

Transition metal complexes with thiosemicarbazide-based ligands. XLIV.¹ Aqua(3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carboxaldehyde 3-methylisothiosemicarbazone- $\kappa^3 O, N^1, N^4$)nitratocopper(II) nitrate

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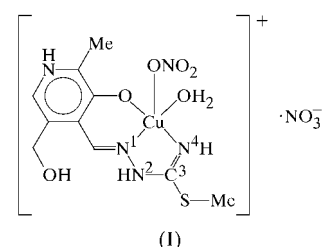
The title complex, $[\text{Cu}(\text{NO}_3)(\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_2\text{S})(\text{H}_2\text{O})](\text{NO}_3)$, is the first metal complex with a Schiff base derived from isothiosemicarbazide and pyridoxal (pyridoxal is 3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carboxaldehyde). The Cu^{II} environment is a square pyramid, the equatorial plane of which is formed by the tridentate *ONN*-coordinated isothiosemicarbazone and one water molecule, while the nitrate ligand is in the apical position. The existence of numerous strong intermolecular hydrogen bonds, and weak $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\pi$ interactions, leads to a three-dimensional supramolecular structure.

Comment

Transition metal complexes with ligands based on thiosemicarbazides (TSC) have been studied for many years because of their interesting structural properties and biological activity (West *et al.*, 1991; Casas *et al.*, 2000). The Cu^{II} metal centre is especially interesting as an essential ion, since its complexes with TSC-based ligands exhibit a wide range of biological effects, such as antiviral, antitumour and anti-inflammatory activity (West *et al.*, 1993). Isothiosemicarbazones (ITSC) can also act as biologically active agents with antibacterial activity (Cardia *et al.*, 2000).

A number of metal complexes with pyridoxal thiosemicarbazone (PxTSC) have been synthesized and structurally characterized to date, namely $[\text{Mn}^{\text{II}}\text{Cl}(\text{PxTSC})(\text{H}_2\text{O})]\text{Cl}$ and $[\text{Cu}^{\text{II}}(\text{PxTSC})(\text{H}_2\text{O})]\text{Cl}\cdot\text{H}_2\text{O}$ (Ferrari *et al.*, 1987), $[\text{Zn}^{\text{II}}\text{Cl}(\text{PxTSC})]\cdot\text{H}_2\text{O}$ (Ferrari *et al.*, 1992), $[\text{Cu}^{\text{II}}\text{Cl}(\text{PxTSC})(\text{H}_2\text{O})]\text{Cl}$

(Ferrari *et al.*, 1994), $[\text{Co}^{\text{III}}(\text{PxTSC})_2]\text{Cl}\cdot\text{EtOH}$ (Ferrari *et al.*, 1995), $[\text{Cu}^{\text{II}}(\text{PxTSC})(\text{H}_2\text{O})_2]\text{SO}_4\cdot\text{H}_2\text{O}$ (Ferrari *et al.*, 1998) and $[\text{Au}^{\text{III}}\text{Cl}(\text{PxTSC})]\text{Cl}_2\cdot\text{MeOH}$ (Abram *et al.*, 2000). PxTSC ligands are usually coordinated as *ONS*-tridentate ligands, the only exception being for the Au^{III} complex, where PxTSC is coordinated as an *NS*-bidentate ligand through the N/S atoms of the thiosemicarbazide fragment. The title complex, $[\text{Cu}^{\text{II}}(\text{NO}_3)(\text{H}_2\text{L})(\text{H}_2\text{O})](\text{NO}_3)$ (H_2L is pyridoxal 3-methylisothiosemicarbazone), (I), represents the first example of a transition metal complex with a pyridoxal isothiosemicarbazone (PxITSC) ligand to be synthesized and characterized by X-ray analysis. The H_2L ligand is coordinated to the Cu^{II} atom through three atoms (O1, N1 and N3), forming two fused chelate rings (Fig. 1), one being five-membered (ITSC) and one six-membered (Px).



The coordination around the Cu^{II} atom in (I) is square-pyramidal, as in all Cu^{II} complexes with PxTSC. The apical $\text{Cu}-\text{O}$ bond is significantly longer than the other bonds in the coordination sphere, as was also observed in the other complexes. The different mode of coordination in complexes involving PxTSC (*ONS*) compared with (I) (*ONN*) leads to a difference in bond lengths in the TSC fragment, associated with a different π -electron delocalization in the $\text{N}^2-\text{C}^3-\text{N}^4$ fragment (the superscript numbering is shown in the *Scheme* and is in accordance with IUPAC rules).

The N^2-C^3 and C^3-N^4 distances in complexes involving the TSC moiety are approximately equal (Bogdanović *et al.*, 2001), whereas in complexes with ITSC-based ligands, and also in (I), the C^3-N^4 bond is significantly shorter (by about 0.08 Å) than the N^2-C^3 bond. As a consequence of the alkylation of the S atom, the C^3-S bond is longer in (I) than in complexes involving PxTSC, whereas all bonds in the Px part of the ligand are of similar length in all complexes.

In the crystal structures reported to date, PxTSC has been coordinated as a neutral molecule in its complexes with Mn^{II} , Cu^{II} and Au^{III} , whereas in the above-mentioned complexes of Sn^{II} and Co^{III} , and in $[\text{Cu}^{\text{III}}(\text{PxTSC})_2]\text{Cl}\cdot\text{H}_2\text{O}$, it is coordinated as the monoanion. In (I), the ligand is coordinated as a neutral molecule and, as with PxTSC, the pyridoxal moiety of the ITSC ligand is in the zwitterionic form, resulting from migration of the phenolic OH H atom to the pyridine N atom. Further, the ITSC moiety, as in isothiosemicarbazides and other isothiosemicarbazones (Bogdanović *et al.*, 2001; Novaković *et al.*, 2002), exists in the imido form.

The chelate rings in (I), with an interplanar angle of 3.2 (1)°, are almost coplanar and, together with the water molecule, form the equatorial coordination plane. All non-H atoms of

¹ Part XLIII: Novaković *et al.* (2002).

the equatorial PxITSC ligand are approximately coplanar, except for the O atoms of the $-\text{CH}_2-\text{OH}$ group, which is almost orthogonally directed out of the coordination plane. The Cu^{II} atom is displaced from this plane towards the apically coordinated NO_3 group by 0.202 (1) Å; the donor atom O8 is displaced from the plane by 2.586 (3) Å. The interplanar angle between the coordinated nitrate and the equatorial plane is 78.6 (1)°.

The complex cation has five hydrogen-bond donor groups (atoms N2, N3, N4, O1W and O2), whereas the two nitrate groups have six O atoms acting as hydrogen-bond acceptors. Consequently, numerous strong intermolecular $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, plus weak $\text{C}-\text{H}\cdots\text{O}$ bonds (Table 2) and intermolecular $\text{C}-\text{H}\cdots\pi$ interactions (see below), give a three-dimensional supramolecular structure.

The crystal packing consists of tapes of molecules parallel to the y axis, which form layers parallel to both (103) and the coordination plane (Fig. 2). Within the tapes, residues are connected by direct $\text{O1W}-\text{H}\cdots\text{O2}$ hydrogen bonds and by hydrogen bonds involving uncoordinated NO_3 groups within the tapes. Although all the tapes are crystallographically equivalent, they are connected in two different ways. Tapes *A* and *B* are connected by hydrogen bonds (two per molecule) which involve coordinated N6O_3 groups (situated between neighbouring *A* and *B* tapes), and tapes *B* and *C* are connected by weak $\text{C2}-\text{H}\cdots\text{O5}$ hydrogen bonds.

The layers are interconnected in several ways: (i) via $\text{O2}-\text{H}\cdots\text{O3}$ hydrogen bonds, (ii) by direct $\text{Cu}-\text{O8}$ bonds from the N6O_3 groups to the Cu^{II} atoms of adjacent layers (the boundary of the reference layer is represented by dashed lines in Fig. 2), (iii) the coordinated nitrate is also hydrogen bonded to atoms N4, C10 and C8 of two tapes (*A* and *B*) in an adjacent layer, and (iv) by $\text{C}-\text{H}\cdots\pi$ interactions (Desiraju & Steiner, 1999; see below) with neighbouring layers, in such a way that

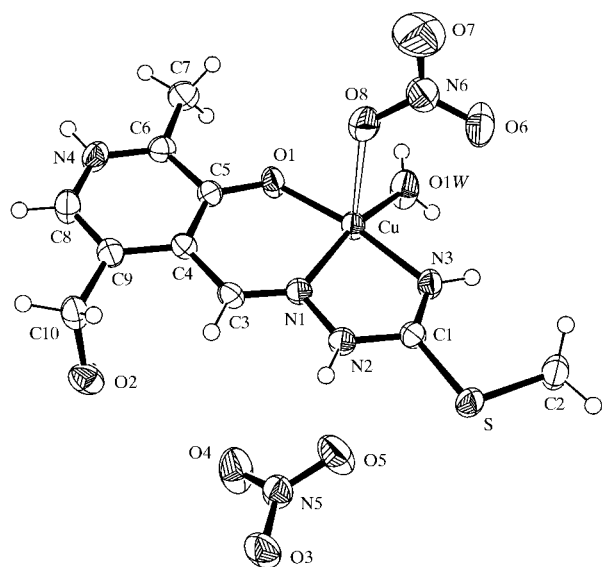


Figure 1

A view of the molecular structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

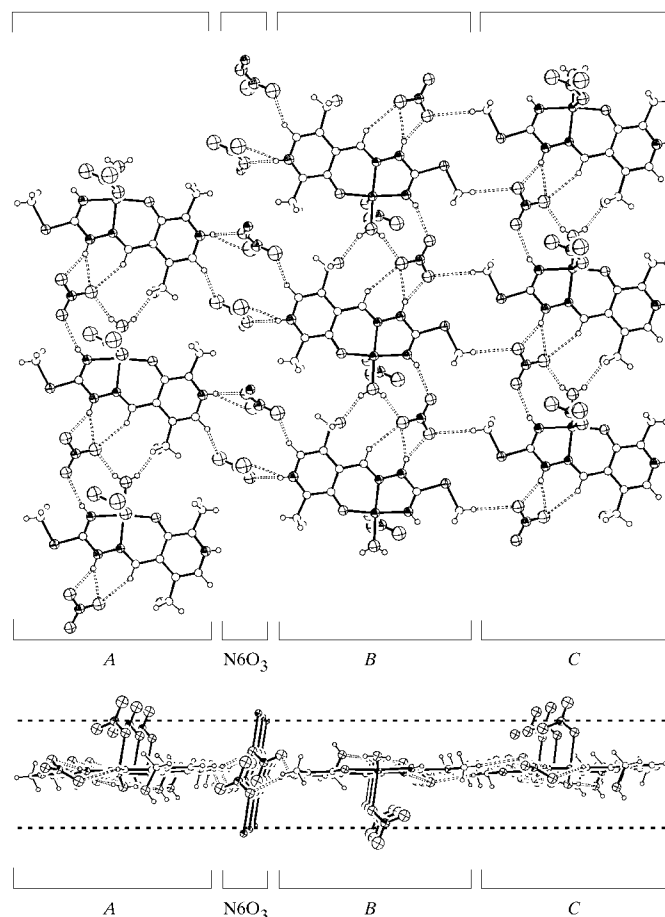


Figure 2

The packing diagram for (I) in two orthogonal projections, showing the intermolecular hydrogen bonds within and between the tapes (*A*, *B* and *C*), which form parallel layers. The longer components of three-centre hydrogen bonds are not shown.

each molecule is involved in two intermolecular $\text{C7}-\text{H}\cdots\pi$ interactions, as both donor and acceptor. In such a three-dimensional network of hydrogen bonds, each formula unit forms 18 intermolecular hydrogen bonds with its neighbours, with two additional hydrogen bonds between the complex cation and the NO_3 anion within the formula unit (Table 2). It may be concluded that the presence of two NO_3 groups in (I) is of crucial significance for the manifestation of the three-dimensional supramolecular crystal structure of this compound.

The intermolecular $\text{C}-\text{H}\cdots\pi$ interactions are such that the C7-methyl group lies above the pyridine ring of the neighbouring ligand at $(-x, 1-y, -z)$, so that one of the H atoms is directed towards the centre of the pyridine ring. Geometric parameters for these $\text{C}-\text{H}\cdots\pi$ interactions are as follows: (i) the distance between the H atom bonded to atom C7 and the centre (C_g) of the C4/C5/C6/N4/C8/C9 aromatic ring is 2.69 (3) Å, (ii) the γ angle between the line connecting the H atom and C_g and the normal to the C4/C5/C6/N4/C8/C9 plane is 3 (2)°, and (iii) the $\text{C7}-\text{H}\cdots\text{C}_g$ angle is 140 (2)°.

Experimental

The pyridoxal 3-methylisothiosemicarbazone ligand, H_2L , was prepared by the reaction of an ethanolic solution of 3-methylisothiosemicarbazide hydroiodide with pyridoxal hydrochloride, and subsequent neutralization with an aqueous solution of Na_2CO_3 . Green single crystals of (I) were obtained by the reaction of a hot ethanolic solution of the ligand with $Cu(NO_3)_2 \cdot 3H_2O$ (molar ratio 1:1).

Crystal data

$[Cu(NO_3)(C_{10}H_{14}N_4O_2S)(H_2O)](NO_3)$	$Z = 2$
$M_r = 459.89$	$D_x = 1.806 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.945 (3) \text{ \AA}$	Cell parameters from 23 reflections
$b = 9.262 (3) \text{ \AA}$	$\theta = 12.0\text{--}16.8^\circ$
$c = 11.701 (3) \text{ \AA}$	$\mu = 1.48 \text{ mm}^{-1}$
$\alpha = 85.13 (2)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 89.34 (3)^\circ$	Prismatic, green
$\gamma = 80.35 (3)^\circ$	$0.40 \times 0.26 \times 0.14 \text{ mm}$
$V = 845.8 (5) \text{ \AA}^3$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.017$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 26^\circ$
Absorption correction: Gaussian (PLATON; Spek, 1990, 1998)	$h = 0 \rightarrow 9$
$T_{\text{min}} = 0.675$, $T_{\text{max}} = 0.815$	$k = -11 \rightarrow 11$
3570 measured reflections	$l = -14 \rightarrow 14$
3316 independent reflections	2 standard reflections
2853 reflections with $I > 2\sigma(I)$	frequency: 60 min
	intensity decay: none

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu—O1	1.8849 (19)	N2—C1	1.365 (3)
Cu—N3	1.932 (2)	N3—C1	1.278 (3)
Cu—O1W	1.955 (2)	C1—S	1.751 (3)
Cu—N1	1.975 (2)	S—C2	1.786 (3)
Cu—O8	2.410 (2)	C3—C4	1.452 (4)
N1—C3	1.286 (3)	C4—C5	1.428 (3)
N1—N2	1.366 (3)	O1—C5	1.293 (3)
O1—Cu—N3	171.27 (9)	O1W—Cu—N1	161.43 (11)
O1—Cu—O1W	91.87 (10)	O1—Cu—O8	84.54 (8)
N3—Cu—O1W	93.71 (11)	N3—Cu—O8	101.30 (9)
O1—Cu—N1	91.49 (9)	O1W—Cu—O8	98.09 (11)
N3—Cu—N1	81.12 (9)	N1—Cu—O8	100.41 (9)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H1N2...O4	0.87 (4)	2.41 (4)	3.174 (3)	147 (3)
N2—H1N2...O5	0.87 (4)	2.03 (4)	2.837 (3)	154 (3)
N3—H1N3...O3 ⁱ	0.80 (4)	2.32 (4)	3.040 (3)	151 (3)
O1W—H1W...O4 ⁱ	0.74 (5)	2.00 (5)	2.698 (3)	158 (5)
O1W—H2W...O2 ⁱ	0.77 (6)	1.98 (6)	2.714 (3)	157 (5)
C2—H3C2...O5 ⁱⁱ	0.84 (4)	2.61 (4)	3.446 (4)	177 (3)
C10—H2C0...O7 ⁱⁱⁱ	1.02 (3)	2.52 (3)	3.404 (4)	145 (2)
O2—H1O2...O3 ^{iv}	0.76 (4)	2.10 (4)	2.862 (3)	174 (4)
N4—H1N4...O7 ^v	0.77 (3)	2.47 (4)	3.078 (4)	137 (3)
N4—H1N4...O8 ^v	0.77 (3)	2.05 (4)	2.795 (3)	164 (3)
C8—H1C8...O6 ^{vi}	0.98 (3)	2.47 (3)	3.248 (4)	135 (2)

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

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 0.3428P]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.095$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.46 \text{ e \AA}^{-3}$
3316 reflections	$\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$
308 parameters	All H-atom parameters refined

All H atoms were found in difference Fourier maps and refined isotropically. A Gaussian-type absorption correction based on the crystal morphology was applied (Spek, 1990, 1998).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*, *PARST* (Nardelli, 1995) and *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1514). Services for accessing these data are described at the back of the journal.

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