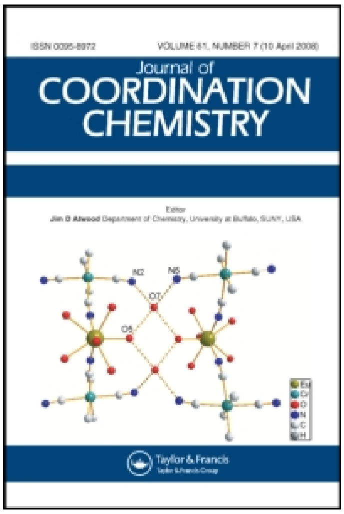

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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Na Li[a]; Sanping Chen[a]; Shengli Gao[a]
[a] Department of Chemistry, Shaanxi Key Laboratory of Physical Inorganic Chemistry, Northwest University, Xi'an, Shaanxi 710069, P.R. China

To cite this Article Li, Na , Chen, Sanping and Gao, Shengli(2007) 'A hydrogen-bonded 3D coordination network in a complex of Cu(II) nitrate with 1,2,4-triazole-5-one and 1,10-phenanthroline', Journal of Coordination Chemistry, 60: 2, 117 — 123

To link to this Article: DOI: 10.1080/00958970600731646

URL: http://dx.doi.org/10.1080/00958970600731646

Journal of Coordination Chemistry
Vol. 60, No. 2, 20 January 2007, 117–123

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A hydrogen-bonded 3D coordination network in a complex of Cu(II) nitrate with 1,2,4-triazole-5-one and 1,10-phenanthroline

NA LI, SANPING CHEN and SHENGLI GAO*

Department of Chemistry, Shaanxi Key Laboratory of Physical Inorganic Chemistry,
Northwest University, Xi'an, Shaanxi 710069, P.R. China

(*Received in final form 23 January 2006*)

A pentacoordinate Cu(II) complex, $[Cu(H_2O)(L1)(L2)(NO_3)](NO_3)(H_2O)$ (**1**; L1 = 1,2,4-triazole-5-one, L2 = 1,10-phenanthroline) has been synthesized and characterized. An X-ray structure analysis of **1** revealed that the Cu(II) centre has a distorted square pyramidal environment, with a second weakly bonded nitrate (Cu–O 2.550 Å) giving rise to a pseudo-octahedral coordination geometry. Weak interactions such as π–π stacking and hydrogen-bonding (especially C–H $\cdots$ O hydrogen bonds) have significant effects in configuring the 3D packing of the complex.

Keywords: Copper; 1,2,4-Triazole-5-one; 1,10-Phenanthroline; Nitrate; X-ray structure; Weak interactions; Packing

1. Introduction

Supramolecular assemblies constructed using hydrogen bonds, π–π and electrostatic interactions are intriguing, because of the diversity of structures found and potential uses of them as functional materials [1–7]. Weak C–H $\cdots$ O hydrogen bonds are of particular importance because they occur in nucleic acids and proteins in biological systems and are involved in substrate–receptor recognition. Just as with N–H $\cdots$ O and O–H $\cdots$ O hydrogen-bonds, C–H $\cdots$ O hydrogen bonds can be used to control crystal packing [8–14]. H-atom acidity, cooperativity, resonance assistance, and the absence or presence of proximal groups are important factors in the bonding scheme [10]. However, the rational design of functional materials through weak C–H $\cdots$ O hydrogen interactions is still at the initial stage and current focus is mainly on understanding the factors that influence crystal packing.

Here, the synthesis and crystal structure of a quaternary complex, $[Cu(TO)(phen)(H_2O)(NO_3)]NO_3 \cdot H_2O$, is reported. The acidic C–H [8–11] atoms of

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*Corresponding author. Email: gaoshli@nwu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970600731646

1,10-phenanthroline and their proximity to O atoms in the structure lead to diverse weak C–H $\cdots$ O hydrogen bonding interactions which control crystal packing. In the solid state, the complex has a 3D network resulting from π–π interactions, and intermolecular and intramolecular hydrogen-bonds; some are bifurcated and involve O $\cdots$ O and C $\cdots$ O groupings.

2. Experimental

2.1. *Materials and measurements*

The ligand 1,2,4-triazole-5-one (TO) was synthesized according to the literatures [15, 16]. All other chemicals were of analytical grade and used without further purification.

C, H, N contents were determined on a Perkin-Elmer 2400 system analyzer. Cu^{2+} was determineded by the iodimertric method. IR specta were measured using a Nicolet 60 SXR FT-IR spectrophotometer in the 4000–400 cm^{-1} region (KBr pellets). All TG-DTG runs were performed with a Perkin-Elmer thermogravimetric system. Single crystal X-ray experiments were performed on a Bruker Smart-1000CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using ω and φ scan modes within the a range of $1.62 < \theta < 25.10°$ at 273 K. The crystal size was $0.23 \times 0.14 \times 0.10$ mm^3. Of 7196 measured reflections, 3238 observed reflections with $I > 2\sigma(I)$ were used in the refinement. The structure was solved by direct methods and refined by full-matrix least-squares based on F^2 using SHELXS-97 [17, 18]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were generated geometrically. Crystal data, data collection parameters and refinement statistics for **1** are listed in table 1.

Table 1. Crystal data and structure refinement details for **1**.

Empirical formula	$CuC_{14}H_{15}N_7O_9$
Formula weight	488.87
Space group	$P\bar{1}$
a (Å)	7.7494(3)
b (Å)	10.0449(4)
c (Å)	12.8028(5)
α (°)	82.149(2)
β (°)	81.058(2)
γ (°)	70.270(2)
V (Å^3)	922.89(6)
Z	2
F(000)	498
Temperature (K)	273(2)
Total reflections	7196
Observed reflections ($I > 2\sigma(I)$)	3238
Goodness-of-fit	1.140
R_{int}	0.0330
R_1, wR_2 ($I > 2\sigma(I)$)	0.0362, 0.0832
R_1, wR_2 (all data)	0.0509, 0.0887
$\Delta\rho_{\max}$ and $\Delta\rho_{\min}$, (e Å^{-3})	0.298, −0.335

2.2. *Synthesis*

TO (0.5 mmol, 0.043 g) and 1,10-phenanthroline monohydrate (1 mmol, 0.198 g) were dissolved in hot absolute ethanol (30 cm^3), and $Cu(NO_3)_2 \cdot 6H_2O$ (0.5 mmol, 0.121 g) dissolved in 10 cm^3 of absolute ethanol added. After stirring for 30 min, the clear blue solution was left to stand at room temperature. A few days later, blue plates suitable for X-ray diffraction were obtained. Anal. Calcd for $CuC_{14}H_{15}N_7O_9$ (%): C, 34.40; H, 3.09; N, 20.06; Cu, 13.00. Found: C, 34.49; H, 2.863; N, 19.87; Cu, 13.08.

3. Results and discussion

In the structure of **1** (figure 1), Cu(II) has a distorted square pyramidal geometry and is coordinated by two nitrogen atoms from phen, one nitrogen atom from TO, one oxygen of a nitrate ion and another oxygen of a water molecule. The Cu–N distances are 1.995(2), 2.004(2) and 2.009(2) Å, and Cu–O distances are 2.302(2) and 1.984(2) Å. In addition, an oxygen atom of the lattice nitrate ion interacts weakly (Cu1–O 2.550 Å) to give overall a pseudo-octahedral coordination geometry. Selected bond lengths and angles are listed in table 2. As shown in figure 2, hydrogen bonds contribute significantly to form an infinite zigzag [N_6–H $\cdots$ O_3, O_8–H $\cdots$ O_7] chain parallel to the *b* direction. These are formed between hydrogen N_6 of TO and O_3 atom of coordinated nitrate, and O_7 of TO ligand and O_8 of coordinated water. Hydrogen bond details are given in table 3. Offset face-to-face π–π stacking interactions involving phen ligands (3.4071 Å) link the zigzag chains to form an infinite two-dimensional plane (figure 2). The conjugated interaction between the 1,2,4-triazole ring and the carbonyl group makes O_7 a good acceptor and it forms a bifurcated hydrogen bond [19–21] with O_8 and O_9, thus generating a six-membered hydrogen bonded ring (figure 3). It is well known that such rings are important in clay-like and zeolite-like supramolecular compounds

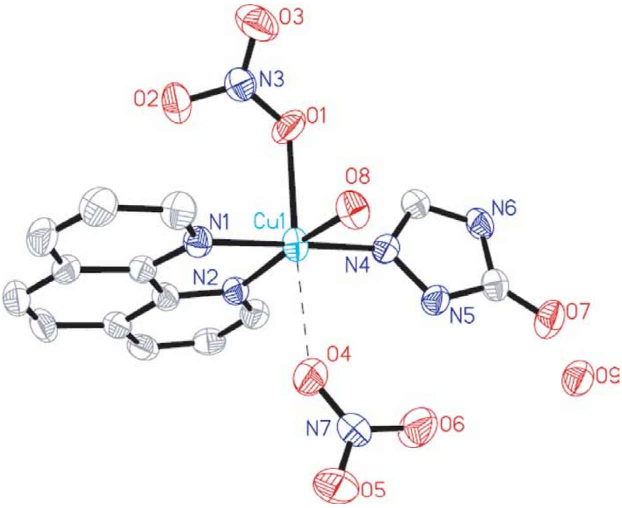

Figure 1. The structure of **1** with 50% thermal ellipsoid probability showing the atom numbering scheme.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Cu(1)–O(8)	1.983(2)	Cu(1)–N(1)	1.995(2)
Cu(1)–N(2)	2.004(2)	Cu(1)–N(4)	2.009(2)
Cu(1)–O(1)	2.362(2)	N(4)–C(13)	1.297(4)
N(4)–N(5)	1.370(4)	N(5)–C(14)	1.344(4)
N(6)–C(13)	1.345(4)	N(6)–C(14)	1.365(4)
N(7)–O(5)	1.219(3)	O(7)–C(14)	1.237(3)
O(8)–Cu(1)–N(1)	90.88(9)	O(8)–Cu(1)–N(2)	168.57(9)
N(1)–Cu(1)–N(2)	82.37(9)	O(8)–Cu(1)–N(4)	90.38(9)
N(1)–Cu(1)–N(4)	178.65(9)	N(2)–Cu(1)–N(4)	96.30(9)
O(8)–Cu(1)–O(1)	88.96(9)	N(1)–Cu(1)–O(1)	95.00(9)
N(2)–Cu(1)–O(1)	100.77(9)	N(4)–Cu(1)–O(1)	85.51(9)
C(5)–N(1)–Cu(1)	112.73(2)	N(1)–C(5)–C(9)	116.2(2)
N(2)–C(9)–C(5)	116.2(2)	C(13)–N(4)–N(5)	104.9(2)
N(4)–C(13)–N(6)	110.6(3)	C(13)–N(6)–C(14)	109.2(3)
N(5)–C(14)–N(6)	103.2(3)	C(14)–N(5)–N(4)	112.1(3)

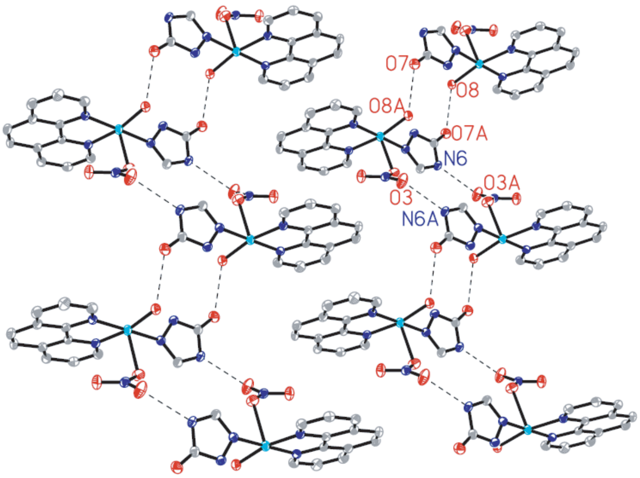

Figure 2. View of the zigzag chain and the two-dimensional planar structure of **1**.

Table 3. Hydrogen bond distances (Å) and angles (°) for **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(8)–H(8A)···O(7)^{i}	0.845(2)	1.96(2)	2.786(3)	165(4)
O(9)–H(9B)···O(7)^{iv}	0.845(2)	1.98(2)	2.788(3)	159(4)
N(5)–H(5B)···O(6)^{ii}	0.770(3)	1.97(3)	2.737(4)	179(3)
O(9)–H(9A)···O(6)^{v}	0.834(2)	1.96(2)	2.752(4)	158(4)
N(6)–H(6B)···O(3)^{iii}	0.760(3)	2.04(3)	2.785(4)	166(3)
O(8)–H(8B)···O(9)^{vi}	0.839(2)	1.88(2)	2.719(3)	175(4)
C(3)–H(3)···O(4)	0.93	2.5592	3.3632	144.94
C(10)–H(10)···O(5)	0.93	2.5493	3.1153	119.59
C(11)–H(11)···O(2)	0.93	2.5044	3.1372	125.50
C(10)–H(10)···O(2)	0.93	2.5309	3.2114	130.27
C(13)–H(13)···O(9)	0.93	2.5589	3.2763	134.25

Symmetry codes used are i: $-x+2, -y+2, -z$; ii: $-x+1, -y+2, -z+1$; iii: $-x+2$, $-y+1$, $-z$; iv: $x-1, y, z+1$; v: $x+1, y, z$; vi: $x, y, z-1$.

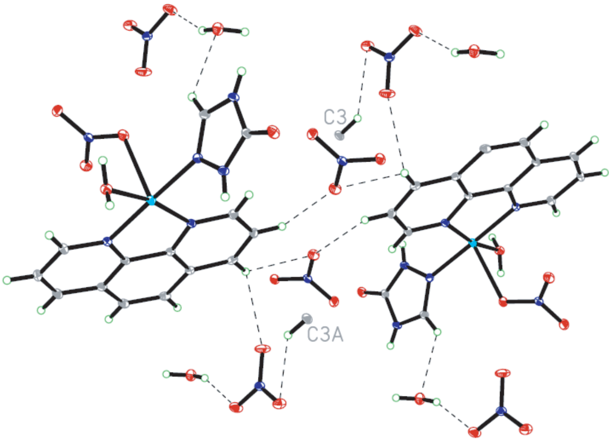

Figure 3. View of intermolecular C–H ··· O hydrogen bonding interactions. C atoms of 1,10-phenanthroline except for C3 are omitted for clarity.

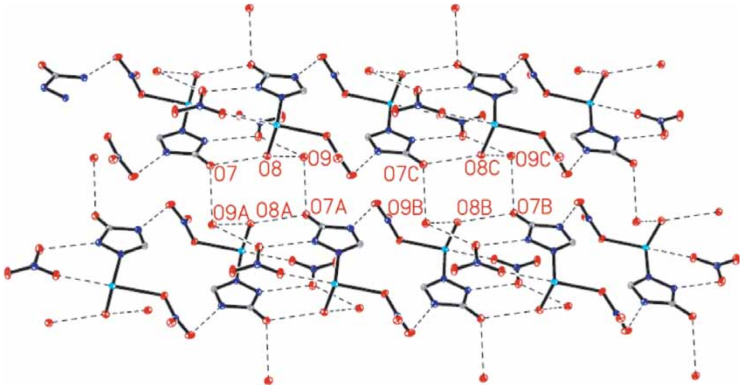

Figure 4. The six-membered ring formed by bifurcated hydrogen bonds. In order for clarity, 1,10-phenanthroline is omitted.

[22]. The nature of C–H ··· O hydrogen-bonding interactions was examined by PLATON 98 (figure 4). Because of the acidity of C(sp2)–H atoms [8–11], strength and directionality are weak, but still clearly noticeable. Interestingly, there is a bifurcated C–H ··· O hydrogen bond formed between C(10)–H as donor and O_2 and O_5 (on the weakly coordinated nitrate group) as acceptors. Hydrogen bond lengths and angles are listed in table 3. The inter- and intramolecular hydrogen bonds together with π–π interactions built up a three dimensional network (figure 5).

The thermal stability of **1** was investigated by therogravimetric methods for a polycrystalline sample under nitrogen. TG-DTG curves show two obvious weight losses, 7.23% between 97 and 140°C, and 17.39% between 140 and 240°C. The first is the loss of water (Calcd 7.36%), and the second the loss of the triazole ring [23] (Calcd 17.39%). In the IR, bands at 1625, 1590, 1574 and 1517 $\mathrm{cm^{-1}}$ are attributed to vibrations of phen. The characteristic C=O stretch at 1743 $\mathrm{cm^{-1}}$ is shifted to higher

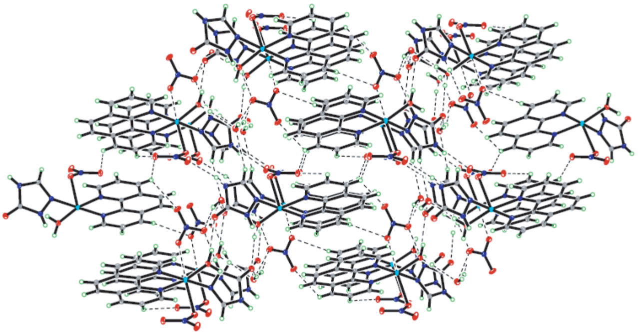

Figure 5. Packing arrangement of the complex [Cu(phen)(TO)(H_2O)(NO_3)](NO_3) · (H_2O).

wave numbers compared to the TO ligand (1696 cm^{-1}), indicating the coordination of the ligand atom with Cu^{2+}. In addition, the C=N stretch shifts to higher frequency (1582 cm^{-1}) because of the coordination of the nitrogen atom of TO. Peaks at 3242, 3015 and 2853 cm^{-1} are assigned C–H, O–H and N–H stretches, respectively.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 294753. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We gratefully acknowledge the financial support of the National Natural Science Foundation of China (Grant No. 20471047), Education Foundation of Shaanxi Province (Grant No. 05JK291), the Natural Science Foundation of Shaanxi Province (Grant No. FF05201 and FF05203) and the Science and Technology Foundation of the National Defense Key Laboratory for Propellants and Explosive Combustion of China (Grant No. 51455010105QT3001).

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