

## An Acetate-Bridged Dicopper(II) Complex of a Binucleating Schiff-Base Chelate

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**Abstract.**  $\mu$ -Acetato-(*O,O'*)- $\mu$ -(5,11-diethyl-6,10-diaza-3,5,10,12-pentadecatetraene-3,8,13-triolato-*O,N,\mu-O',N',O''*)-dicopper(II),  $[\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)(\text{C}_{17}\text{H}_{27}\text{N}_2\text{O}_3)]$ ,  $M_r = 493.54$ , monoclinic,  $C2/c$ ,  $a = 16.034$  (5),  $b = 17.481$  (3),  $c = 9.205$  (4) Å,  $\beta = 123.76$  (3)°,  $V = 2144.9$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.529$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 19.4$  cm<sup>-1</sup>,  $F(000) = 1024$ ,  $T = 297$  K,  $R = 0.031$  for 1521 independent observed reflections. The molecule crystallizes as discrete neutral binuclear Cu<sup>II</sup> units, with crystallographically imposed twofold symmetry. The Cu atoms are bridged endogenously by the alkoxide O of the pentafunctional chelate ligand and exogenously by an acetate ligand. The coordination sphere is four-coordinate, planar with an NO<sub>3</sub> donor set.

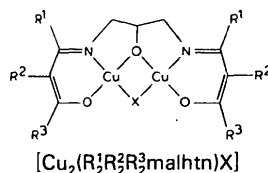
**Introduction.** Binuclear transition-metal centers in biological systems displaying unusual physical properties have been at the center of attention of many chemists and biologists for the last decade. Investigations into the native molecules and model systems have led to a variety of interesting results on both the biological and fundamental physical levels.

An example of the latter can be found in the discussions of the structures of two isomeric forms of an asymmetrically bridged dicopper(II) complex,  $[\text{Cu}_2(\text{Me}_2\text{H}_2\text{Me}_2\text{htn})(\text{OAc})]$  (Nishida, Takeuchi, Takahashi & Kida, 1983; Fallon, Murray, Mazurek & O'Connor, 1985).† These complexes differ primarily in their degree of hydration and magnetic properties, although no direct interrelationship has been established. Here we wish to report the structure of a structurally similar molecule,  $[\text{Cu}_2(\text{Et}_2\text{H}_2\text{Et}_2\text{malhtn})(\text{OAc})]$ .

**Experimental.** Addition of two equivalents of 3,5-heptanedione (Eastman) to 1,3-diamino-2-propanol (Aldrich) in the presence of one equivalent of triethyl orthoformate (Aldrich) affords, following work-up with diethyl ether, the ligand  $\text{H}_3[\text{Et}_2\text{H}_2\text{Et}_2\text{malhtn}]$ . Reaction of this ligand with cupric acetate dihydrate (J. T. Baker; molar ratio 1:2) in methanol gives a deep-blue solution. Removal of solvent followed by recrystallization from heptane/ $\text{CH}_2\text{Cl}_2$  results in the title compound. A second recrystallization from the same solvent system gives deep-blue needles; crystal size  $0.075 \times 0.125 \times 0.55$  mm; cell constants and e.s.d.'s at 297 K from the least-squares refinement of 25 reflections with  $25 \leq 2\theta \leq 30^\circ$ . Data collection on an Enraf–Nonius CAD-4-F11  $\kappa$ -geometry diffractometer using monochromated Mo  $K\alpha$  radiation. A total of 2858 reflections were collected with  $4 \leq 2\theta \leq 50^\circ$  ( $\pm h, +k, +l$ ) including six standard reflections measured every 3 h of exposure; no decay was observed. There were 1792,  $R_{\text{int}} = 0.013$ , unique reflections; 1521 observed with  $F \geq 6\sigma(F)$ . Absorption correction was not applied. The direct methods of *SHELX76* (Sheldrick, 1976) were used to solve the structure. Neutral-atom scattering factors taken from *International Tables for X-ray Crystallography* (1974) were used for non-H atoms. H-atom scattering factors were taken from the standard reference (Stewart, Davidson & Simpson, 1965). All H atoms were placed in calculated positions ( $d_{\text{C-H}} = 0.95$  Å),  $U = 0.07$  Å<sup>2</sup> except the methyl H atoms that had  $U = 0.10$  Å<sup>2</sup>. The remaining non-H atoms were refined as anisotropic scatterers;  $\sum w(|F_o| - |F_c|)^2$  minimized,  $w = 1/\sigma^2(F)$ ; the largest peak on final difference Fourier map amounted to  $0.30 \text{ e } \text{Å}^{-3}$ . The refinement of 136 parameters gave  $R = 0.031$  and  $wR = 0.031$ ; the largest shift/e.s.d. was 0.15. Table 1 contains final positional and equivalent isotropic thermal parameters.‡ All calculations were performed on an IBM 3081-D computer using *SHELX76*.

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† The notation used to describe the complexes is as follows:



‡ Lists of observed and calculated structure factors, anisotropic thermal parameters for non-H atoms, H-atom positions, remaining interatomic distances and angles, least-squares planes and a stereoview of the unit-cell packing have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43554 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional atomic positions and equivalent isotropic thermal parameters for [Cu<sub>2</sub>(Et<sub>2</sub>H<sub>2</sub>-Et<sub>2</sub>malhtn)(OAc)]

The numbers in parentheses are the e.s.d.'s in the last significant digit(s).  $B_{eq} = \frac{1}{3}(\pi^2) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$ .

	x	y	z	$B_{eq}(\text{\AA}^2)$
Cu	0.10649 (3)	0.02374 (2)	0.24103 (6)	3.38 (2)
O(1)	0.00000	-0.01896 (17)	0.25000	4.09 (15)
O(2)	0.06785 (18)	0.12889 (13)	0.24296 (36)	4.28 (11)
O(3)	0.21388 (19)	0.06595 (13)	0.23552 (35)	4.16 (11)
N(1)	0.13696 (20)	-0.08046 (15)	0.21792 (37)	3.26 (11)
C(1)	0.07438 (27)	-0.13507 (20)	0.23519 (56)	4.29 (16)
C(2)*	0.01623 (89)	-0.09572 (34)	0.29539 (73)	3.13 (33)
C(11)	0.29948 (29)	-0.22267 (22)	0.33847 (58)	5.43 (20)
C(12)	0.22019 (27)	-0.18629 (20)	0.16651 (54)	4.28 (17)
C(13)	0.20264 (27)	-0.10264 (20)	0.18571 (49)	3.47 (15)
C(14)	0.26474 (29)	-0.04987 (21)	0.17367 (53)	4.29 (17)
C(15)	0.26916 (27)	0.02716 (23)	0.20138 (49)	4.04 (16)
C(16)	0.34627 (31)	0.07498 (23)	0.19670 (62)	5.57 (21)
C(17)	0.41916 (32)	0.11103 (29)	0.36325 (69)	8.56 (30)
C(21)	0.00000	0.16058 (28)	0.25000	3.70 (21)
C(22)	0.00000	0.24705 (26)	0.25000	4.75 (24)

\* Atom is positionally disordered as a consequence of space-group symmetry. See text for details.

**Discussion.** The title compound crystallizes as discrete neutral binuclear Cu<sup>II</sup> complexes that possess crystallographically imposed twofold symmetry. An ORTEP (Johnson, 1965) drawing of the molecule, in which the atomic-labeling scheme is displayed, is depicted in Fig. 1. Selected interatomic distances and angles are listed in Table 2.

As is evident from Fig. 1, the two Cu<sup>II</sup> ions are bridged by the internal alkoxide O, O(1), of the pentafunctional chelate ligand as well as by an acetate anion. Completing the coordination sphere of the metal are the imino N, N(1), and the enonato O, O(3), atoms. The coordination geometry is square planar as is made evident by the slight deviations from the plane defined by all five atoms: Cu, 0.027; O(1), 0.041; O(2), -0.054; O(3), 0.041; and N(1), -0.055 Å. Angles within the coordination sphere are consistent with the square-planar description.

Another important feature is the geometry of the bridging O atom, O(1). The angles about this atom clearly indicate a trigonal-planar geometry, sum of the three X—O(1)—Cu angles, 358.5°. This geometry is chiefly responsible for the pronounced planarity of the molecule. Atoms Cu, O(1), O(2), O(3), N(1), C(13), C(14), C(15), C(21) and C(22) and the atoms related by  $-x, y, \frac{1}{2}-z$ , lie within  $\pm 0.22$  Å of the mutually defined plane. The maximum deviation of any atom not included in the aforementioned plane is 1.44 Å for C(17).

A consequence of the crystallographically imposed twofold symmetry in the title molecule is the disorder of atom C(2). This atom is unequivocally an  $sp^2$ -hybridized moiety and cannot possess such symmetry. Initial location of this atom on difference Fourier maps

indicated a position coincident with the twofold axis. However, refinement of the atom, with no constraints, led to the chemically realistic position that we report.

The contacts  $<4.0$  Å between binuclear units *via* the metal and bridging O atom, O(1), are the only unusual long-range interactions between non-H atoms within 4.0 Å. No evidence for hydrogen bonding was observed.

The structure of the title molecule is similar to that of the complex reported by Nishida *et al.* (1983) and hence it is not surprising that it has similar magnetic properties (Davis, Busch, Helms & Hatfield, 1985, unpublished results).

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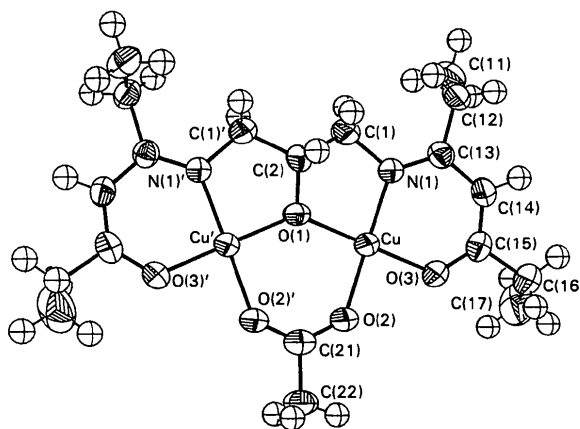


Fig. 1. ORTEP drawing of the title molecule with the labeling scheme used in the text. Thermal ellipsoids are of the 40% probability level. H-atom thermal parameters arbitrarily set at 1.0 Å<sup>2</sup>. Primed atoms at  $-x, y, \frac{1}{2}-z$ .

Table 2. Selected interatomic distances (Å) and angles (°) for [Cu<sub>2</sub>(Et<sub>2</sub>H<sub>2</sub>Et<sub>2</sub>malhtn)(OAc)]

The numbers in parentheses are the e.s.d.'s in the last significant digit.

Cu—O(3)	1.901 (3)	Cu—O(1)	1.908 (1)
Cu—N(1)	1.930 (3)	Cu—O(2)	1.943 (2)
Cu—Cu <sup>i</sup>	3.512 (1)	Cu—Cu <sup>ii</sup>	3.9865 (9)
	Cu—O(1 <sup>ii</sup> )	3.9700 (6)	
O(3)—Cu—O(1)	179.2 (1)	O(3)—Cu—N(1)	94.2 (1)
O(3)—Cu—O(2)	86.1 (1)	O(1)—Cu—N(1)	85.7 (1)
N(1)—Cu—O(2)	175.0 (2)	C(2)—O(1)—Cu	111.9 (6)
C(2)—O(1)—Cu <sup>i</sup>	112.5 (6)	Cu—O(1)—Cu <sup>i</sup>	133.9 (2)

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

## References

- FALLON, G. D., MURRAY, K. S., MAZUREK, W. & O-CONNOR, C. J. (1985). *Inorg. Chim. Acta*, **96**, L53–L55.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1965). *ORTEP*. ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- NISHIDA, Y., TAKEUCHI, M., TAKAHASHI, K. & KIDA, S. (1983). *Chem. Lett.* pp. 1815–1818.
- SHELDRICK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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## Structure of Dichlorobis(1,3-thiazolidine-2-thione-S)zinc(II)

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**Abstract.**  $[\text{ZnCl}_2(\text{C}_3\text{H}_5\text{NS}_2)_2]$ ,  $M_r = 374.7$ , monoclinic,  $P2_1/n$ ,  $a = 8.773$  (3),  $b = 11.274$  (3),  $c = 13.877$  (4) Å,  $\beta = 99.44$  (3)°,  $U = 1353.9$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.82$  (2),  $D_x = 1.84$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 2.81$  mm<sup>-1</sup>,  $F(000) = 752$ ,  $T = 293$  K, final  $R = 0.038$  for 2486 observed reflections. The Zn atom is tetrahedrally coordinated by two 1,3-thiazolidine-2-thione ligands and two Cl atoms. The ligands are bonded through the thione S atom to the metal with Zn–S 2.361 (1) and 2.369 (1) Å. The crystal structure is stabilized by intra- and intermolecular N–H...Cl hydrogen bonds.

**Introduction.** Compounds like 1,3-thiazolidine-2-thione (ttz), containing a secondary thioamide group, are of considerable interest as ligands since they are found to provide potential binding sites for metal ions in many physiological systems (Raper, 1985). The ttz ligand is also of great interest in the chemistry of coordination compounds since it can act either as a neutral molecule or as a deprotonated anion, possessing in both forms more than one donor atom (Raper, Oughtred & Nowell, 1983).

Our crystallographic studies of the Pd<sup>II</sup> (Kubiak & Głowiak, 1982) and Cd<sup>II</sup> (Kubiak & Głowiak, 1985) complexes have shown that ttz is S-bonded to the metal. To check the possibilities of metal–N bond formation by ttz (Preti & Tosi, 1976) we have studied also the interaction of Zn<sup>II</sup> with this ligand and the X-ray structure of such a system is presented here.

**Experimental.** Clear colourless crystals from zinc(II) chloride and ttz, at room temperature (293 K), dimensions 0.3 × 0.3 × 0.4 mm;  $D_m$  by flotation in carbon tetrachloride/ethylene bromide; monoclinic from Weissenberg photographs,  $P2_1/n$ ; Syntex  $P2_1$

computer-controlled four-circle diffractometer, scintillation counter, Mo  $K\alpha$  radiation, graphite monochromator; cell parameters by least squares from setting angles of 15 reflections; 3132 independent reflections; variable  $\theta/2\theta$  scan, scan rate 2.0–29.3° min<sup>-1</sup> (depending on intensity),  $2\theta_{\text{max}} = 55.0^\circ$ ; two standards measured every 30 reflections, no significant change; correction for Lorentz and polarization effects, not for absorption; 2486 reflections with  $F > 6\sigma(F)$  used for structure determination; index range  $h$  0–11,  $k$  0–14,  $l$  –18–17; calculations performed on a Nova 1200 computer with programs supplied by Syntex (1976); neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); heavy-atom method, full-matrix least squares (on  $F$ ); non-H atoms refined with anisotropic and H atoms with fixed positional and one overall isotropic thermal parameter ( $B = 4.8$  Å<sup>2</sup>), 136 variables;  $(\Delta/\sigma)_{\text{max}} = 0.1$ ;  $\Delta\rho_{\text{max}} = \pm 0.5$  e Å<sup>-3</sup>;  $R = 0.038$ ,  $wR = 0.046$ ,  $S = 3.70$ ,  $w = 1/\sigma^2(F)$ .

**Discussion.** Final atomic parameters are given in Table 1\* and interatomic distances and selected angles in Table 2. A view of the complex and the atom-numbering scheme is shown in Fig. 1. Fig. 2 is a stereoscopic view of the molecular packing.

The ttz ligands are monodentate and S-bonded to the Zn<sup>II</sup> ion is coordinated in a tetrahedral manner to two thiazolidine-2-thione ligands and two Cl atoms.

\* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, bond angles, least-squares-plane calculations and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43503 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.