metal-organic compounds

A novel three-dimensional copper(II) network *via* hydrogen bonds: diaqua-bis[bis(pyrazol-1-yl-κN^2)methane]-copper(II) diperchlorate

Lei Zhang,* Miao Du, Liang-Fu Tang, Xue-Bing Leng and Zhi-Hong Wang

Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China
Correspondence e-mail: lzhang@nankai.edu.cn

The crystal structure of the title complex, $[Cu(C_7H_8N_4)_2(H_2O)_2](ClO_4)_2$, consists of a discrete centrosymmetric $[Cu(C_7H_8N_4)_2(H_2O)_2]^{2+}$ cation and two perchlorate anions. The Cu^{II} centre is six-coordinated by four N donors from the two pyrazole rings [Cu—N 1.998 (2) and 2.032 (3) Å] and two O atoms from the water molecules occupying the apical sites [Cu—O 2.459 (3) Å]. The coordination geometry of the complex can be described as octahedral. There is a unique three-dimensional network in which the perchlorate units are linked by a combination of strong O—H···O and weak C—H···O hydrogen bonds.

Comment

The self-assembly of metal compounds into one-, two- and three-dimensional supramolecular architectures is of considerable current interest for potential applications because the macroscopic physical properties of crystals are defined by the intermolecular electronic interactions presented in the solid state (Lehn, 1990; Burrows *et al.*, 1995). Consequently, there is a need for the development and study of strong and highly directional intermolecular interactions, which are able to generate predetermined molecular arrangements. The high directionality of strong (O—H···O) and weak (C—H···O) hydrogen bonds makes them useful in crystal design for the preparation of molecular materials with controlled physical properties (Etter, 1991; Desiraju, 1991; Desiraju & Steiner, 1999). The interactions of strong and weak hydrogen bonds play vital roles in molecular recognition in a wide variety of biological systems (Chao & Chen, 1996; Reddy *et al.*, 1993), as well as influencing crystal packing in crystallography, and some important results have been reviewed by Chen & Suslick (1993) and Hanck *et al.* (1988). The lengths, angles, directional properties of C—H···O bonds have been described by Pedireddi & Desiraju (1992) and Steiner & Desiraju (1998). Although it has long been known that

perchlorate anions can form hydrogen bonds in crystals, the tetradentate perchlorate-bridged three-dimensional structure has not been reported. We describe herein the title compound, (I), which forms a unique three-dimensional network by means of strong and weak hydrogen bonds with tetradentate perchlorate in bridging mode.


(I)
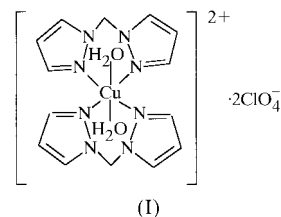
The X-ray structure analysis of (I) shows that the Cu^{II} atom is six-coordinated by four N atoms, originating from two chelated bis(pyrazol-1-yl)methane rings interacting at 60.26°, and by two O atoms from water molecules (Fig. 1). The axial Cu—O bond distance of 2.459 (3) Å is significantly longer than the Cu—N bond lengths of 1.998 (2) and 2.032 (3) Å in the equatorial plane, due to the pronounced Jahn–Teller effect. The bis(pyrazol-1-yl)methane ligands are in six-membered boat configurations in the complex, as observed in the analogous Ni^{II} complex (Langenberg *et al.*, 1997).
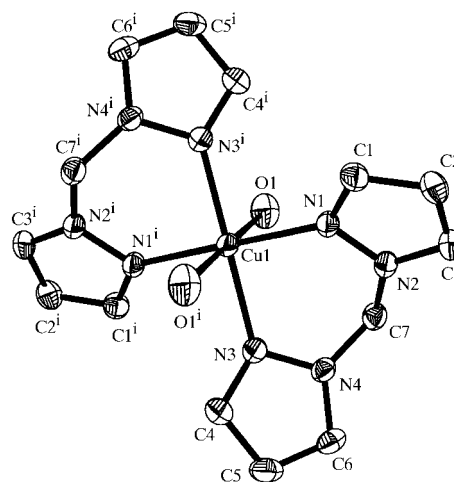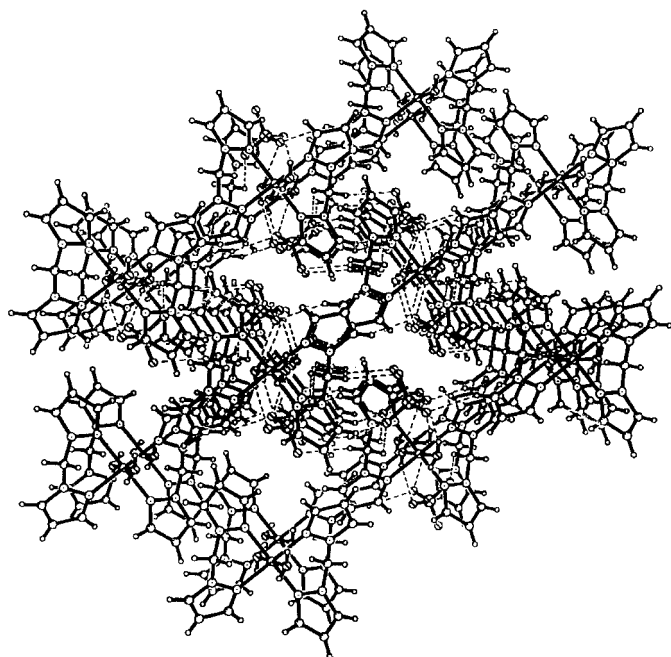

Figure 1
An *ORTEP* (Johnson, 1965) drawing of the cation of (I) with 30% probability displacement ellipsoids. H atoms have been omitted for clarity (symmetry code as in Table 1).

The most striking feature of complex (I) is seen in its ability to form three types of hydrogen bonds (Fig. 2). The H atoms of the ligand in the $[Cu(C_7H_8N_4)_2(H_2O)_2]^{2+}$ cation unit have been activated by the positive charge due to the coordination of N atoms to the Cu^{II} cation. Each perchlorate anion forms acceptors of hydrogen bonds with three adjacent $[Cu(C_7H_8N_4)_2(H_2O)_2]^{2+}$ cations, giving a three-dimensional network (Fig. 3). The lengths of the hydrogen bonds are variable due to differences in C—H and/or O—H acidity. The C···O separations occur in the range 3.0–3.5 Å, well within the range of 3.0–4.0 Å reported for C···O separations (Desiraju, 1991). The smallest bond angle is 114 (3)°. The O···O distances of 2.847 (7) and 2.923 (7) Å are shorter than the C···O distances.
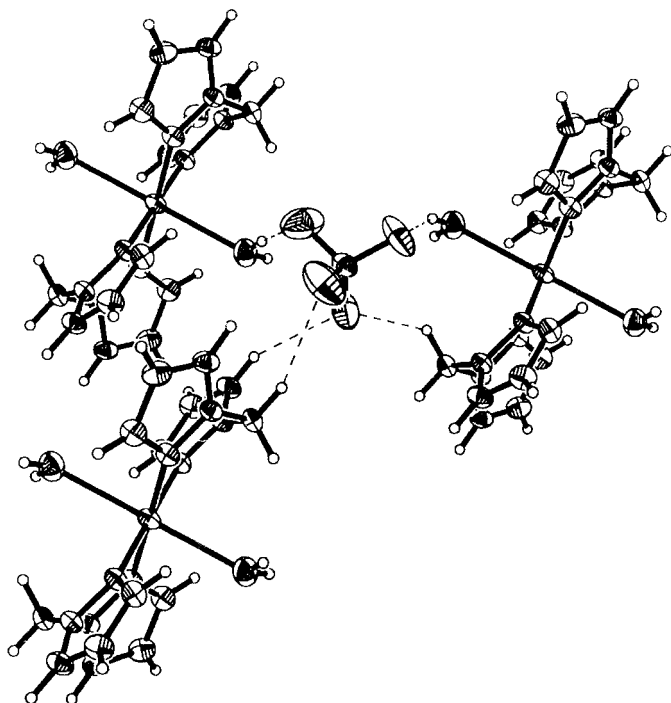
Figure 2
A view of the hydrogen bonding in (I) involving the perchlorate anion.

The C—H···O contacts primarily indicate electrostatic rather than van der Waals character and govern the crystal packing. Transmission of magnetic interactions through hydrogen bonds was first observed in transition metal complexes (Figgis *et al.*, 1993), but hydrogen-bonded organic ferromagnets have now become the focus of interest (Zhang &

Figure 3
A packing diagram showing the three-dimensional network in (I).

Baumgarten, 1997). The work described here is a unique case of perchlorate forming a component of a supramolecular network.

Experimental

The bis(pyrazol-1-yl)methane ligand was prepared according to the method described by Tang *et al.* (1998). An aqueous solution (5 ml) of $[Cu(ClO_4)_2]\cdot6H_2O$ (180.6 mg, 0.5 mmol) was added dropwise to a stirred methanol solution (5 ml) of bis(pyrazol-1-yl)methane (241 mg, 1.0 mmol). The clear dark-blue solution was left in the refrigerator for two weeks. Dark-blue single crystals of (I) were then obtained by slow evaporation. The crystals were filtered off, washed with water and methanol and dried *in vacuo* (yield 74%). Analysis calculated for $C_{14}H_{20}Cl_2CuN_8O_{10}$: C 28.27, H 3.39, N 18.84%; found: C 28.63, H 3.79, N 18.42%. FT–IR data (KBr pellet, cm^{-1}): 2968 (*w*), 1519 (*vs*), 1458 (*s*), 1394 (*m*), 1338 (*s*), 1282 (*s*), 1094 (*s*).

Crystal data

$[Cu(C_7H_8N_4)_2(H_2O)_2](ClO_4)_2$	$Z = 1$
$M_r = 594.82$	$D_x = 1.726$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.221$ (1) Å	Cell parameters from 2357
$b = 9.223$ (1) Å	reflections
$c = 9.483$ (1) Å	$\theta = 2.46$–$25.02°$
$\alpha = 109.144$ (2)°	$\mu = 1.257$ mm^{-1}
$\beta = 101.536$ (2)°	$T = 298$ (2) K
$\gamma = 114.010$ (2)°	Block, dark blue
$V = 572.25$ (12) Å^3	$0.20 \times 0.15 \times 0.10$ mm

Data collection

Bruker SMART 1000 diffractometer	$R_{int} = 0.014$
	$\theta_{max} = 25.02°$
ω scans	$h = -8 \rightarrow 9$
Absorption correction: by integration (North *et al.*, 1968)	$k = -10 \rightarrow 10$
	$l = -11 \rightarrow 11$
$T_{min} = 0.787$, $T_{max} = 0.885$	4 standard reflections
2407 measured reflections	every 400 reflections
2012 independent reflections	intensity decay: none
1771 reflections with $I > 2\sigma(I)$	

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.998 (2)	Cu1—N3	2.032 (3)
N1—Cu1—N1^i	180.00 (10)	N1—Cu1—N3^i	90.69 (11)
N1—Cu1—N3	89.31 (11)		

Symmetry code: (i) $-x, -y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O3^{ii}	0.90 (6)	2.08 (7)	2.923 (7)	155 (7)
O1—H2O···O5^{iii}	0.89 (4)	1.98 (4)	2.847 (7)	165 (6)
C3—H3···O2	0.94 (5)	2.40 (4)	3.278 (6)	157 (5)
C6—H6···O5^{iv}	0.92 (5)	2.52 (5)	3.208 (7)	132 (4)
C7—H7A···O4	0.98 (4)	2.48 (5)	3.434 (8)	163 (4)
C7—H7B···O1	0.99 (4)	2.52 (4)	3.325 (6)	138 (3)
C7—H7B···O2^{ii}	0.99 (4)	2.47 (4)	3.015 (6)	114 (3)

Symmetry codes: (ii) $1 - x, -y, 1 - z$; (iii) $x - 1, y, z$; (iv) $2 - x, 1 - y, 1 - z$.

metal-organic compounds

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0850P)^2$
$R(F) = 0.042$	$+ 0.3155P]$
$wR(F^2) = 0.124$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.019$	$(\Delta/\sigma)_{max} = 0.036$
2012 reflections	$\Delta\rho_{max} = 0.55$ e Å^{-3}
200 parameters	$\Delta\rho_{min} = -0.46$ e Å^{-3}
H atoms: see below	

All H atoms were located geometrically and refined in calculated positions.

Data collection: *SMART* 1000 *Operation Manual* (Bruker, 1998); cell refinement: *SMART* 1000 *Operation Manual*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1144). Services for accessing these data are described at the back of the journal.

References

Bruker (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1998). *SMART* 1000 *Operation Manual* and *SAINT* (Version 5.00). Bruker AXS Inc., Madison, Wisconsin, USA.

Burrows, A. D., Chan, C. M., Chowdhry, M. M., McGrady, J. E. & Mingos, D. M. P. (1995). *Chem. Soc. Rev.* **24**, 329–339.

Chao, I. & Chen, J.-C. (1996). *Angew. Chem.* **108**, 200–204.

Chen, C. T. & Suslick, K. S. (1993). *Coord. Chem. Rev.* **128**, 293–316.

Desiraju, G. R. (1991). *Acc. Chem. Res.* **24**, 290–295.

Desiraju, G. R. & Steiner, T. (1999). In *The Weak Hydrogen Bond in Structural Chemistry and Biology*. Oxford University Press.

Etter, M. C. (1991). *J. Phys. Chem.* **95**, 4601–4610.

Figgis, B. N., Kucharski, E. S. & Vrtis, M. (1993). *J. Am. Chem. Soc.* **115**, 176–181.

Hanck, M., Deger, S. & Lange, A. (1988). *Coord. Chem. Rev.* **83**, 115–136.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Langenberg, K. V., Batten, S. R., Berry, K. J., Hockless, D. C. R., Moubaraki, B. & Murray, K. S. (1997). *Inorg. Chem.* **36**, 5006–5015.

Lehn, J. M. (1990). *Angew. Chem. Int. Ed. Engl.* **29**, 1304–1308.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Pedireddi, V. R. & Desiraju, G. R. (1992). *J. Chem. Soc. Chem. Commun.* pp. 988–990.

Reddy, D. S., Goud, B. S., Panneerselvam, K. & Desiraju, G. R. (1993). *J. Chem. Soc. Chem. Commun.* pp. 663–664.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Steiner, T. & Desiraju, G. R. (1998). *J. Chem. Soc. Chem. Commun.* pp. 891–892.

Tang, L. F., Wang, Z. H., Xu, Y. M., Wang, J. T., Wang, H. G. & Yao, X. K. (1998). *Polyhedron*, **7**, 3765–3769.

Zhang, J. & Baumgarten, M. (1997). *Chem. Phys.* **222**, 1–8.