

Diaquabis(nitrato- κ O)bis(4,7-dihydro-1,2,4-triazolo[1,5-a]pyrimidin-7-one- κ N³)copper(II)

Mohammad Abul-Haj,^a Miguel Quirós^{b*} and Juan M. Salas^b

^aDepartment of Chemistry and Chemical Technology, Faculty of Science and Technology, Al-Quds University, PO Box 20002, Abu Dis, Jerusalem, Palestinian Authority, and

^bDepartamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

Correspondence e-mail: mquiros@ugr.es

Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

R factor = 0.057

wR factor = 0.166

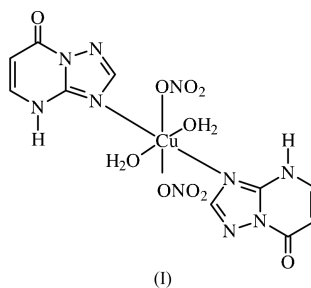
Data-to-parameter ratio = 20.8

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

The molecule of the title compound, $[\text{Cu}(\text{7HtpO})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$, contains two neutral 4,7-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidin-7-one (7HtpO) ligands, coordinated through the N atom in position 3, two nitrate ions each coordinated through one of the O atoms, and two water molecules, completing the octahedral environment around the copper atom which lies on an inversion centre, thus defining the all-*trans* isomer. The intramolecular N—H \cdots O hydrogen bond involving the nitrate oxygen atom linked to the metal atom stabilizes the structure. Distances in the coordination sphere are Cu—N(7HtpO) = 2.003 (2), Cu—O(nitrate) = 2.410 (2) and Cu—O(water) = 1.977 (2) Å.

Comment

The coordination chemistry of 1,2,4-triazolo[1,5-*a*]pyrimidine derivatives displays great versatility, binding metal ions in several different ways (Salas *et al.*, 1999), either in a monodentate (usually through the N atom in position 3) or in a bidentate fashion, bridging metal atoms and leading to dinuclear (Navarro *et al.*, 1996) or polynuclear (Navarro *et al.*, 1997) species with interesting metal–metal interactions. Regarding copper(II), examples have been described of mononuclear complexes (Dirks *et al.*, 1987) as well as di- or polynuclear, either bridged by the auxiliary ligands (Biagini-Cingi *et al.*, 1983; Grodzicki *et al.*, 1999) or by the triazolo-pyrimidine derivative, as is the case in the 5-oxo isomer of the ligand present in the title compound, (I) (Abul Haj *et al.*, 2002).



Following this line of research, we have studied the interaction of Cu(II) with the 4,7-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidin-7-one (7HtpO) ligand in acidic medium, yielding a simple mononuclear compound with formula $[\text{Cu}(\text{7HtpO})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$, the structure of which is described here. The measured magnetic moment of the compound is 1.94 BM. The crystal structure comprises discrete molecules, in which the metal ion is located in a tetragonally distorted octahedral

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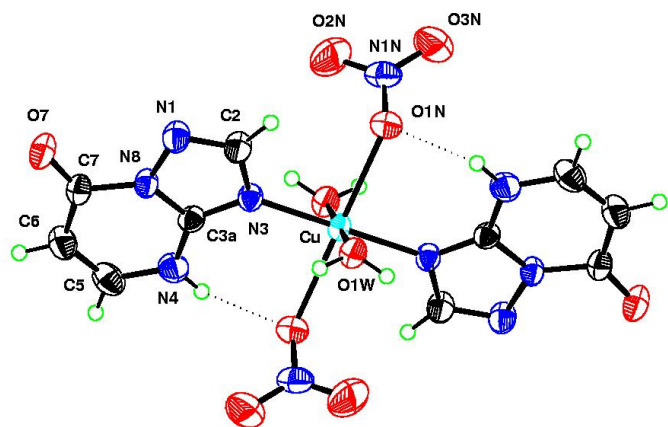


Figure 1
View of the title compound, with the non-H atoms drawn as 50% probability ellipsoids.

environment, defined by two 7HtpO ligands, coordinated through the nitrogen atom in position 3, two water molecules, and two O atoms from the nitrate anions at a longer distance in a normal Jahn–Teller distortion. The copper atom lies on a crystallographic inversion centre; therefore the disposition of the ligands is all-*trans*. A view of the molecular structure is shown in Fig. 1, which also gives the labelling scheme. Distances and angles in the coordination sphere are listed in Table 1.

The Cu–N3 bond distance is within the range found for copper complexes with the related 7-hydroxy-5-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine (HmtpO) ligand (Navarro *et al.*, 1998), either in molecular or anionic form. Coordination does not appreciably affect the geometry of 7HtpO, the differences in bond distances and angles compared with the free ligand (Abul Haj *et al.*, 2000) being less than 0.02 Å and 1°, respectively. The ligand is in its neutral form, the hydrogen in position 4 remaining in place, which is confirmed by the formation of an intramolecular hydrogen bond with the oxygen of the nitrate anion bound to the copper atom [N4...O1N(1 - *x*, 1 - *y*, 1 - *z*), 2.769 (4) Å], thereby closing a six-membered pseudo-chelate ring. The orientation of the plane of the organic ligand [C3A–N3–Cu–O1N(1 - *x*, 1 - *y*, 1 - *z*) –18.3 (3)°] and the N1N–O1N–Cu bond angle are such as to optimize this interaction. The water molecule is likewise involved in hydrogen bonding with neighbouring units [O1W...O7(*x*, ½ - *y*, *z* + ½) 2.727 (3) and O1W...O3N(*x* + ½, ½ - *y*, 1 - *z*) 2.797 (4) Å].

Experimental

The 7HtpO ligand was prepared according to the published method (Abul Haj *et al.*, 2000) from 3-amino-1,2,4-triazole and malic acid in a strong acidic medium. The copper complex was prepared by mixing 1 mmol (240 mg) of Cu(NO₃)₂·3H₂O dissolved in 1 M nitric acid and 2 mmol (290 mg) of 7 HtpO dissolved in 1 M nitric acid, giving a blue solution. This was filtered and left to evaporate at room temperature. Blue crystals of the compound were obtained after 24 h and were collected by filtration and air-dried.

Crystal data

[Cu(NO₃)₂(C₅H₄N₄O)₂(H₂O)₂]
 $M_r = 495.84$
 Orthorhombic, *Pbca*
 $a = 14.4717$ (5) Å
 $b = 6.4247$ (2) Å
 $c = 18.4846$ (6) Å
 $V = 1718.63$ (10) Å³
 $Z = 4$
 $D_x = 1.916$ Mg m⁻³

Mo *K*α radiation
 Cell parameters from 40 reflections
 $\theta = 12.7$ –17.6°
 $\mu = 1.36$ mm⁻¹
 $T = 293$ (2) K
 Brick, blue
 0.55 × 0.38 × 0.25 mm

Data collection

Stoe Stadi4 four-circle diffractometer
 ω scans
 Absorption correction: ψ scan (*X-RED*; Stoe, 1996)
 $T_{\min} = 0.569$, $T_{\max} = 0.704$
 3096 measured reflections
 3096 independent reflections

2141 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 32.5^\circ$
 $h = 0 \rightarrow 21$
 $k = 0 \rightarrow 9$
 $l = 0 \rightarrow 27$
 3 standard reflections
 frequency: 60 min
 intensity decay: 4%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.166$
 $S = 1.08$
 3096 reflections
 149 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.065P)^2 + 3.5P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.94$ e Å⁻³
 $\Delta\rho_{\min} = -0.65$ e Å⁻³
 Extinction correction: *SHELXL*
 Extinction coefficient: 0.0078 (11)

Table 1

Selected geometric parameters (Å, °).

Cu–O1W	1.977 (2)	Cu–O1N	2.410 (2)
Cu–N3	2.003 (2)		
O1W–Cu–N3	87.75 (9)	N3–Cu–O1N	91.59 (9)
O1W–Cu–O1N	85.44 (9)	N1N–O1N–Cu	122.3 (2)

H atoms of the organic moiety were idealized (C–H 0.93 Å). Those of the water molecule were located in a difference Fourier map and refined with a restrained O–H distance (0.86 Å). Isotropic displacement parameters of all H atoms fixed at 1.2 times U_{eq} of the parent atom.

Data collection: *STADI4* (Stoe, 1996); cell refinement: *STADI4*; data reduction: *X-RED* (Stoe, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XtalGX* (Hall & du Boulay, 1997); software used to prepare material for publication: *SHELXL97*.

References

- Abul Haj, M., Quirós, M., Salas, J. M., Dobado, J., Molina, J., Basallote, M. G. & Máñez, M. A. (2002). *Eur. J. Inorg. Chem.* pp. 811–818.
 Abul Haj, M., Salas, J. M., Quirós, M., Molina, J. & Faure, R. (2000). *J. Mol. Struct.* **519**, 165–172.
 Biagini-Cingi, M., Manotti-Lanfredi, A. M., Tiripicchio, A., Haasnoot, J. G. & Reedijk, J. (1983). *Inorg. Chim. Acta*, **72**, 81–88.
 Dirks, E. J., Haasnoot, J. G., Kinneging, A. J. & Reedijk, J. (1987). *Inorg. Chem.* **26**, 1902–1906.
 Grodzicki, A., Szyk, E., Wojtczak, A., Wrzeszcz, G., Pazderski, L. & Muziol, T. (1999). *Polyhedron*, **18**, 519–527.
 Hall, S. R. & du Boulay, D. (1997). *XtalGX*. University of Western Australia, Australia.
 Navarro, J. A. R., Romero, M. A., Salas, J. M., Faure, R. & Solans, X. (1997). *J. Chem. Soc. Dalton Trans.* pp. 2321–2326.

Navarro, J. A. R., Romero, M. A., Salas, J. M., Molina, J. & Tiekink, E. R. T. (1998). *Inorg. Chim. Acta*, **274**, 53–63.

Navarro, J. A. R., Romero, M. A., Salas, J. M., Quirós, M., El Bahraoui, J. & Molina, J. (1996). *Inorg. Chem.* **35**, 7829–7835.

Salas, J. M., Romero, M. A., Sánchez, M. P. & Quirós, M. (1999). *Coord. Chem. Rev.* **193**, 1119–1142.

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

Stoe & Cie (1996). *X-RED* and *STADI4*. Stoe & Cie, Darmstadt, Germany.