Asian Journal of Chemistry Vol. 19, No. 7 (2007), 5360-5364

A Novel Metal-Organic 1D-Supramolecular Complex from the Self-Assembly of Copper(II) with 1,10-Phenanthroline and Biphthalate

JIAN-HONG BI*, FU-HOU YAO†, ZI-XIANG HUANG‡,
HONG-LIANG WANG† and NAI-LANG HU†
Department of Chemistry, Anhui Institute of Education, Hefei-230061, P.R. China
E-mail: bijianhong@ahieedu.net.cn

A new copper(II) complex of formula [Cu(phen)(BPT)H_2O]·0.5H_2O (phen = 1,10-phenanthroline, BPT = biphthalate) has been synthesized under the ambient conditions and the crystal structure was determined by single crystal X-ray diffraction. The compound crystallizes in the system and belongs to space group: orthorhombic Pca2(1) with a = 11.14770(10)Å, b = 11.63650(10)Å, c = 14.03150 (10)Å, β = 90º, γ = 90º, V = 1820.17(3)Å^3, Z = 4, Dc = 1.587 g/cm^3, Mr = 434.88, μ(moKo) = 1.239 mm^{-1}, F(000) = 888. The final R = 0.0450 and wR = 0.1166 for 3012 observed reflections with I > σ(I). The crystal structure analysis indicates that the copper(II) ion is five-coordinated in a square pyramidal geometry. The BPT and phen molecules are connected by copper(II) and form zigzag chain-like structure, then pack in 1D-supramolecular complex.

Key Words: Copper(II), Biphthalate, 1,10-Phenanthroline, Supramolecular, Crystal structure.

INTRODUCTION

Supramolecular chemistry and crystal engineering of coordination compounds have attracted considerable interests nowadays owing to the fascinating structural diversity and potential applications as functional materials[1-3]. In this field, using large special ligands and metal ions through self-assembly to form supramolecular compounds is in a period of remarkable growth and this kind of molecule is supposed to offer functional materials for catalysis, molecule selection, ion exchange and specific chemical transformations[4-8].

†School of Chemistry and Chemical Engineering, Anhui University, Hefei-230039, P.R. China.

‡Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou-350002, P.R. China.

Recently, many supramolecular compounds containing copper(II) have been synthesized, because Cu ions are soft acid and it favour to be coordinated by soft base such as S and unsaturated N-containing ligands[6-8]. Herein, the synthesis and crystal structure of the supramolecular compound $[Cu(phen)(BPT)H_2O]\cdot 0.5H_2O$ is reported.

EXPERIMENTAL

All reagents were of AR grade and used without further purification. IR spectra were record on a Nexus-870 spectrophotometer, Elemental analyses for C, H and N were performed on a Elementar Vario EL-III analyzer.

Synthesis: A solution of 10 mmol phen in 15 mmol ethanol, a solution of 5 mmol $Cu(SO_4)_2\cdot 5H_2O$ in 10 mL water and a solution of 5 mmol potassium biphthalate in 10 mL water were mixed together under stirring condition. The solution became blue. After being filtered, the solution was kept at room condition for 10 d and then the four-prism shaped blue crystals resulted from it. IR (KBr, cm^{-1}): 3430 (m, ν_{OH}), 3060 (m, $\nu_{Ar\text{-}H}$), 1660 (s, $\nu_{C=N}$), Anal. Calcd. for $C_{20}H_{15}N_2O_{5.5}Cu$: C, 55.24; H, 3.48; N, 6.44 %. Found: C, 55.06; H, 3.65; N, 6.37 %.

Crystal structure determination: A single crystal of compound with dimensions of 0.50 mm × 0.34 mm × 0.26 mm was selected for crystallographic data collection at 293(2)K and structure determination on a Seimens SMART CCD area-detector diffractometer with graphite-monochromatic MoKα radiation (λ = 0.71073Å). A total of 3012 reflections were collected in the range of $2.53 < \theta < 25.11^o$, of which 3102 reflections were unique with R_{int} = 0.0401. Lp effects and empirical absorption were applied in data corrections. The strucutre was solved by direct methods and expanded using Fourier techniques and SHELXS-97 program system was used in the solution and refinement of the structure. The non-hydrogen atoms were refined anisotroically. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 269 variable parameters for 3012 reflections with $I > \sigma(I)$ and gave the final R = 0.0450, wR = 0.1166. The weighting scheme was $w = 1/[s^2(F_0^2) + (0.0522P)^2 + 2.7539P]$, where $P = (F_0^2 + 2Fc^2)/3\}$, s = 1.196. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.830 and -0.441 e/$Å^3$, respectively.

RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters obtained are given in Table-1. The selected bond length and bond angles are listed in Table-2. Hydrogen bonds are given in Table-3. Fig. 1 shows the molecular structure of the compound. Fig. 2 shows the packing arrangement of the unit cell of the compound. There are two crystallographically independent molecules,

TABLE-1
NON-HYDROGEN ATOMIC COORDINATES (× 10^4) AND
THERMAL PARAMETERS (× 10^3Å^2)

Atom	X	Y	Z	U(EQ)
Cu	1135(1)	233(1)	2072(2)	25(1)
N(1)	963(6)	-1054(5)	3039(5)	24(2)
N(2)	970(6)	-1059(8)	1158(5)	33(2)
C(1)	999(6)	-1026(6)	3940(5)	18(1)
C(2)	674(8)	-2027(10)	4506(7)	43(2)
C(9)	794(9)	-1961(8)	-376(5)	34(2)
C(10)	964(9)	-1056(11)	149(8)	53(3)
C(11)	663(7)	-2118(6)	1568(6)	29(2)
C(12)	686(8)	-2012(6)	2587(5)	26(2)
C(13)	2256(6)	1513(6)	633(5)	21(1)
C(14)	2350(7)	2611(7)	48(6)	25(2)
C(19)	2600(7)	2615(6)	-920(5)	21(2)
O(1)	1355(6)	1441(6)	1124(4)	35(2)
O(2)	3116(5)	826(5)	571(4)	32(1)
O(3)	3653(6)	1404(5)	-1989(5)	35(2)
O(4)	1850(5)	828(6)	-1453(4)	38(2)
O(5)	-1005(3)	505(3)	2017(7)	33(1)
O(6)	-641(7)	1967(13)	1967(13)	54(3)

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (º)

Bond	Bond length (Å)	Angle	(º)	Angle	(º)
Cu-O(3)#1	1.910(7)	O(3)#1-Cu-O(1)	86.61(13)	N(2)-Cu-N(1)	82.22(15)
Cu-O(1)	1.951(6)	O(3)#1-Cu-N(2)	176.0(3)	O(3)#1-Cu-O(5)	92.9(3)
Cu-N(1)	2.031(7)	O(1)-Cu-N(2)	96.7(4)	O(1)-Cu-O(5)	90.5(2)
Cu-N(2)	1.985(9)	O(3)#1-Cu-N(1)	94.4(3)	N(2)-Cu-O(5)	89.3(3)
Cu-O(5)	2.407(3)	O(1)-Cu-N(1)	177.8(3)	N(1)-Cu-O(5)	91.4(3)

TABLE-3
HYDROGEN BOND LENGTHS (Å) AND BOND ANGLES (º)
(A = Acceptor, D = Donor)

D-H···A	d(D-H)	d(H···A)	d(D···A)	< (DHA)
O(5)-H(1)···O(4)#4	0.95(2)	1.94(4)	2.811(9)	152(5)
O(5)-H(2)···O(2)#5	0.95(2)	1.93(4)	2.735(10)	141(5)

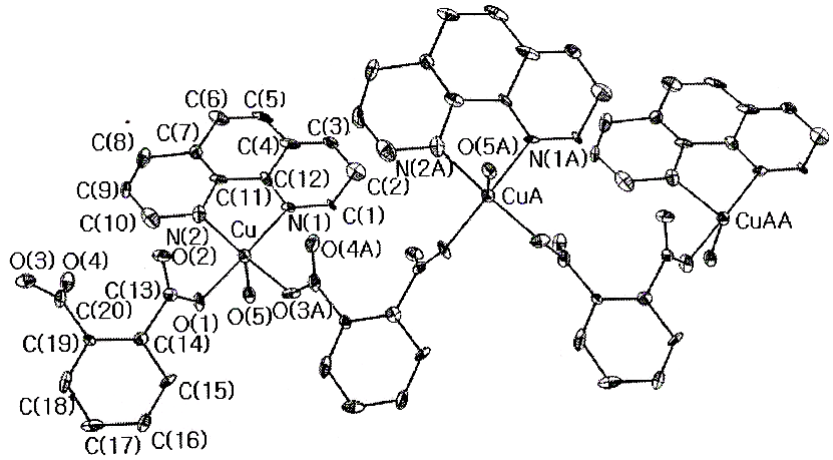

Fig. 1. Molecular structure of [Cu(phen)(BPT)H_2O]·0.5H_2O complex

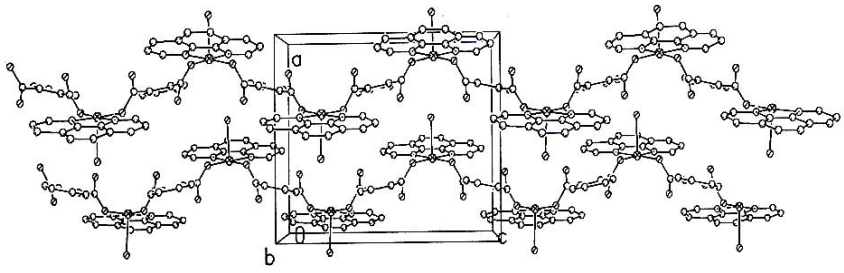

Fig. 2. Molecular packing arrangement in the unit cell

Cu(phen)(BPT)H_2O and one lattice water in an asymmetric unit. In the unit, the coordination geometries of the two Cu atoms (Cu and CuA) in the two molecules are both distorted square pyramids, in which copper cation is five-coordinated in a slightly distorted square plane defined by N(1)-N(2)-O(1)-O(2) and the two molecules have similar bond distances and bond angles. However, the dihedral angle between these two basal planes of the two distorted square pyramids is about 42.36º, which means the two distorted square pyramids have different orientations. Therefore, it is enough to describe the structure of one molecule Cu(phen)(BPT)H_2O here. As illustrated in Fig. 1, Cu(II) is coordinated by N(1) and N(2) atoms from one molecule of phen. The bond lengths of Cu-N(1) and Cu-N(2) are 2.031(7) and 1.985(9) Å. O(1) is from COO^- groups of one BPT molecule and O(3A) is from COO^- groups of another BPT molecule. The bond length

of Cu-O(1) and Cu-O(3) are 1.951(6) and 1.910(7) Å. The O(5) comes from a solvent H_2O molecule and the length of Cu-O(5) is 2.407(3) Å. It is obviously longer than that of the rest. The bond angles of O(1)-Cu-O(5), O(3A)-Cu-O(5), N(1)-CuO(5), N(2)-Cu-O(5) are in the range from 89.3(3) to 92.9(3)º. A conclusion can be reached that the Cu(II) ion is five-coordinated in a distorted square pyramidal geometry and the axial position is occupied by O(5) atom. Fig. 2 depicts the molecules packing in the unit cell, indicating that the BPT and phen molecules are connected by copper(II) and from a zigzag (123.5º) chain-like structure. The distance between two chains is 6.003-15.912 Å. Many of these chains packed in 1D-supramolecular complex[8-11].

Conclusion

Crystal structure of novel copper(II) complex with BPT and 1,10-phenanthroline has been synthesized and characterized by IR, elemental analysis and X-ray diffraction analysis. The studies of the absorption and catalysis characteristics about this complex are in progress.

Supplementary material

Crystallographic data for the structure reported in this communication have been deposited with the Cambridge Crystallorgaphic Data Center as supplementary publication No. CCDC 266938.

ACKNOWLEDGEMENT

This work is financially supported by the foundation of 2006 Anhui province key research project (06022020).

REFERENCES

1. S. Leininger, B. Olenyuk and P.J. Stang, *Chem. Rev.*, **100**, 853 (2000).
2. N.L. Hu, H.Z. Dong, Z.X. Huang and F.X. Xie, *Asian J. Chem.*, **17**, 1276 (2005).
3. J.H. Bi, J.M. Song, Z.X. Huang, Y.H. Wang and L.T. Kong, *Asian J. Chem.*, **18**, 2365 (2006).
4. B.F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, **119**, 2952 (1997).
5. J.H. Bi, L.Q. Chen, Z.Q.F.X. Xie, X.D. Zhao, S.S. Ni and J.D. Xu, *Asian J. Chem.*, **14**, 1621 (2002).
6. N.F. Curtis, *Inorg. Chim. Acta*, **317**, 27 (2001).
7. J.H. Bi, X.L. Cheng, Z.X. Huang and N.L. Hu, *Asian J. Chem.*, **18**, 2371 (2006).
8. J.H. Bi, F.X. Xie, X.D. Zhao, Q. Chen, J.D. Xu and S.S. Ni, *Asian J. Chem.*, **16**, 137 (2004).
9. K.L. Zhang, Y. Zu, Z. Wang, X.M. Jin and X.Z. You, *Transition Met. Chem.*, **27**, 95 (2002).
10. Y. Kim and D.Y. Jung, *Inorg. Chem.*, **39**, 1470 (2000).
11. F. Yun-Long and L. Shi-Xiong, *Chin. J. Struct. Chem.*, **2**, 142 (2002).

(*Received*: 12 October 2006; *Accepted*: 16 June 2007) AJC-5711