Dibromo(pyridoxal semicarbazone-$\kappa^3N^1,O^3,O^{3'}$)copper(II)

Dejan Poleti,[a] Ljiljana Karanović,[b]* Vukadin M. Leovac[c] and Violeta S. Jevtović[c]

[a]Department of General and Inorganic Chemistry, Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Yugoslavia, [b]Faculty of Mining and Geology, Laboratory of Crystallography, Djušina 7, 11000 Belgrade, Yugoslavia, and [c]Institute of Chemistry, Faculty of Natural Sciences, Trg Dositeja Obradovića 4, 21000 Novi Sad, Yugoslavia
Correspondence e-mail: ljika2002@yahoo.com

The title compound, dibromo(3-hydroxy-5-hydroxymethyl-2-methyl-4-pyridinecarboxaldehyde semicarbazone-$\kappa^3N^1,O^3,O^{3'}$)copper(II), [CuBr$_2$(C$_9$H$_{12}$N$_4$O$_3$)], consists of discrete complex units with the tridentate pyridoxal semicarbazone ligand as a zwitterion in an almost planar configuration. The Cu^{II} ions are in a distorted square-pyramidal coordination, with the equatorial Br atom at a distance of 2.4017 (6) Å and the apical Br atom at a distance of 2.6860 (6) Å.

Comment

Semicarbazones (sc) and thiosemicarbazones (tsc) are excellent chelating ligands of different denticity, and a great number of transition metal complexes containing these ligands have been described in the literature (Campbell, 1975; Padhye & Kauffman, 1985; Casas *et al.*, 2000). Many of these sc and tsc complexes, especially those with tsc, possess a broad spectrum of biological activity (West *et al.*, 1991). In addition, since both kinds of ligands form very stable and intensely coloured complexes, some of them have been suggested as analytical reagents (Singh *et al.*, 1978).

The synthesis, properties and structures, as well as the biological activities, of some transition metal complexes with pyridoxal (3-hydroxy-5-hydroxymethyl-2-methyl-pyridine-4-carbaldehyde) thiosemicarbazone (Pxtsc) have already been described (Belicchi Ferrari *et al.*, 1987, 1994, 1995, 1998). Most of them are copper(II) complexes, where Pxtsc in the neutral or deprotonated form acts as a tridentate chelate ligand.

It would be of interest to compare copper(II) complexes containing pyridoxal thiosemicarbazone as an *O,N,S*-ligand with related complexes containing pyridoxal semicarbazone (Pxsc) as a potential *O,N,O*-ligand. However, to the best of our knowledge, no structures of Pxsc complexes have been

described to date. In order to make possible the comparison of Pxsc and Pxtsc complexes, the title compound, (I), has been prepared and its crystal structure is described in this paper.

(I)
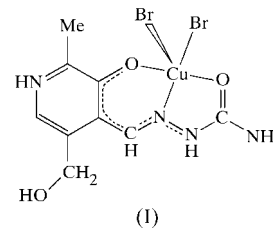
Compound (I) consists of discrete complex units, with Pxsc coordinated as a neutral tridentate ligand (Fig. 1). As expected, the phenolic O atom (O2) is deprotonated, but this H atom is shifted to N4; therefore, Pxsc is zwitterionic. Similar behaviour has already been observed in Cu^{II}–Pxtsc complexes (Belicchi Ferrari *et al.*, 1987, 1995, 1998), while in only one case is Pxtsc deprotonated (Belicchi Ferrari *et al.*, 1987). Nearly all the bond distances in the Pxsc ligand in (I) are very close to the corresponding values found previously in Pxtsc ligands. One of the exceptions is O3—C7, which seems a little short [1.362 (4) Å]. This can be attributed to the unresolved disorder (see *Experimental*) of the alcohol group, since a riding-motion calculation (Busing & Levy, 1964) gives a quite reasonable value of 1.412 Å. The other exception is N2—C9, which is about 0.02 Å longer than the mean value in corresponding Pxtsc complexes. This may be a consequence of the absence of an S atom in the vicinity.

The whole ligand in (I) is very close to coplanarity; if only skeletal atoms are considered, the greatest deviation from the least-squares plane is only 0.031 (2) Å for atom O2. At the same time, atoms C6, C7 and Cu deviate from this plane by 0.046 (3), 0.206 (4) and −0.1757 (4) Å, respectively.

The dihedral angles between the pyridoxal moiety (*A*), and the six- (*B*) and five-membered (*C*) chelate rings (Fig. 1) are *A*–*B* 4.70 (6), *A*–*C* 4.27 (7) and *B*–*C* 6.57 (5)°. On average, these values are smaller than the corresponding values in Cu^{II}–Pxtsc complexes, which, very probably, can be ascribed to the more extended electron delocalization in the Pxsc ligand.

The Cu^{II} atoms in (I) are in a distorted square-pyramidal environment, with atoms Br1, N1, O1 and O2 in the basal plane (Fig. 1). The Cu—O2(phenol) bond is shorter than both Cu—O1 and Cu—N1 (Table 1). Both these observations are in agreement with similar features found in Cu^{II}–Pxtsc complexes. The Cu—O2 bond distance is close to the value found recently in a Cu^{II} *N*-salicylidene-*rac*-alaninate complex [1.965 (2) Å; Warda, 1998], where the ligand has a very similar skeleton. The basal and apical Cu—Br distances are significantly different (Table 1) and, using the criteria of Orpen *et al.* (1989), they belong to the classes of short and long Cu—Br bonds, respectively. The experimental distances for (I) are very close to the mean values listed in the paper cited above.

The basal plane of the coordination polyhedron of (I) is tetrahedrally deformed, with a maximum distance from the least-squares plane of 0.209 (2) Å for N1. As expected, the Cu atom is displaced towards the apical Br2 atom by 0.3585 (4) Å.

metal-organic compounds

With respect to the plane defined by atoms N1, O1 and O2, the basal Br1 atom is displaced outwards by 0.6405 (4) Å.

Possible hydrogen bonds are listed in Table 2. Due to the presence of the N2—H2N···O3 bond, a centrosymmetric
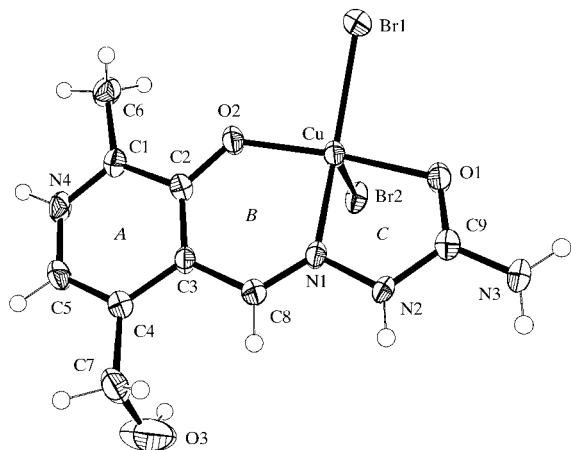
Figure 1
The molecular structure of (I), with the atom- and ring-labelling schemes. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

dimer with almost coplanar chelate ligands is formed. The O3—H3O···Br1 and N3—H3AN···Br1 hydrogen bonds further join such dimers into sheets approximately parallel to the $(3\bar{5}\bar{5})$ plane. However, the apically coordinated Br2 atoms belong to neighbouring sheets, where they take part in two additional hydrogen bonds, connecting the sheets and stabilizing the overall structure (Table 2).

Experimental

The title complex was prepared by the reaction of $CuBr_2 \cdot 2H_2O$ and Pxsc in a 1:1 molar ratio, using warm MeOH as the solvent. Green single crystals of (I) of suitable size were obtained after allowing the reaction mixture to stand overnight.

Crystal data

[CuBr$_2$(C$_9$H$_{12}$N$_4$O$_3$)]
$M_r = 447.59$
Triclinic, $P\bar{1}$
$a = 7.5764$ (10) Å
$b = 8.7614$ (11) Å
$c = 10.8154$ (14) Å
$\alpha = 92.965$ (3)°
$\beta = 97.881$ (2)°
$\gamma = 108.709$ (3)°
$V = 670.05$ (15) Å^3

$Z = 2$
$D_x = 2.218$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 769
  reflections
$\theta = 4.9–56.7°$
$\mu = 7.60$ mm^{-1}
$T = 298$ (1) K
Plate, green
$0.18 \times 0.14 \times 0.07$ mm

Data collection

Bruker SMART CCD area-detector
  diffractometer
φ and ω scans
Absorption correction: empirical
  (*XPREP* in *SHELXTL*;
  Bruker, 1997)
$T_{min} = 0.291$, $T_{max} = 0.587$
7646 measured reflections

4057 independent reflections
2678 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 30.5°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.063$
$S = 0.85$
4057 reflections
174 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0213P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.16$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}
Extinction correction: *SHELXL*97
  (Sheldrick, 1997)
Extinction coefficient: 0.0016 (3)

Table 1
Selected geometric parameters (Å, °).

Br1—Cu	2.4017 (6)	Cu—O1	1.980 (2)
Br2—Cu	2.6860 (6)	Cu—N1	1.990 (2)
Cu—O2	1.895 (2)		
O2—Cu—O1	165.90 (9)	N1—Cu—Br1	154.38 (7)
O2—Cu—N1	89.77 (9)	O2—Cu—Br2	97.85 (7)
O1—Cu—N1	80.23 (9)	O1—Cu—Br2	93.30 (6)
O2—Cu—Br1	91.72 (7)	N1—Cu—Br2	97.30 (7)
O1—Cu—Br1	93.06 (6)	Br1—Cu—Br2	107.81 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3O···Br1^i	0.82	2.77	3.358 (3)	130
N2—H2N···O3^{ii}	0.86	1.90	2.752 (4)	174
N3—H3AN···Br1^{iii}	0.86	2.61	3.457 (2)	170
N3—H3BN···Br2^{iv}	0.86	2.65	3.338 (3)	138
N4—H4N···Br2^v	0.86	2.39	3.226 (3)	165

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

With the exception of the H atoms belonging to the hydroxymethyl group (Fig. 1), it was possible to find all H atoms in the ΔF maps. However, at the final stage of the refinement, the H atoms were positioned geometrically (N—H = 0.86, O—H = 0.82 and C—H = 0.93–0.97 Å) and refined using a riding model, with fixed isotropic displacement parameters 20% larger than those of the parent atoms. The H atom of the OH group was modelled using option HFIX 143 in *SHELXL*97 (Sheldrick, 1997). It is worth noting that an attempt to model this H atom with the program *HYDROGEN* (Nardelli, 1999) resulted in a nearly identical geometry. Two electron-density peaks in the final ΔF map (1.16 and 0.85 e Å^{-3}, located near atoms O3 and C7, respectively), together with an elongated O3 ellipsoid (Fig. 1), indicated disorder of the alcohol group. However, all attempts to model this disorder were unsuccessful. Similar disorder has also been observed in Pxtsc complexes (Belicchi Ferrari *et al.*, 1987).

Data collection: *SMART–NT* (Bruker, 1998); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *ORTEX*8a (McArdle, 1995; Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1983, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1591). Services for accessing these data are described at the back of the journal.

References

Belicchi Ferrari, M., Gasparri Fava, G., Pelizzi, C., Pelosi, G. & Tarasconi, P. (1998). *Inorg. Chim. Acta*, **269**, 297–301.

Belicchi Ferrari, M., Gasparri Fava, G., Pelizzi, C., Tarasconi, P. & Tosi, G. (1987). *J. Chem. Soc. Dalton Trans.* pp. 227–233.

Belicchi Ferrari, M., Gasparri Fava, G., Pelosi, G., Rodriguez-Arguelles, M. C. & Tarasconi, P. (1995). *J. Chem. Soc. Dalton Trans.* pp. 3035–3040.

Belicchi Ferrari, M., Gasparri Fava, G., Tarasconi, P., Albertini, R., Pinelli, S. & Starcich, R. (1994). *J. Inorg. Biochem.* **53**, 13–25.

Bruker (1997). *SHELXTL.* Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1998). *SMART–NT.* Version 5.00. Bruker AXS Inc., Madison, Wisconsin, USA.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142–146.

Campbell, M. J. M. (1975). *Coord. Chem. Rev.* **15**, 279–319.

Casas, J. S., García-Tasende, M. S. & Sordo, J. (2000). *Coord. Chem. Rev.* **209**, 197–261.

McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Nardelli, M. (1999). *J. Appl. Cryst.* **32**, 563–571.

Orpen, G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–83.

Padhye, S. & Kauffman, G. B. (1985). *Coord. Chem. Rev.* **63**, 127–160.

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

Siemens (1996). *SAINT.* Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Singh, R. B., Garg, B. S. & Singh, R. P. (1978). *Talanta*, **25**, 619–632.

Warda, S. A. (1998). *Acta Cryst.* C**54**, 304–306.

West, D. X., Padhye, S. B. & Sonawane, P. B. (1991). *Struct. Bonding* (*Berlin*), **76**, 1–50.