unit cell dimensions	a = 17.2402(19) Å $\alpha = 90^\circ$ b = 25.712(3) Å $\beta = 90^\circ$ c = 16.1672(18) Å $\gamma = 90^\circ$
Volume	0.40
Z	7166.6(14) Å <sup>3</sup>
Density (calculated)	1.436 Mg/m <sup>3</sup>
Absorption coefficient	0.985 mm <sup>-1</sup>
F(000)	3184
Crystal size	0.18 × 0.15 × 0.11 mm <sup>3</sup>
Theta range for data collection	1.42 to 27.16°
Index ranges	-22 ≤ h ≤ 22, -33 ≤ k ≤ 32, -20 ≤ l ≤ 20
Reflections collected	72188
Independent reflections	7930 [R(int) = 0.1101]
Observed reflections [I > 2σ(I)]	4341
Completeness to theta = 27.16°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.899 and 0.843
Data/restraints/parameters	7930 / 0 / 455
Goodness-of-fit on F <sup>2</sup>	1.000
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0459, wR <sub>2</sub> = 0.0918
R indices (all data)	R <sub>1</sub> = 0.1086, wR <sub>2</sub> = 0.1131
Largest diff. peak and hole	0.365 and -0.333 e.Å <sup>-3</sup>

## Results and discussion

It should be pointed out that  $[\text{Co}(\text{Pht})(1\text{-MeIm})_2]_n$  compound is insoluble in common organic solvents, a common property of coordination polymers, but their poor solubility in water allows us to grow single crystals of  $[\text{Co}(\text{Pht})(1\text{-MeIm})_2]_n$  for X-ray investigations as well as possible.

The most features of their IR spectra are the absorptions due to the symmetric and asymmetric stretching of the coordinated COO groups in the 1610–1579 and 1380 cm<sup>-1</sup> regions, respectively. Their positions and intensities are similar to those reported for other phthalate complexes having polymeric structures [12–20].

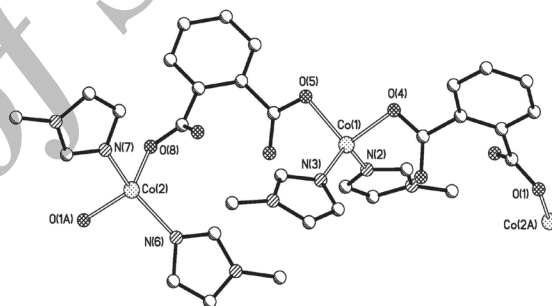
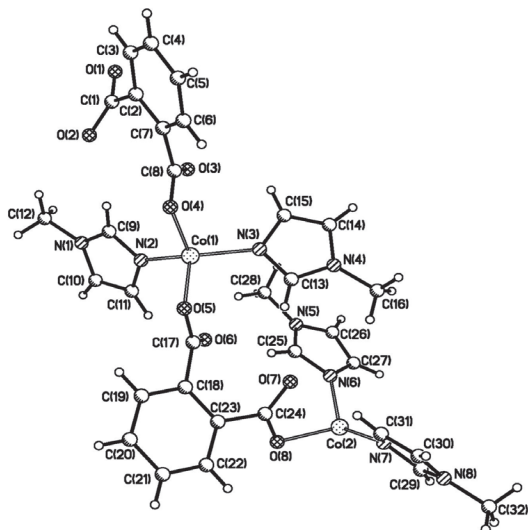


Figure 2 The overview of Co coordination in  $[\text{Co}(\text{Pht})(1\text{-MeIm})_2]_n$ . Hydrogen atoms are omitted for clarity. Only atoms linked to Co are labeled. Symmetry transformations used to generate equivalent atoms:  $-x, y+1/2, -z+1/2$  for O(1A) and  $-x, y-1/2, -z+1/2$  for Co(2A)

Table 2 Selected bond distances (Å) and bond angles (°)

Co(1)-O(4)	1.981(2)	O(4)-Co(1)-O(5)	100.85(10)
Co(1)-O(5)	1.988(2)	O(4)-Co(1)-N(2)	106.42(10)
Co(1)-N(2)	2.017(3)	O(5)-Co(1)-N(2)	107.89(11)
Co(1)-N(3)	2.020(3)	O(4)-Co(1)-N(3)	107.88(11)
Co(2)-O(8)	1.991(2)	O(5)-Co(1)-N(3)	105.65(10)
Co(2)-O(1)#1	1.996(2)	N(2)-Co(1)-N(3)	125.51(11)
Co(2)-N(6)	2.020(3)	O(8)-Co(2)-O(1)#1	102.58(10)
Co(2)-N(7)	2.025(3)	O(8)-Co(2)-N(6)	105.98(11)
		O(1)#1-Co(2)-N(6)	102.79(11)
		O(8)-Co(2)-N(7)	102.02(11)
		O(1)#1-Co(2)-N(7)	105.60(11)
		N(6)-Co(2)-N(7)	134.17(12)



Figure 3 The independent part of unit cell of  $[\text{Co}(\text{Pht})(1\text{-MeIm})_2]_n$ .

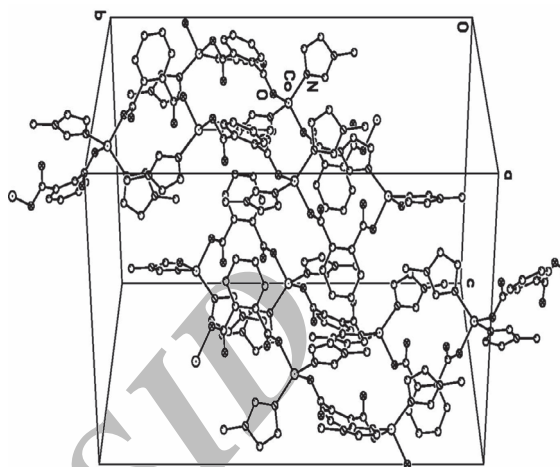
### Crystal structure

The X-ray diffraction analysis indicates that complex  $[\text{Co}(\text{Pht})(1\text{-MeIm})_2]_n$  possesses an infinite 1-D polymeric chain consisting of  $[\text{Co}(1\text{-MeIm})_2]$  units linked by 1,6-bridging Pht ligands into an infinite chain. There are two crystallographically independent Co(II) centers (Co(1) and Co(2)) within the chain; both Co(II) atoms are tetrahedrally coordinated by two O atoms from different Pht ligands and two N atoms of two 1-MeIm molecules. The Co(1)–O(4,5) distances are 1.981(2) and 1.988(2) Å, and Co(1)–N(2,3) are 2.017(3) and 2.020(3) Å, whereas Co(2)–O(8,1) and Co(2)–N(6,7) bond distances are slightly longer 1.991(2) and 1.996(2), and 2.020(3) and 2.025(3) Å, respectively. The bond angles lie in the range of 100.85(10)–125.51(11)° for Co(1) and 102.58(10)–134.17(12)° for Co(2) (Table 2).

The C–O distances lie in the range from 1.230(4) to 1.277(4) Å. The absorption frequencies of the aromatic hydrogen atoms C–H of 1-MeIm are located in the 3120–2941  $\text{cm}^{-1}$  region in the IR spectra.

### Conclusion

This study demonstrates a synthetic approach for the construction of coordination polymer consist-

Figure 4 The overview of crystal packing in  $[\text{Co}(\text{Pht})(1\text{-MeIm})_2]_n$ .

ing of  $[\text{Co}(\text{Pht})(1\text{-MeIm})_2]$  building units connected through 1,6-bridging o-phthalate ligands. This coordination polymer was synthesized from reactions of 1-MeIm and o-phthalic acid and the metal nitrate salt. A systematic investigation on the use of the phthalate linker in the synthesis of other new polymers as well as their properties is under way.

### Supplementary data

A figure and full lists of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and observed and calculated factors are available from the authors.

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