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Journal of Molecular Structure 831 (2007) 114–118

Journal of
MOLECULAR
STRUCTURE

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Self assembly of a novel mixed-ligand hydrogen bonding three dimensional supramolecular network $[Co(Phmal)(Him)_4]$

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Received 23 April 2006; received in revised form 20 July 2006; accepted 22 July 2006

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.

Keywords: Cobalt complex; Crystal structure; Mixed-ligand; Supramolecular network; Infrared spectra

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, H_2Phmal) 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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doi:10.1016/j.molstruc.2006.07.033

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 $Co(NO_3)_2 \cdot 6H_2O$ (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 $C_{21}H_{22}CoN_8O_4$: 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–Kα) 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. 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.

Table 1
Crystallographic data and structure refinement for the title complex

Empirical formula	$C_{21}H_{22}CoN_8O_4$
Formula weight	509.39
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$P2(1)2(1)2(1)$
a (Å)	8.569(6)
b (Å)	13.411(10)
c (Å)	20.795(16)
α (°)	90
β (°)	90
γ (°)	90
Volume	2389.5(3) Å^3
Z	2
Calculated density	1.405 Mg/m^3
Absorption coefficient	0.762 mm^{-1}
$F(000)$	1036
Theta range for data collection (°)	1.81–25.02
Limiting indices	$-10 \leqslant h \leqslant 9, -15 \leqslant k \leqslant 15,$ $-19 \leqslant l \leqslant 24$
Reflections collected/unique	13112/4216 [$R(\text{int}) = 0.0382$]
Completeness to $\theta = 25.06°$	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 R indices [$I > 2\sigma(I)$]	$R_1 = 0.0378$, $wR_2 = 0.0936$
R indices (all data)	$R_1 = 0.0500$, $wR_2 = 0.0989$
Largest diff. peak and hole (e Å^{-3})	0.395 and −0.202

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

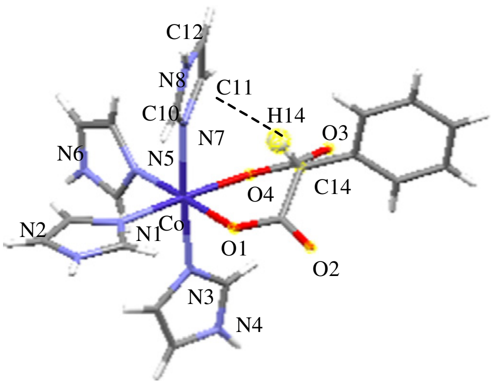

Fig. 1. Molecular structure of the title complex. The dashed line indicates the intramolecular C–H···π interaction. Hydrogen atom participating in C–H···π interactions is indicated as ball.

one Co atom, one phmal ligand and four imidazole ligands in each independent crystallographic unit (Fig. 1). The Co atom, which is in a distorted octahedral environment, is coordinated by four nitrogen atoms from four Him ligands [Co(1)–N(1) 2.130(3) Å; Co(1)–N(5) 2.151(3) Å; Co(1)–N(3) 2.152(3) Å; Co(1)–N(7) 2.167(3) Å] and two carboxylate oxygen atoms from the Phmal ligand [Co(1)–O(4) 2.084(2) Å; Co(1)–O(1) 2.122(2) Å]. Selected bond distances and angles are listed in Table 2. The angles subtended the Co atom ranges from 84.99(9)° to 175. 86(10)°. The Phmal group in the title complex adopts a bidentate coordination mode and exhibits the same boat conformation as in the reported complex [Cu(2,2′-bipy)(Phmal)(H_2O)]·$2H_2O$] [23]. Whereas the Phmal group in the reported complex $\{[Cu(H_2O)_3][Cu(Phmal)_2]\}_n$ simultaneously exhibits both bidentate (through two oxygen atoms of the two carboxylate groups) and bis(monodentate) (through two *trans* carboxylate oxygen atoms from two Phmal ligands) coordination mode. Furthermore, the two Phmal ligands have different conformation: one has the boat conformation while the other exhibits the envelope one [24]. The distance, 2.770 Å, between the H(14) atom attached to the C(14) atom and the centroid of Him [N(8)–C(12)–C(11)–N(7)–C(10)] shows that there is intramolecular C(14)–H(14)···π interactions in the title complex [d (C–H···C_g) = 3.672 Å; ∠(C–H···C_g) = 153.38°]. This kind of contact further stabilizes the molecule. There are five strong hydrogen bonds in the present supramolecular complex. The system of hydrogen bonds, which includes carboxylate oxygen atoms [O(1), O(2) and O(3)] and nitrogen atoms [N(2), N(4), N(6) and N(8)] from Him ligands, is very complicated. This system of hydrogen bridges can be regarded as a superposition of two different layers. The layer parallel to (0 1 0) plane is defined by the N(2)–H(2A)···O(4)#1 and N(6)–H(6A)···O(2)#3 hydrogen bonds (Fig. 2), while that parallel to (0 0 1) plane is defined by the N(8)–H(8A)···O(1)#4 and N(4)–H(4A)···O(3)#2 hydrogen bonds (Fig. 3) [N(2)–H(2A)···O(4)#1 = 2.836(3) Å #1: 1 + *x*,*y*,*z*; N(4)–H(4A)···O(3)#2 = 2.775(4) Å #2: −*x*, −1/2 + *y*,3/2 − *z*; N(6)–H(6A)···O(2)#3 = 2.725(4) Å #3:1/2 − *x*, 1 − *y*, 1/2 + *z*; N(8)–H(8A)···O(1)#4 = 2.929(4) Å #4: 1 − *x*,

Table 2
Selected bond lengths (Å) and angles (°) for the title complex

Bond distances	
Co(1)–O(4)	2.084(2)
Co(1)–O(1)	2.122(2)
Co(1)–N(1)	2.130(3)
Co(1)–N(5)	2.151(3)
Co(1)–N(3)	2.152(3)
Co(1)–N(7)	2.167(3)
Bond angles	
O(4)–Co(1)–O(1)	84.99(9)
O(4)–Co(1)–N(1)	175.86(10)
O(1)–Co(1)–N(1)	90.87(10)
O(4)–Co(1)–N(5)	92.58(9)
O(1)–Co(1)–N(5)	175.66(11)
N(1)–Co(1)–N(5)	91.56(10)
O(4)–Co(1)–N(3)	88.06(11)
O(1)–Co(1)–N(3)	86.13(10)
N(1)–Co(1)–N(3)	91.90(12)
N(5)–Co(1)–N(3)	90.19(12)
O(4)–Co(1)–N(7)	88.03(11)
O(1)–Co(1)–N(7)	91.95(10)
N(1)–Co(1)–N(7)	91.89(12)
N(5)–Co(1)–N(7)	91.57(12)
N(3)–Co(1)–N(7)	175.78(11)

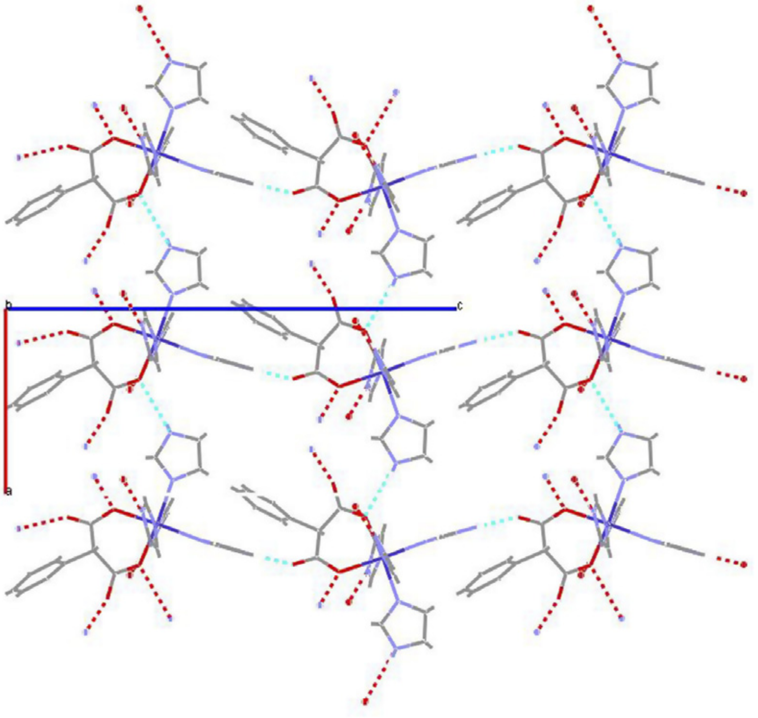

Fig. 2. View of the layer parallel to the (0 1 0) plane linked by strong intermolecular N(2)···O(4) and O(2)···N(6) hydrogen bonds.

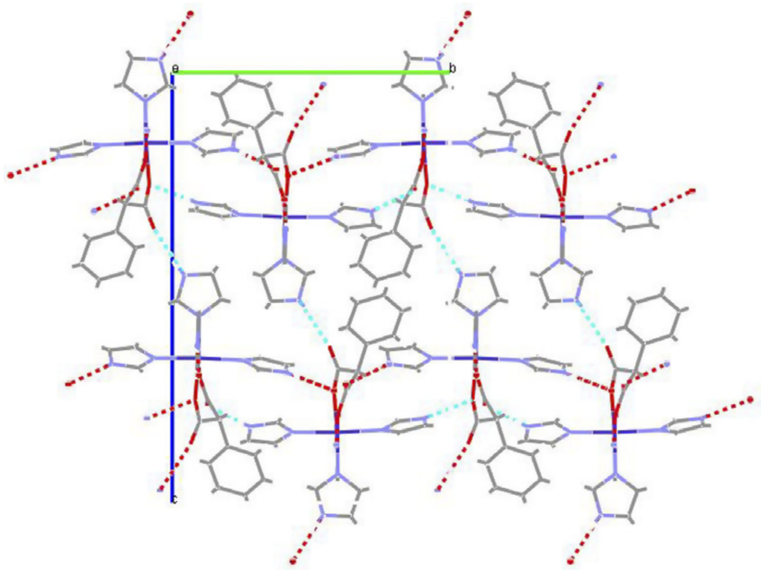

Fig. 3. View of the layer parallel to the (0 0 1) plane formed by strong intermolecular N(3)···O(4) and O(1)···N(8) hydrogen bonds.

$1/2 + y, 3/2 - z$]. The details of the hydrogen bonds are listed in Table 3. Thus, a novel three dimensional supramolecular network was formed as a result of strong intermolecular hydrogen bonding. Hydrogen bonding interactions are very important in the preparation of supramolecular architectures [26]. Undoubtedly, the hydrogen bonding plays important roles in the stabilization of the title coordination compound.

3.2. FT-IR spectra

The FT-IR spectra of the title compound show characteristic bands of carboxylate groups at 1614 cm^{-1} for asymmetric stretching and that at 1410 cm^{-1} for symmetric stretching, respectively [27]. The value of $\Delta v(\mathrm{COO}) = v_{\mathrm{as}}(\mathrm{COO}) - v_{\mathrm{s}}(\mathrm{COO})$, which is usually used in determining the coordination mode of carboxylate, follows the order $\Delta v_{\mathrm{monodentate}} > \Delta v_{\mathrm{ionic}} > \Delta v_{\mathrm{bridging}} > \Delta v_{\mathrm{chelate}}$ [28]. However, it is known that strong hydrogen bonding with monodentate carboxylate group can decrease the Δv value. The Δv value corresponding to the monodentate carboxylate group in the title complex, which equals to 204 cm^{-1}, is significantly smaller than expected. In the title complex, strong intermolecular hydrogen bond between the coordinated Him molecule and the carboxylate oxygen atom has been found (Table 3). Such low values of Δv have been reported for other monodentate carboxylates with $\mathrm{C{=}O}$ group involved in strong hydrogen bonding [29]. In all these cases, the results of the X-ray analysis allowed to assign unambiguously the binding mode of carboxylate group. The broad band around 3135 cm^{-1} may be assigned to the stretching vibrations of N–H group in the Him ring with intermolecular hydrogen bonds.

Table 3
The details of the hydrogen bonds for the title complex

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<DHA
N(2)–H(2A)···O(4)#1	0.8600	1.9900	2.836(3)	168.00
N(4)–H(4A)···O(3)#2	0.8600	1.9200	2.775(4)	173.00
N(6)–H(6A)···O(2)#3	0.8600	1.8700	2.725(4)	171.00
N(8)–H(8A)···O(1)#4	0.8600	2.0700	2.929(4)	176.00
N(8)–H(8A)···O(2)#4	0.8600	2.5200	3.083(5)	124.00

Symmetry transformations used to generate equivalent atoms: #1 $1 + x, y, z$; #2 $-x, -1/2 + y, 3/2 - z$; #3 $1/2 - x, 1 - y, 1/2 + z$; #4 $1 - x, 1/2 + y, 3/2 - z$.

3.3. UV-Vis spectra

In the UV-Vis spectra in methanol, three absorption bands centered at 202, 204 and 208 nm were observed. They may be due to the π–π^* and n-π^* transitions of the ligands. No *d–d* transition bands were observed. This indicates that the concentration of methanolic solution is quite low. While in the UV-Vis spectra of the present complex in solid state, two absorption bands centered at 222 and 507 nm were observed. The band around 222 nm may arise from the π–π and n-π^* transitions of the ligands and that centered at 507 nm may be due to the *d–d* transition band of the Co^{2+} ion.

3.4. Thermogravimetric analysis

The thermal behavior of the title coordination compound has been deduced from the TG analysis. The weight loss of 57.80% in the temperature range 169–403 °C can be attributed to the removal of four Him ligands. The total weight loss of 85.20% in the temperature range 169–505 °C, which is in agreement with the weight loss calculated for the loss of all organic moieties leading to the formation of CoO as final residuals above 505 °C (Calcd 85.29%).

4. Conclusion

In conclusion, the mixed ligand complex of cobalt has been obtained by self assembly. The Phmal ligand and imidazole molecules complete the distorted octahedral coordination sphere around Co^{2+}. It has been shown that the determination of the coordination mode of the carboxylate group can not be made on the basis of its IR spectra only. Strong hydrogen bonds severely influence the vibrational characteristics of the carboxylate group. The intramolecular C–H$\cdots\pi$ contacts exists in the title complex. The complex forms a novel 3D supramolecular structure due to the strong intermolecular hydrogen bonds.

Acknowledgements

We gratefully acknowledge the Foundation of Jiangsu Provinicial Key Program of Physical Chemistry in Yangzhou University and the National Natural Science Foundation of China (Grant No. 20373060) for the financial support of this work.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2006.07.033.

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