

C(40)	-0.0646 (10)	0.5141 (9)	0.1296 (14)	0.051 (10)
C(41)	0.0272 (11)	0.5573 (8)	0.1806 (14)	0.050 (10)
C(42)	0.3094 (10)	0.4782 (9)	0.1809 (12)	0.051 (9)
C(43)	0.3484 (11)	0.4064 (10)	0.2200 (13)	0.062 (10)
C(44)	0.4144 (12)	0.3436 (9)	0.1582 (15)	0.073 (12)
C(45)	0.4335 (13)	0.3601 (10)	0.0456 (13)	0.062 (4)†
C(46)	0.3970 (11)	0.4310 (9)	0.0063 (13)	0.063 (10)
C(47)	0.3317 (11)	0.4960 (9)	0.0679 (12)	0.057 (10)

† Refined isotropically.

Table 2. Selected geometric parameters (Å, °)

Cu(1)···Cu(1 <sup>i</sup> )	2.624 (4)	O(5)—C(4)	1.250 (17)
Cu(1)—O(1)	1.975 (11)	C(4)—C(5)	1.511 (16)
Cu(1)—O(2 <sup>i</sup> )	1.975 (8)	C(5)—C(6)	1.39 (2)
Cu(1)—O(3)	1.947 (7)	O(7)—C(7)	1.308 (14)
Cu(1)—O(5 <sup>i</sup> )	1.987 (10)	O(8)—C(7)	1.195 (17)
Cu(1)—O(7)	2.092 (8)	C(7)—C(8)	1.517 (16)
Cu(2)—O(8)	2.075 (8)	C(8)—C(9)	1.436 (16)
Cu(2)—O(9)	2.183 (7)	O(9)—C(10)	1.406 (16)
Cu(2)—P(1)	2.238 (4)	C(10)—C(11)	1.25 (3)
Cu(2)—P(2)	2.222 (3)	P(1)—C(12)	1.769 (17)
O(1)—C(1)	1.244 (18)	P(1)—C(18)	1.825 (10)
O(2)—C(1)	1.214 (16)	P(1)—C(24)	1.849 (10)
C(1)—C(2)	1.52 (3)	P(2)—C(30)	1.854 (17)
C(2)—C(3)	1.41 (3)	P(2)—C(36)	1.821 (14)
O(3)—C(4)	1.258 (14)	P(2)—C(42)	1.844 (11)
O(1)—Cu(1)—O(2 <sup>i</sup> )	167.2 (5)	O(9)—Cu(2)—P(1)	102.6 (3)
O(1)—Cu(1)—O(3)	90.4 (4)	O(9)—Cu(2)—P(2)	109.7 (2)
O(1)—Cu(1)—O(5 <sup>i</sup> )	88.9 (4)	P(1)—Cu(2)—P(2)	126.8 (2)
O(2 <sup>i</sup> )—Cu(1)—O(5 <sup>i</sup> )	91.0 (4)	Cu(2)—P(1)—C(12)	116.1 (4)
O(2 <sup>i</sup> )—Cu(1)—O(3)	87.4 (4)	Cu(2)—P(1)—C(18)	112.6 (5)
O(3)—Cu(1)—O(5 <sup>i</sup> )	169.2 (4)	Cu(2)—P(1)—C(24)	113.7 (4)
O(1)—Cu(1)—O(7)	99.8 (4)	Cu(2)—P(2)—C(30)	113.5 (5)
O(2 <sup>i</sup> )—Cu(1)—O(7)	93.0 (4)	Cu(2)—P(2)—C(36)	115.8 (4)
O(3)—Cu(1)—O(7)	101.5 (3)	Cu(2)—P(2)—C(42)	114.1 (3)
O(5 <sup>i</sup> )—Cu(1)—O(7)	89.3 (4)	C(12)—P(1)—C(24)	105.2 (6)
O(1)—C(1)—O(2)	125.8 (17)	C(12)—P(1)—C(18)	104.7 (6)
O(3)—C(4)—O(5)	127.8 (10)	C(18)—P(1)—C(24)	103.5 (5)
O(7)—C(7)—O(8)	126.7 (11)	C(30)—P(2)—C(36)	107.1 (7)
O(8)—Cu(2)—O(9)	93.9 (3)	C(30)—P(2)—C(42)	102.3 (6)
O(8)—Cu(2)—P(1)	106.6 (3)	C(36)—P(2)—C(42)	102.6 (6)
O(8)—Cu(2)—P(2)	111.9 (2)		

Symmetry code: (i)  $-x, 2 - y, -z$ .

The crystal specimen was of poor quality and no correction was made for crystal decomposition. Cu-atom positions were obtained from a Patterson function and other non-H-atom positions were obtained from Fourier syntheses. H atoms were placed in calculated positions. Calculations were performed using *SHELX76* (Sheldrick, 1976).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: MU1081). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Drew, M. G. B., Othman, B. A. H., Edwards, D. A. & Richards, R. (1975). *Acta Cryst.* **B31**, 2695–2697.  
 Koman, M., Valigura, D., Ďurčanská, E. & Ondrejovič, G. (1984). *J. Chem. Soc. Chem. Commun.* pp. 381–383.  
 Koman, M., Valigura, D. & Ondrejovič, G. (1988). *Acta Cryst.* **C44**, 601–603.  
 Meester, P. de, Fletcher, S. R. & Skapski, A. C. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2575–2578.  
 Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.

*Acta Cryst.* (1995). **C51**, 1084–1087

## *trans*-Dichlorobis(1-ethyltetrazole-*N*<sup>4</sup>)-copper(II)

ALEXANDER V. VIROVETS, NINA V. PODBEREZSKAYA  
AND LUDMILA G. LAVRENOVA

*Institute of Inorganic Chemistry SD RAS,  
Prospekt Lavrent'ev 3, Novosibirsk 630090, Russia*

GALINA A. BIKZHANOVA

*Novosibirsk State University, Prospekt Pirogov 2,  
Novosibirsk 630090, Russia*

(Received 27 June 1994; accepted 22 November 1994)

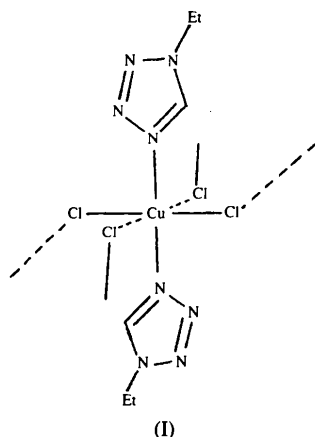
## Abstract

In the title compound, [CuCl<sub>2</sub>(C<sub>3</sub>H<sub>6</sub>N<sub>4</sub>)<sub>2</sub>], the tetrazole ligand is coordinated terminally by the N<sup>4</sup> ring atom. The coordination polyhedron of the Cu atom takes the form of an elongated square bipyramid with  $\bar{1}$  site symmetry. The equatorial positions are occupied by two Cl atoms [Cu—Cl 2.290 (1) Å] and two ethyltetrazole ligands [Cu—N 1.990 (4) Å]. In addition, there are two Cl atoms in axial positions [Cu—Cl 2.993 (1) Å]. Hence, the Cl atoms play the role of non-symmetrical bridges and connect the molecules into infinite layers located in the *yz* plane.

## Comment

The tetrazoles (Tz) are an interesting class of ligands which have various coordination abilities because of the presence of four N atoms. There are only a few reports of substituted tetrazoles being unable to coordinate to metal atoms (Baenziger & Schultz, 1971; van den Meuveld, Franke, Verschoor & Zuur, 1983; Aliev, Goncharov, Grachev & Roschupkin, 1990; Aliev, Goncharov, Grachev, Kurmaz & Roschupkin, 1991). It can be concluded that these ligands have a tendency towards terminal monodentate coordination, whereas their nearest analogues, the 1,2,4-triazoles, typically form bridges between two metal atoms (Bietmeijer, Van Albada, de Graaff, Haasnoot & Reedijk, 1985; Sinditskii *et al.*, 1987; Vreugdenhil, Haasnoot & Reedijk, 1990; Grap, Kuz'mina, Porai-Koshits, Kurbakova & Efimenko, 1993). Previously, we found that in *trans*-[Cu(1-PhTz)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], where 1-PhTz is 1-phenyltetrazole (Lavrenova, Virovets, Podbereskaya & Bikzhanova, 1994), the Cu atom has two terminal *N*<sup>4</sup>-coordinated 1-PhTz ligands and two water molecules in equatorial positions, and two NO<sub>3</sub><sup>-</sup> ligands in axial positions. We thought it of interest to investigate the structure of a complex of copper(II) chloride with another 1-

substituted tetrazole, such as 1-ethyltetrazole (1-EtTz), and to compare the ligand coordination modes. The synthesis of  $[\text{CuCl}_2(1\text{-EtTz})_2]$ , (I), has been described previously by Gaponik, Degtjarik & Sviridov (1982), but its structure was unknown.



It was found that the 1-EtTz ligand, containing a nearly planar heterocycle, is coordinated terminally to Cu by the N4 atom of the ring. The coordination polyhedron of Cu takes the form of an elongated square bipyramid with  $\bar{1}$  site symmetry. The equatorial positions are occupied by two Cl atoms and two 1-EtTz ligands. In addition, there are two Cl atoms in

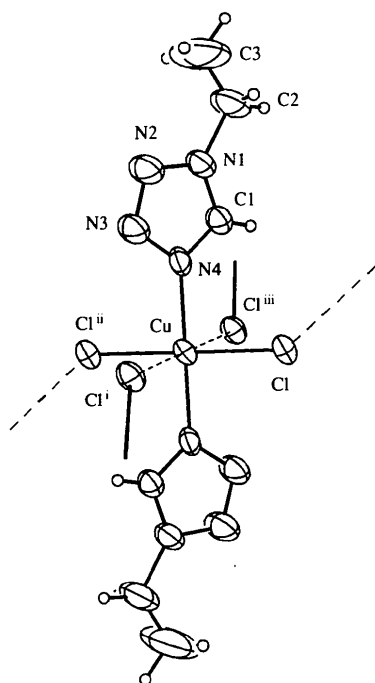


Fig. 1. ORTEP (Johnson, 1976) drawing of the molecular fragment of the title compound. Displacement ellipsoids are plotted at the 50% probability level.

axial positions (Fig. 1). Hence, the Cl atoms have a non-symmetrical bridging role and connect the molecules into infinite layers located in the  $yz$  plane (Fig. 2). Geometrical characteristics of the Tz cycle show good distinction between the  $\text{C}-\text{N}$  and  $\text{C}=\text{N}$ , and  $\text{N}-\text{N}$  and  $\text{N}=\text{N}$  bond lengths (Table 2), and are in agreement with the bond lengths found for  $[\text{Zn}(1\text{-MeTz})_2\text{Cl}_2]$  (Baenziger & Schultz, 1971) and  $[\text{Fe}(1\text{-PrTz})_6](\text{BF}_4)_2$  [Franke, 1982 (data taken from JANSAS in the Cambridge Structural Database; Allen *et al.*, 1979)]. In both compounds, the Tz ligands are also terminally coordinated to the metal atom through the N4 atom. On this basis, we can conclude that the structure of the title compound confirms the tendency of Tz ligands towards terminal  $N^4$ -coordination with substituents unable to coordinate to metal atoms.

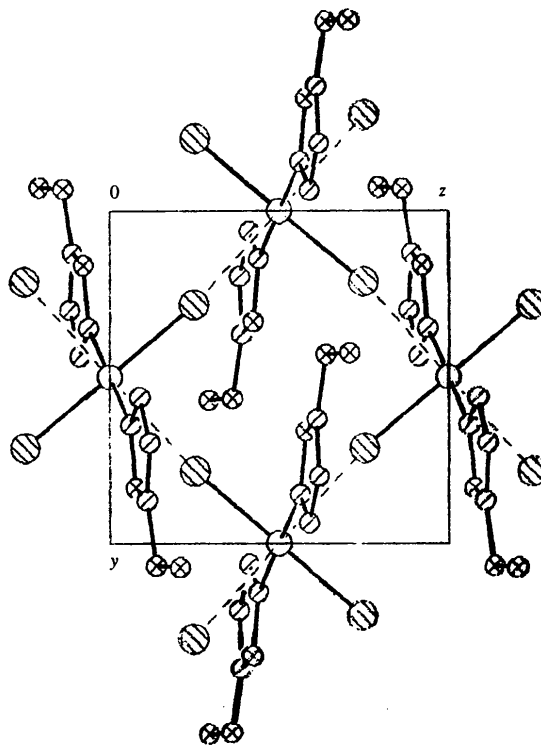


Fig. 2. The crystal packing of the title compound projected along the  $x$  axis. H atoms have been omitted for clarity.

## Experimental

Synthesis of the title compound (m.p. 483 K) was carried out by reaction of  $\text{CuCl}_2$  with 1-ethyltetrazole (molar ratio 1:2) in EtOH. Recrystallization was from ethanol.

### Crystal data

$[\text{CuCl}_2(\text{C}_3\text{H}_6\text{N}_4)_2]$   
 $M_r = 330.68$

Cu  $K\alpha$  radiation  
 $\lambda = 1.54178 \text{ \AA}$

## Monoclinic

$P2_1/c$   
 $a = 13.247(3) \text{ \AA}$   
 $b = 6.769(1) \text{ \AA}$   
 $c = 7.302(1) \text{ \AA}$   
 $\beta = 107.39(2)^\circ$   
 $V = 624.8(2) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 1.758 \text{ Mg m}^{-3}$

## Cell parameters from 20

reflections  
 $\theta = 12\text{--}27^\circ$   
 $\mu = 6.364 \text{ mm}^{-1}$   
 $T = 298(2) \text{ K}$   
 Plate  
 $1.00 \times 0.80 \times 0.08 \text{ mm}$   
 Green

Cl—Cu—Cl <sup>i</sup>	92.68(2)	N3—N4—Cu	125.4(3)
Cl—Cu—Cl <sup>iii</sup>	87.32(2)	N4—Cl—N1	109.7(5)
C1—N1—N2	107.8(5)	N4—Cl—H1	128(5)
C1—N1—C2	128.5(6)	N1—Cl—H1	128(5)
N2—N1—C2	123.8(5)	C3—C2—N1	118.8(9)

Symmetry codes: (i)  $-x, y - \frac{1}{2}, \frac{3}{2} - z$ ; (ii)  $-x, -y, 1 - z$ ; (iii)  $x, \frac{1}{2} - y, z - \frac{1}{2}$ .

## Data collection

Syntex  $P2_1$  diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction:  
 by integration from crystal shape  
 $T_{\min} = 0.082, T_{\max} = 0.595$   
 984 measured reflections  
 839 independent reflections  
 783 observed reflections  
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0568$   
 $\theta_{\text{max}} = 56.93^\circ$   
 $h = -14 \rightarrow 13$   
 $k = 0 \rightarrow 7$   
 $l = 0 \rightarrow 7$   
 3 standard reflections monitored every 97 reflections  
 intensity decay: none

The scan rate varied in the range  $1.98\text{--}14.5^\circ \text{ min}^{-1}$  and background counts for 25% of the total scan time were taken on each side. The scan width was  $[1.9 + 2\theta(\alpha_2) - 2\theta(\alpha_1)]^\circ$ . The absorption correction was applied using distances between crystal faces. Refinement was by full-matrix least-squares method on  $F^2$  using all reflections with  $I_{hkl} > 0$ .

Data collection: *Recentering  $\theta/2\theta$  Collection Program* from the XTL tape system (Syntex, 1973). Cell refinement:  $P2_1$  from the XTL disk system. Data reduction: *TAPER* from the XTL disk system. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

## Refinement

Refinement on  $F^2$   
 $R(F) = 0.0611$   
 $wR(F^2) = 1.663$   
 $S = 1.065$   
 839 reflections  
 92 parameters  
 All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.1315P)^2 + 0.8672P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.654$

$\Delta\rho_{\text{max}} = 0.655 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.252 \text{ e \AA}^{-3}$   
 Extinction correction:  
*SHELXL93* (Sheldrick, 1993)  
 Extinction coefficient:  
 0.0099 (22)  
 Atomic scattering factors from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)

We are grateful to Dr Yu. V. Gatilov (Novosibirsk Institute of Organic Chemistry) for putting at our disposal a single-crystal diffractometer. The research described in this publication was made possible in part by grant No. RC3000 from the International Science Foundation. EtTz was kindly donated by Dr P. N. Gaponik from the Institute of Physical and Chemical Problems, Belorussian St. Univ.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: VS1015). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{eq}}$
Cu	0	0	1/2	0.0358 (6)
Cl	0.06912 (9)	0.2148 (2)	0.7481 (2)	0.0369 (6)
N1	-0.2537 (4)	0.3725 (7)	0.3892 (7)	0.0465 (13)
N2	-0.3038 (4)	0.1998 (7)	0.3822 (11)	0.067 (2)
N3	-0.2334 (4)	0.0616 (8)	0.4115 (9)	0.0573 (15)
N4	-0.1366 (3)	0.1456 (6)	0.4384 (6)	0.0352 (11)
C1	-0.1526 (4)	0.3351 (8)	0.4223 (8)	0.0393 (13)
C2	-0.3076 (7)	0.5662 (12)	0.3625 (18)	0.087 (3)
C3	-0.4062 (10)	0.5711 (19)	0.293 (4)	0.250 (15)

Table 2. Selected geometric parameters ( $\text{\AA}, ^\circ$ )

Cu—N4	1.990 (4)	N1—C2	1.478 (9)
Cu—Cl	2.290 (1)	N2—N3	1.293 (8)
Cu—Cl <sup>i</sup>	2.993 (1)	N3—N4	1.362 (7)
N1—C1	1.313 (7)	N4—C1	1.300 (7)
N1—N2	1.338 (7)	C2—C3	1.25 (2)
N4—Cu—Cl	89.2 (1)	N3—N2—N1	107.5 (5)
N4—Cu—Cl <sup>ii</sup>	90.8 (1)	N2—N3—N4	108.9 (4)
N4—Cu—Cl <sup>i</sup>	91.93 (13)	C1—N4—N3	106.1 (4)
N4—Cu—Cl <sup>iii</sup>	88.07 (13)	C1—N4—Cu	128.4 (4)

## References

- Aliev, Z. G., Goncharov, T. K., Grachev, B. M., Kurmaz, S. V. & Roschupkin, V. P. (1991). *Koord. Khim.* **17**, 1101–1109.
- Aliev, Z. G., Goncharov, T. K., Grachev, B. M. & Roschupkin, V. P. (1990). *Koord. Khim.* **16**, 570–573.
- Allen, F. H., Bellard, O., Brice, M. D., Cartwright, B. A., Doubleday, A., Higgs, H., Hummerlink, T., Hummerlink-Peters, B. G., Kennard, O., Motherwell, W. D. S., Rodgers, J. R. & Watson, D. J. (1979). *Acta Cryst.* **B35**, 2331–2339.
- Baenziger, N. C. & Schultz, R. J. (1971). *Inorg. Chem.* **10**, 661–667.
- Bietmeijer, F. J., Van Albada, G. A., de Graaff, R. A. G., Haasnoot, J. G. & Reedijk, J. (1985). *Inorg. Chem.* **24**, 3597–3601.
- Franke, P. L. (1982). Thesis, Rijks Univ., Leiden, The Netherlands.
- Gaponik, P. N., Degtjarik, M. N. & Sviridov, V. V. (1982). *Dokl. Akad. Nauk SSSR*, **26**, 716–718.
- Grap, S. R., Kuz'mina, L. G., Porai-Koshits, M. A., Kurbakova, A. P. & Efimenko, I. A. (1993). *Koord. Khim.* **19**, 566–570.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Lavrenova, L. G., Virovets, A. V., Podberzskaya, N. V. & Bikzhanova, G. A. (1994). *Polyhedron*. In the press.
- Meuvel, E. J. van den, Franke, P. L., Verschoor, G. C. & Zuur, A. P. (1983). *Acta Cryst.* **C39**, 337–339.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

Sinditskii, V. P., Sokol, V. I., Vogelzang, A. E., Dutov, M. D., Serushkin, V. V., Porai-Koshits, M. A. & Svetlov, B. S. (1987). *Zh. Neorg. Khim.* **32**, 1950–1955.  
 Syntex (1973). *XTL Structure Determination System*. Syntex Analytical Instruments, Cupertino, California, USA.  
 Vreugdenhil, W., Haasnoot, J. G. & Reedijk, J. (1990). *Inorg. Chim. Acta*, **167**, 109–113.

*Acta Cryst.* (1995). **C51**, 1087–1089

**Aqua[1,3-propanediyl-diiminobis(1,3-dimethyl-5-nitrosouracilato)- $\kappa^4N^5, N^6, N^{15}, N^{16}$ ]copper(II) Monohydrate**

RAIKKO KIVEKÄS AND MARTTI KLINGA

*Inorganic Chemistry Laboratory, Box 55, FIN-00014, University of Helsinki, Finland*

ENRIQUE COLACIO AND JOSE M. DOMINGUEZ-VERA

*Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain*

ANTONIO ROMEROSA

*Departamento de Química Inorgánica, Facultad de Ciencias Experimentales, Universidad de Almería, 04071 Almería, Spain*

(Received 14 June 1994; accepted 25 November 1994)

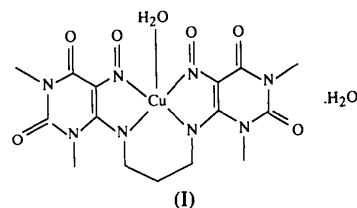
**Abstract**

The versatile  $C_{15}H_{20}N_8O_6$  ligand is coordinated through four of its N atoms to the  $Cu^{II}$  atom in a double-deprotonated tetradentate fashion to give the title complex, aqua[1,3-propanediyl-diimino- $\kappa^2N$ -bis(1,3-dimethyl-5-nitroso-2,4(1*H*,3*H*)-pyrimidinedionato- $\kappa^2N^5, N^6(2-)$ ]copper(II) monohydrate,  $[Cu(C_{15}H_{18}N_8O_6)(H_2O)] \cdot H_2O$ . A water molecule occupies the axial position of the distorted square-pyramidal coordination environment of the Cu atom.

**Comment**

In a previous report we showed that  $\alpha, \omega$ -bis(1,3-dimethyl-5-nitrosouracil-6-ylamino)propane ( $H_2L$ ), a dioxime pyrimidine ligand, reacts with copper(II) in basic medium giving the mononuclear complex  $[Cu(L)(H_2O)] \cdot 3H_2O$  (Colacio, Dominguez-Vera, Escuer, Kivekäs & Romerosa, 1994). In this compound, the  $Cu^{II}$  atom occupies the  $N_4$  inner site of the ligand and a water

molecule coordinates at the axial position. The three lattice water molecules and the  $[Cu(L)(H_2O)]$  complex unit are involved in an extended network of hydrogen bonds, which is responsible for the weak antiferromagnetic interaction observed for the compound. In this paper, we describe the preparation and present the X-ray results for the monohydrated complex,  $[Cu(L)(H_2O)] \cdot H_2O$ , (I).



The  $H_2L$  ligand is coordinated through four of its N atoms to the  $Cu^{II}$  atom in a double-deprotonated tetradentate fashion ( $L^{2-}$ ), the deprotonated N atoms being N(6) and N(16). The complex unit of the present compound is essentially similar to that of  $[Cu(L)(H_2O)] \cdot 3H_2O$  (Colacio, Dominguez-Vera, Escuer, Kivekäs & Romerosa, 1994), the Cu atom occupying the inner site of the tetradentate  $L^{2-}$  ligand. The complex unit is approximately coplanar and the six-membered ring [Cu, N(6), C(7), C(8), C(17), N(16)] has a boat conformation. The C—O distances are typical for C=O bonds. Moreover, the distances and angles in the CNO groups are approximately similar in both compounds and the values agree quite well with those reported for oximate complexes (Korvenranta, Saarinen & Näsäkkälä, 1982) and also with those observed for 6-amino-3-methyl-5-nitrosouracil complexes (Romero, Moreno, Ruiz, Sanchez & Nieto, 1986).

The coordination of the  $Cu^{II}$  atoms in the title compound and in  $[Cu(L)(H_2O)] \cdot 3H_2O$  is quite similar, the polyhedra being distorted square-based pyramids. However, there are also some significant differences between the two coordination spheres. The basal plane of the coordination sphere is more planar in the title compound than in  $[Cu(L)(H_2O)] \cdot 3H_2O$ , the greatest deviation of an

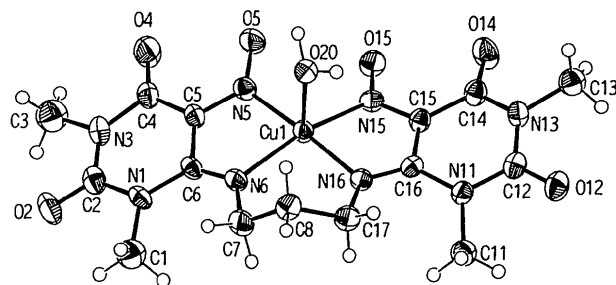


Fig. 1. ORTEP (Johnson, 1976) plot of the title compound. Displacement ellipsoids are shown at the 50% probability level; H atoms are shown as spheres of arbitrary radii.