Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Aquabis(2,2′-biimidazole)copper(II) dinitrate

Ruili Sang and Li Xu*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou, Fujian 350002, People's Republic of China

Correspondence e-mail: xli@fjirsm.ac.cn

Received 24 January 2005
Accepted 16 March 2005
Online 31 March 2005

The crystal structure of the title compound, $[Cu(C_6H_6N_4)_2(H_2O)](NO_3)_2$, has been determined from single-crystal X-ray diffraction data. The five-coordinate geometry of the copper(II) centre comprises four N atoms from two biimidazole ligands and a water molecule in a distorted square-based pyramidal coordination. Cu and the aqua ligand lie on a twofold rotation axis.

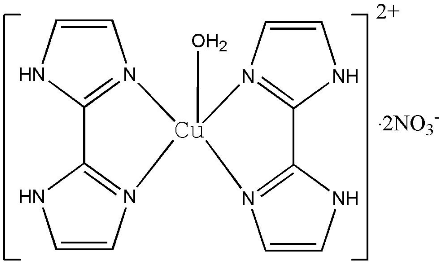
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.039
wR factor = 0.136
Data-to-parameter ratio = 11.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Biimidazole is of great interest as a biomimetic ligand since the imidazole ring of histidine has been frequently found in a variety of proteins and metalloenzymes (Freeman, 1975). 2,2′-Biimidazole (H_2biim) can be coordinated to transition metals in non-deprotonated (H_2biim), mono-deprotonated (Hbiim$^-$) and di-deprotonated (biim^{2-}) forms. The monoanion Hbiim$^-$ is able to form complementary intermolecular hydrogen bonds (Tadokoro *et al.*, 1999; Tadokoro & Nakasuji, 2000). Coordinated H_2biim usually forms hydrogen bonds with counteranions and solvent molecules (Ye *et al.*, 1999; Cancela *et al.*, 2001; Dance *et al.*, 1980). Hydrogen bonds of this type have been postulated to play a role in the activation of coordinated aqua ligands (Ye *et al.*, 1999).



(I)

The synthesis and crystal structure of a copper(II) compound with neutral H_2biim, $[Cu(H_2biim)_2(H_2O)](NO_3)_2$, (I), is reported in this paper. To the best of our knowledge, only two examples of aqua-coordinated H_2biim-containing copper compounds have been reported (Carranza *et al.*, 2003; Haj *et al.*, 2002). The metal-bound water molecule is important in the functional unit at the active site of proteins and metalloenzymes (Freeman, 1975).

The structure of (I) consists of the cation $[Cu(H_2biim)_2(H_2O)]^{2+}$ and nitrate ions interconnected by hydrogen bonds. The structure is shown in Fig. 1. Selected interatomic distances and angles are listed in Table 1.

An extensive hydrogen-bonded network links cations and anions into an infinite three-dimensional network (Table 2 and

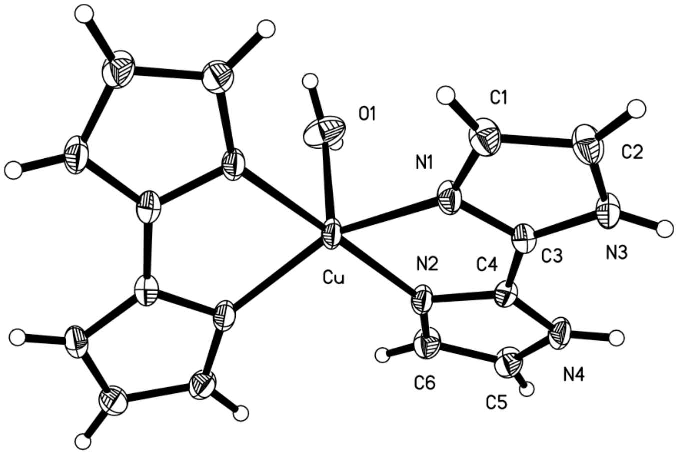


Figure 1
A view of the molecular structure of the title cation, with displacement ellipsoids drawn at the 30% probability level and H atoms shown as small spheres of arbitrary radii. Unlabelled atoms are related to labelled atoms by the symmetry operation $-x, y, \frac{1}{2} - z$.

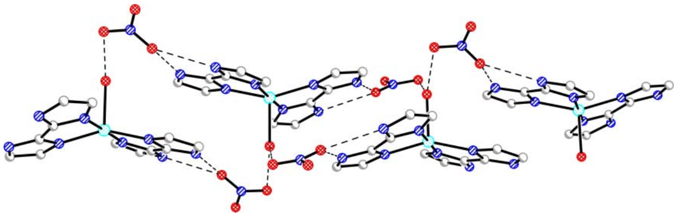


Figure 2
A view of the one-dimensional structure of (I), showing the hydrogen-bonding scheme (dashed lines).

Fig. 3). The packing of the molecules is driven by three kinds of hydrogen bonds: (i) hydrogen bonds between H_2biim and the nitrate, (ii) hydrogen bonds between the coordinated water molecule and H_2biim, and (iii) hydrogen bonds between the aqua ligand and the nitrate. In the crystal structure, the complex units are arranged in parallel layers. The layers are alternately connected through weak H_2biim$\cdots$nitrate [N4$\cdots$O4 = 3.089 (5) Å] hydrogen bonds. Within the layers, the nitrate, H_2biim and coordinated water form hydrogen bonds (Fig. 2).

The Cu atom has a distorted square-pyramidal coordination geometry (τ = 0.45; Addison *et al.*, 1984) formed by four N atoms of two symmetry-related 2,2′-biimidazole molecules [Cu1—N1 = 2.034 (3) Å and Cu1—N2 = 2.004 (3) Å] and a water ligand [Cu—O1 = 2.208 (4) Å]. The two chelating 2,2′-biimidazole ligands occupy the basal sites and the aqua molecule takes up the apical position. The apical Cu1—O1 bond is the longest of the copper-ligand bonds at 2.208 (4) Å, while the average Cu1—N bond length is 2.019 (3) Å. The mean copper–imidazole nitrogen distance is in accordance with those in $[Cu(H_2biim)_2]^{2+}$ [2.01 (1) Å; Dencini & Mani, 1988] and $[Cu(Me_4biim)ONO_2]^+$ [2.009 (5) Å; Bernarducci *et al.*, 1983]. The value of the inter-ring C3—C4 bond distance of H_2biim in (I) [1.442 (5) Å] is close to that found for free bi-imidazole (1.423 Å; Cromer *et al.*, 1987) and coordinated bi-imidazole {1.441 (3) Å in $[Cu(H_2biim)_2]^{2+}$ (Dencini & Mani, 1988) and $[VOCl(H_2biim)_2]Cl$ (Cancela *et al.*, 2001)}. The short single C—C bond that connects the two imidazole rings, together with their near coplanarity, reveal the importance of resonance in the bonding description of this molecule.

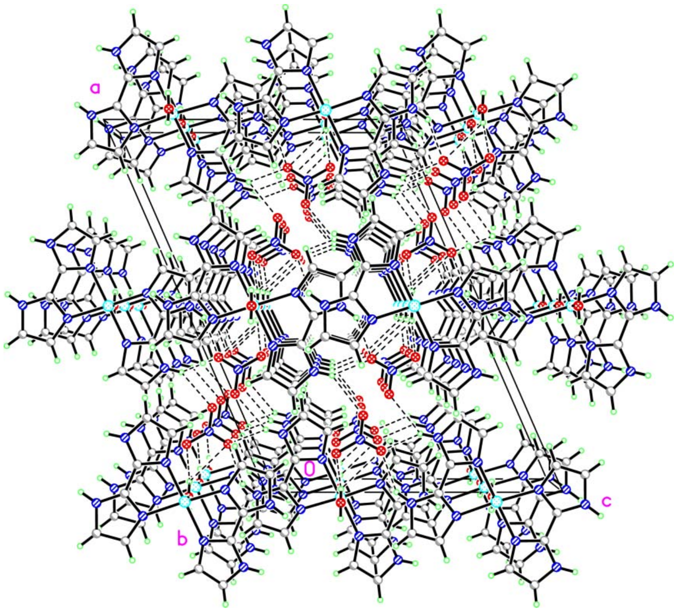


Figure 3
Packing diagram of the title compound, viewed along the *b* axis. Dashed lines represent hydrogen bonds.

Angles in the coordination sphere [82.09 (11)–104.40 (9)°] deviate appreciably from the ideal values, the maximum deviation being N1—Cu—O1 [104.40 (9)°]. The bite angle subtended at the Cu atom by the H_2biim ligands is 82.09 (11)°. The atoms defining the basal plane of copper have a significant tetrahedral distortion [the torsion angle is 17.8 (1)°] and the metal is displaced by 0.266 (2) Å. The mean N—Cu1—O1 angle [97.63 (9)°] is larger than the average N—Cu1—N angles [89.78 (11)°]. Both imidazole rings are planar, with no atoms deviating by more than 0.005 Å from the least-squares plane. The two rings of H_2biim are nearly coplanar, making an angle of 7.63 (13)°. This value is larger than that reported for the mononuclear copper(II) species $[Cu(H_2biim)_2]^{2+}$are in a strictly planar environment (Dencini & Mani, 1988), and that observed in the free H_2biim molecule (1.2°; Cromer *et al.*, 1987), but it compares well with that found for the mononuclear oxovanadium(IV) species $[VOCl(H_2biim)_2]Cl$ [9.90 (9) and 9.2 (1)°; Cancela *et al.*, 2001].

Experimental

H_2biim was synthesized in accordance with a published procedure (Thummel *et al.*, 1989). A suspension of H_2biim (0.268 g, 2 mmol) in water (30 ml) was added slowly to $Cu(NO_3)_2.6H_2O$ (0.242 g, 1 mmol) dissolved in water (20 ml) with stirring. The mixture was stirred at 353 K for 30 min. The resulting solution was filtered. The filtrate was left in air to evaporate and the crystals were obtained after a few days. Green crystals were collected by filtration, washed with water and dried under vacuum. Analysis found (%): C 30.37, H 3.03, N 29.50; calculated for $C_{12}H_{14}CuN_{10}O_7$: C 30.41, H 2.98, N 29.56.

Crystal data

$[Cu(C_6H_6N_4)_2(H_2O)](NO_3)_2$
$M_r = 473.88$
Monoclinic, $C2/c$
$a = 19.6113$ (19) Å
$b = 6.8168$ (7) Å
$c = 14.2923$ (14) Å
$\beta = 113.551$ (2)°
$V = 1751.5$ (3) Å^3
$Z = 4$

$D_x = 1.797$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2339 reflections
$\theta = 2.3$–25.0°
$\mu = 1.31$ mm^{-1}
$T = 293$ (2) K
Block, green
0.40 × 0.32 × 0.10 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.747$, $T_{\max} = 1.000$
2908 measured reflections

1525 independent reflections
1387 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\max} = 25.0°$
$h = -23 \rightarrow 12$
$k = -6 \rightarrow 8$
$l = -16 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.136$
$S = 1.01$
1525 reflections
138 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0934P)^2 + 5.5585P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.63$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—N2	2.004 (3)	Cu—O1	2.208 (4)
Cu—N1	2.034 (3)	C3—C4	1.442 (5)
N2^{i}—Cu—N1	97.47 (11)	N2—Cu—O1	90.86 (8)
N2—Cu—N1	82.09 (11)	N1—Cu—O1	104.40 (9)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O3^{ii}	0.86	2.03	2.790 (4)	147
N3—H3···O1^{iii}	0.86	2.64	3.237 (3)	128
N4—H4···O3^{ii}	0.86	2.07	2.821 (5)	146
N4—H4···O4	0.86	2.52	3.089 (5)	125
O1—H1A···O2^{iv}	0.82	1.96	2.769 (4)	171
O1—H1A···O3^{iv}	0.82	2.54	3.126 (4)	130
O1—H1A···N5^{iv}	0.82	2.61	3.379 (4)	157

Symmetry codes: (ii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (iii) $-x, 1 - y, -z$; (iv) $x - \frac{1}{2}, \frac{1}{2} + y, z$.

H atoms attached to C, N and O atoms were placed in calculated positions (C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.82 Å), with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$ of their respective parent atoms.

Data collection: *SMART* (Siemens, 1994); cell refinement: *SAINT*(Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL*.

This work was supported by the National Natural Science Foundation of China and 'One Hundred Talent Program' of the Chinese Academy of Science.

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

Bernarducci, E. B., Bharadwaj, P. K., Lalancette, R. A., Krogh-Jespersen, K., Potenza, J. A. & Schugar, H. J. (1983). *Inorg. Chem.* **22**, 3911–3920.

Cancela, J., Gonalez Garmendia, M. J. & Qurs, M. (2001). *Inorg. Chim. Acta*, **313**, 156–159.

Carranza, J., Brennan, C., Sletten, J., Vangdal, B., Rillerna, P. & Julve, M. (2003). *New J. Chem.* **27**, 1775–1783.

Cromer, D. T., Ryan, R. R. & Storm, C. B. (1987). *Acta Cryst.* C**43**, 1435–1437.

Dance, I. G., Abushamleh, A. S. & Goodwin, H. A. (1980). *Inorg. Chim. Acta*, **43**, 217–221.

Dencini, A. & Mani, F. (1988). *Inorg. Chim. Acta*, **154**, 215–219.

Freeman, H. C. (1975). *Inorganic Biochemistry*, edited by G. L. Eichorn. Amsterdam: Elsevier.

Haj, M. A., Quiros, M., Salas, J. M., Dobado, J. A., Molina, J. M., Basallote, M. G. & Manez, M. A. (2002). *Eur. J. Inorg. Chem.* pp. 811–818.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (1999). *SHELXTL/PC*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1994). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Tadokoro, M., Isobe, K., Uekysa, H., Ohashi, Y., Toyoda, J., Tashiro, K. & Nakasuji, K. (1999). *Angew. Chem. Int. Ed.* **38**, 95–98.

Tadokoro, M. & Nakasuji, K. (2000). *Coord. Chem. Rev.* **198**, 205–218.

Thummel, R. P., Goulle, V. & Chen, B. (1989). *J. Org. Chem.* **54**, 3057–3061.

Ye, B. H., Xue, F., Xue, G. Q., Ji, L. N. & Mak, T. C. W. (1999). *Polyhedron*, **18**, 1785–1790.