Synthesis, Structure and Characterization of Two-dimensional Network Copper Complex [Cu$_3$(nta)$_2$(azpy)$_2$(H$_2$O)$_2$]·6H$_2$O

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The copper(II) complex [Cu$_3$(nta)$_2$(azpy)$_2$(H$_2$O)$_2$]·6H$_2$O (nta = nitrilotriacetate, azpy = 4,4'-azobispyridine) has been synthesized and characterized. The X-ray analysis reveals that there are two kinds of copper(II) coordination environments. Cu(1) has a distorted square plane symmetry and Cu(2) has a distorted octahedral symmetry. Cu(1) is linked to Cu(2) through nta and bound to Cu(1C) by azpy, and Cu(2) is linked to Cu(2A) through azpy, which extends to two-dimensional network with large rhombus 1.2 nm × 1.7 nm.

Keywords   crystal structure, two-dimensional network, copper complex, azobispyridine

Introduction

Crystal engineering of supramolecular architectures sustained by coordinate covalent bonds or hydrogen bonds represents a rapidly expanding field that offers potential for development of new classes of functional solids.[1,2] The architectures of coordination polymers can be reliably predicted, since previously known metal coordination environments are propagated into one-, two-, and three-dimensional motifs with rigid multitopic organic "spacer" ligands. The formation of open framework structure based on coordination chemistry with zeolite-like molecule-sized channels, cavities and pores is current interest.[3-5] A convenient path to obtain polymetric structure is to employ some bifunctional ligands such as pyrazine, 4,4'-bipyridine and 4,4'-azobispyridine to link metal ions to form an infinite configuration.[6-10]

A coordination polymer containing two different organic ligands is so far less explored, and it is generally impossible to predict either the composition or structure of the product. In order to achieve predictive power, people must establish a much large structural database for this type. However, several very interesting examples of combination of two different ligands have so far been reported including oxalate and pyrazine;[11] oxalate and bipyridine;[12] pyridine-4-carboxylate and bipyridine;[13] malonate and bipyridine;[14] nitrilotriacetate and bipyridine;[15] phthalate, malonate and bipyridine.[16] In the present work, by using a flexible ligand nitrilotriacetate (nta) and a rigid ligand 4,4'-azobispyridine (azpy) as a mixed ligand system, complex [Cu$_3$(nta)$_2$(azpy)$_2$(H$_2$O)$_2$]·6H$_2$O (1) has been synthesized and characterized.

Experimental

All reagents were of AR grade and were used without further purification. 4,4'-Azobispyridine (azpy) was prepared following the literature method.[17] Elemental analyses for C, H and N was performed on a Perkin-Elmer 240C analyser. IR spectra were obtained on a Nicolet 170SX FT-IR spectrophotometer in the 4000—400 cm^{-1} region for KBr pellets. ESR spectra were recorded in solid state on an Er2000-SRC instrument. Magnetic susceptibilities were measured in the solid state using a CAHN-2000 Faraday balance with [Ni(en)$_2$]-

S_2O_3 as a standard at 6000 G magnetic field.

Synthesis of $[Cu_3(nta)_2(azpy)_2(H_2O)_2] \cdot 6H_2O$ (1)

A solution of $Cu_3(nta)_2 \cdot H_2O$ (0.121 g, 0.2 mmol) in 20 mL of $H_2O/EtOH$ (1:1, V/V) was added to one side of H-shape tube, and a solution of 4,4'-azobispyridine (azpy) (0.074 g, 0.4 mmol) in 20 mL of $H_2O/$
EtOH (1 : 1 , V/V) was added to the another side. After about one month, the dark prismatic single crystals suitable for X-ray diffraction were obtained by the careful diffusion method. Anal. calcd for $C_{32}H_{44}Cu_3N_{10}O_{20}$: C 35.61, H 4.11, N 12.98; found C 35.43, H 4.12, N 13.14.

X-Ray structure determination

A single crystal of the compound **1** with dimensions 0.52 mm × 0.36 mm × 0.28 mm was selected for data collection at 293(2) K, using a SIEMENS P4 four-circle diffractometer with graphite monochromated Mo K_α radiation ($\lambda = 0.071073$ nm). Data were collected by ω-2θ scan technique. The structure was solved by direct methods (SHELXS-86[18]) and refined with full-matrix least-squares technique (SHELXL-93[19]). The positions of all remaining non-H atoms were obtained from successive Fourier syntheses. No attempt was made to locate the hydrogen atoms of water except the coordination water. The positions of hydrogen atoms were calculated using idealized geometry except H(7B), H(31), H(32),

H(34) and H(35), which were obtained from successive Fourier syntheses. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) (E-mail: deposit@ccdc.cam.ac.uk) as supplementary publication, deposition code is 149036.

Results and discussion

Crystal structure

The crystallographic data and the selected bond lengths and angles are listed in Tables 1 and 2, respectively. The molecular configuration is shown in Fig. 1. There are two kinds of copper(II) coordination environments in complex **1**. The Cu(1) atom lies on the crystallographic center and has a distorted square coordination, two carboxylate oxygen atoms [O(6) and O(6a)] are from the two symmetry-related nta ligand [Cu(1)—O(6), 0.1949(3) nm], two nitrogen atoms [N(4) and N(4a)] are from the two symmetry-related azpy ligands [Cu(1)—N(4), 0.2021(4) nm]. However, Cu(2) atom has a elongated octahedral geometry. The equatorial plane is defined by N(1), O(1) and O(3) atoms of the nta ligand [Cu(2)—N(1), 0.2024(3) nm; Cu(2)—O(1), 0.1965(3) nm; Cu(2)—O(3), 0.1960(3) nm] and N(2) atom of the azpy ligand [Cu(2)—N(2), 0.1990(3) nm], while the axial positions being occupied by carboxylate O(5) and water O(7) atoms [Cu(2)—O(5), 0.2419(4) nm; Cu(2)—O(7), 0.2340(4) nm]. Azpy ligand molecule exhibits a *trans*-form in complex **1**.

Table 1 Crystallographic data for complex $[Cu_3(nta)_2(azpy)_2(H_2O)_2] \cdot 6H_2O$

Formula	$C_{32}H_{44}Cu_3N_{10}O_{20}$	Absorption coefficient (mm^{-1})	1.514
M	1079.40	Absorption correction:	empirical
Crystal system	Triclinic	T_{min}	0.524
Space group	$P\bar{1}$	T_{max}	0.751
a (nm)	1.0273(2)	F (000)	553
b (nm)	1.1060(2)	2θ Range (°)	3.80—49.94
c (nm)	1.1617(2)	Index ranges	$0 \le h \le 12$, $-13 \le k \le 11$, $-13 \le l \le 13$
α (°)	98.28(3)	Reflections collections	4127
β (°)	105.54(3)	Independent reflections	3890
γ (°)	114.37(3)	Data/restrains/parameters	3890/0/334
V (nm^3)	1.1086(4)	Goodness-of-fit on F^2	1.054
Z	2	Final R $[I > 2\sigma(I)]$ indices	$R_1 = 0.0472$, $wR_2 = 0.1167$
$D_{calc.}$ (g/cm^3)	1.617	R indices (all data)	$R_1 = 0.0553$, $wR_2 = 0.1280$

$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 3.6920P]$, $P = [F_o^2 + 2F_c^2]/3$.

Table 2 Selected bond lengths (nm) and angles (°) for complex **1**

|			
Cu(1)—O(6)	0.1949(3)	Cu(1)—N(4)	0.2021(4)
Cu(2)—O(1)	0.1965(3)	Cu(2)—O(3)	0.1960(3)
Cu(2)—N(2)	0.1990(3)	Cu(2)—N(1)	0.2024(3)
Cu(2)—O(7)	0.2340(4)	Cu(2)—O(5)	0.2419(4)
O(6)-Cu(1)-O(6a)	180.0	O(6)-Cu(1)-N(4)	92.11(14)
N(4)-Cu(1)-N(4a)	180.0	O(6)-Cu(1)-N(4a)	87.89(14)
O(3)-Cu(2)-O(1)	167.77(13)	O(3)-Cu(2)-N(2)	96.2(2)
O(1)-Cu(2)-N(2)	95.94(14)	O(3)-Cu(2)-N(1)	82.88(14)
O(1)-Cu(2)-N(1)	85.41(13)	N(2)-Cu(2)-N(1)	171.25(14)
O(3)-Cu(2)-O(7)	91.0(2)	O(1)-Cu(2)-O(7)	86.15(14)
N(2)-Cu(2)-O(7)	95.8(2)	N(1)-Cu(2)-O(7)	92.96(14)
O(3)-Cu(2)-O(5)	98.6(2)	O(1)-Cu(2)-O(5)	82.43(14)
N(2)-Cu(2)-O(5)	92.89(14)	N(1)-Cu(2)-O(5)	78.70(12)
O(7)-Cu(2)-O(5)	166.3(2)		

Symmetry code: $a - x + 1$, $-y$, $-z + 1$.
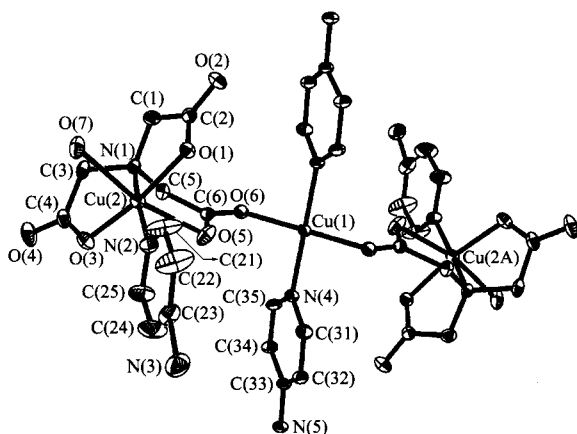
Fig. 1 Local coordination of Cu(1) and Cu(2) in complex **1** with 30% thermal ellipsoids.

Cu(1) is linked to Cu(2) through nta and bound to Cu(1C) by azpy to form a chain with arms. The distances of Cu(1)—Cu(2) and Cu(1)—Cu(1C) are 0.5375 nm and 1.2965 nm, respectively. Cu(2) is linked to Cu(2A) by azpy with separation of 1.2972 nm to form a 2D network as shown in Fig. 2. Four Cu(1) atoms locate at the corners of the rhombus and four Cu(2) atoms occupy at the two longer sides of the rhombus. The shorter side length is 1.2965 nm and the longer side length is 1.7934 nm. The interior angles of rhombus are 82.5° and 97.5°, the diagonal lengths are 2.3457 nm and 2.0717 nm. The two-dimensional network is an undulated layer. The two-dimensional layers stack with the hydrogen bond interactions between coor-

dination water and carboxylate oxygen atoms of adjacent layer [O(7)—O(2) 0.2751 nm, O(7)—O(4) 0.2813 nm] (Fig. 3).
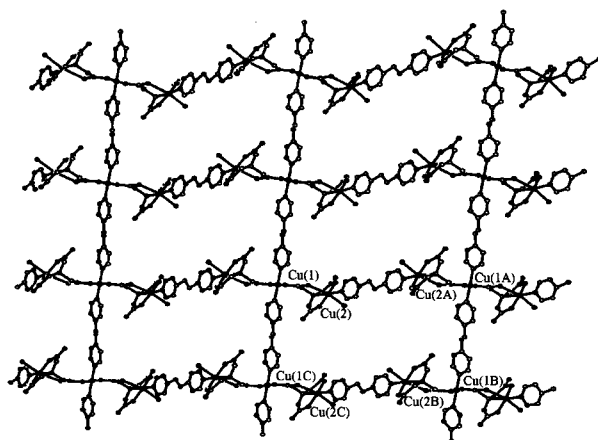

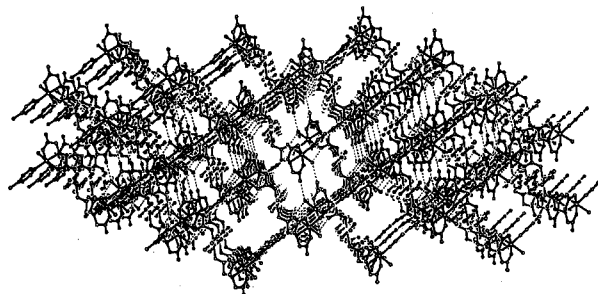**Fig. 2** View of the two-dimensional network in complex **1**.

Fig. 3 Stack figure of the complex **1** showing the hydrogen bonding interactions.

Infrared spectrum and magnetic measurement

IR spectra shown the bands are as follows: 3600—3100v, 1658—1603v, 1494w, 1422v, 1396v, 1334m, 1305s, 1226m, 1107m, 1051s, 917s, 848s, 746m, 627w, 846s, 578m, 562m, 530m and 500w cm^{-1}. The strong peaks at 1422 cm^{-1} and 1396 cm^{-1} belong to the N=N stretch vibration of azo group.[17,20] The absorbed bands 1658—1603 cm^{-1} are attributed to coordinated carboxylate of nta.[21]

The ESR spectrum of complex **1** in solid shows a typical axically symmetric signal with $g_\parallel = 2.250$ and $g_\perp = 2.083$.

Variable-temperature magnetic susceptibility in the range of 75—300 K shows that the title complex obeys the Curie-Weiss law, $\chi_m = C/(T - \theta)$, with values of $\theta = -16.9$ K, $C = 1.226$ emu·K·mol^{-1} (Fig. 4).

There is a weak anti-ferromagnetic interaction between the copper(II) ions through nta bridging in the complex **1**.
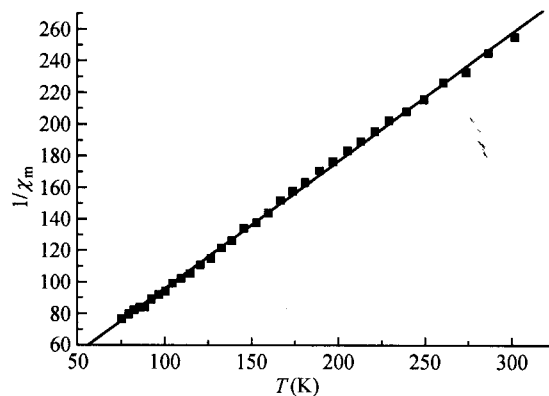

Fig. 4 Plot of $1/\chi_m$ vs. T for complex **1**.

References

1   Lehn, J. M. *Supramolecular Chemistry*: *Concepts and Perspectives*, VCH: Weinheim, **1995**, Chapter 9.

2   Aakeroy, C. B.; Seddon, K. R. *Chem. Soc. Rev.* **1993**, 397.

3   Yaghi, O. M.; Li, G. *Nature* **1995**, *378*, 703.

4   Schwarz, P.; Stebel, E.; Fisher, R. D.; Apperley, D. C.; Davies, N. A.; Harris, R. K. *Angew. Chem.*, *Int. Ed. Engl.* **1995**, *34*, 1197.

5   Hirsch, K. A.; Venkataraman, D.; Wilson, S. R.; Moore, J. S.; Lee, S. *J. Chem. Soc., Chem. Commun.* **1995**, 2199.

6   Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *166*, 1151.

7   Yugen, Z.; Jianmin, L.; Wei, D.; Nishiura, M.; I-mamoto, T. *Chem. Lett.* **1999**, 195.

8   MacGillivary, L. R.; Groeneman, R. H.; Atwood, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 2676.

9   Mitsuru, K.; Mariko, S.; Shin-ichiro, N.; Tomomichi, Y.; Seika, M.; Susumu, K. *Chem. Lett.* **1999**, 285.

10 Lucia, C.; Gianfranco, C.; Davide, M. P. *J. Chem. Soc., Dalton Trans.* **1999**, 1799.

11 Kitagawa, S.; Okubo, T.; Kawata, S.; Kondo, M.; Katada, M.; Kobayashi, H. *Inorg. Chem.* **1995**, *34*, 4790.

12 Lu, J. Y.; Lawandy, M. A.; Li, J.; Yuan, T.; Lin, C. L. *Inorg. Chem.* **1999**, *38*, 2695.

13 MacGillivray, L. R.; Groeneman, R. H.; Attwod, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 2676.

14 Li, J.; Zeng, H.; Wang, Q.; Wu, X. *Chem. Commun.* **1997**, 1213.

15 Wang, Q.-M.; Wu, X.-T.; Zhang, W.-J.; Sheng, T.-L.; Lin, P.; Li, J.-M. *Inorg. Chem.* **1999**, *38*, 2223.

16 Lightfoot, P.; Snedden, A. *J. Chem. Soc., Dalton Trans.* **1999**, 3549.

17 Beadle, P. J.; Goldstein, M.; Goodgame, D. M. L.; Grzeskowiak, R. *Inorg. Chem.* **1969**, *8*, 1490.

18 Sheldrick, G. M. *SHELXS-86 User Guide*, University of Göttingen; Göttingen, Germany, **1990**.

19 Sheldrick, G. M. *SHELXL-93*, *Program for X-ray Crystal Structure Refinement*, Göttingen, Germany, **1993**.

20 Grzeskowiak, R.; Whatley, C.; Goldstein, M. *Spectrochim. Acta* **1975**, *31A*, 1577.

21 Tomita, Y.; Ueno, K. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 1069.