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Structure of Bis(dimethylglyoximato-*N*,*N*′)(thiourea-*S*)copper(II)

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Abstract. Bis(2,3-butanedione dioximato-*N*,*N*′)(thiourea-*S*)copper(II), $[\mathrm{Cu(C_4H_7N_2O_2)_2(CH_4N_2S)}]$, $M_r = 369{\cdot}88$, monoclinic, $P2_1/c$, $a = 15{\cdot}117\,(14)$, $b = 11{\cdot}569\,(6)$, $c = 8{\cdot}882\,(4)$ Å, $\beta = 103{\cdot}73\,(6)^\circ$, $V = 1508{\cdot}9\,(1{\cdot}7)$ Å^3, $Z = 4$, $D_m = 1{\cdot}63$, $D_x = 1{\cdot}63$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 35{\cdot}261$ cm^{-1}, $F(000) = 764$, $T = 293$ K, $R = 0{\cdot}055$ for 1306 observed reflections. The coordination polyhedron around Cu$^{\mathrm{II}}$ is a distorted tetragonal pyramid with four N atoms of the dioximato ligands forming the basal plane [Cu—N distances in the range 1·946 (3)–1·956 (3) Å] and thiourea S-bonded at the apex [Cu—S 2·484 (1) Å].

Introduction. In our investigation of factors determining the stabilizing influence of dioximato ligands on Cu$^{\mathrm{II}}$ relative to Cu$^{\mathrm{I}}$, several dioximato copper(II) complexes with reductive ligands, *e.g.* thiourea and its derivatives, triphenylphosphine and triphenylarsine, have been prepared. In order to clarify the bonding of the reductive ligands in these complexes, the crystal structure determination of the title complex was undertaken.

Experimental. Dark brown prismatic crystals, 0·30 × 0·40 × 0·20 mm; D_m measured by flotation: Weissenberg photographs indicated space group $P2_1/c$, Syntex $P2_1$ diffractometer; cell parameters by least squares from 15 reflections with $9{\cdot}69 \le 2\theta \le 31{\cdot}02^\circ$; intensity measurements from θ–2θ scans carried out for $0 \le 2\theta \le 100^\circ$; range of *hkl*: $h\ -17 \rightarrow 17$, $k\ 0 \rightarrow 13$, $l\ 0 \rightarrow 10$. Two standard reflections after every 98 intensity measurements, no significant intensity variation; no correction for absorption; 2030 unique reflections; 1306 independent reflections with $I \ge 3\sigma(I)$; Cu position from Patterson function, other non-H atoms from difference syntheses. Methyl and thiourea H atoms in calculated positions, oxime H atoms from difference syntheses. Anisotropic full-matrix refinement (except H atoms) based on F. $R = 0{\cdot}055$, $wR = 0{\cdot}060$, $w = k/[\sigma^2(F_o) + g(F_o)^2]$, $k = 1{\cdot}0763$ and $g = 0{\cdot}003101$; $(\Delta/\sigma)_{\max}$ in final least-squares cycle 0·30; max. and min. heights in final difference Fourier synthesis = 0·8 and −0·4 e Å^{-3}. Calculations performed with *SHELX76* (Sheldrick, 1976); scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates of non-H atoms are given in Table 1; selected interatomic distances and bond angles are listed in Table 2.† The crystal structure consists of neutral square-pyramidal $\mathrm{Cu(Hdmg)_2(tu)}$ molecules with dioximato (Hdmg) ligands N-bonded in the equatorial plane and thiourea (tu) S-bonded in the apical position (Fig. 1).

The mean Cu—N distance [1·952 (4) Å] and the bond lengths and angles within the dioximato ligands agree well with those found in other five-coordinate complexes $\mathrm{Cu_2(Hdmg)_4}$ (Vaciago & Zambonelli, 1970), $\mathrm{Cu(Hdmg)_2(im)}$ (im = imidazole) (Morehouse, Polychronopoulou & Williams, 1980) and $\mathrm{Cu(Hdpg)_2(H_2O)}$ (Hdpg = diphenylglyoxime) (Boualam & Gleizes, 1983).

The O—H···O hydrogen bonds appear to be asymmetric with both H atoms bonded to the same

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† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52401 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters for non*-H *atoms, with e.s.d.'s in parentheses*

	x	y	z	B_{eq}*(Å^2)
Cu(1)	0·2419 (1)	0·0696 (1)	0·4136 (1)	3·41 (3)
N(1)	0·3510 (4)	0·1625 (5)	0·4783 (6)	3·53 (18)
N(2)	0·3151 (4)	0·0067 (5)	0·2793 (6)	3·31 (17)
N(3)	0·1636 (5)	0·1677 (5)	−0·5043 (7)	3·89 (18)
N(4)	0·1227 (4)	0·0269 (5)	0·2882 (7)	3·85 (19)
O(1)	0·3594 (4)	0·2495 (4)	0·5859 (6)	4·84 (17)
O(2)	0·2830 (4)	−0·0785 (5)	0·1773 (6)	5·16 (17)
O(3)	0·1989 (4)	0·2404 (5)	0·6225 (7)	5·36 (19)
O(4)	0·1083 (4)	−0·0538 (5)	0·1699 (6)	5·27 (20)
C(1)	0·4182 (5)	0·1392 (6)	0·4168 (8)	3·83 (25)
C(2)	0·3964 (5)	0·0464 (6)	0·2998 (8)	3·32 (20)
C(3)	0·5051 (6)	0·2021 (7)	0·4535 (10)	4·94 (28)
C(4)	0·4640 (5)	0·0054 (7)	0·2150 (9)	4·29 (25)
C(5)	0·0770 (5)	0·1571 (6)	0·4523 (9)	3·75 (22)
C(6)	0·0540 (5)	0·0711 (6)	0·3244 (8)	3·73 (22)
C(7)	0·0101 (7)	0·2215 (8)	0·5134 (12)	6·36 (33)
C(8)	−0·0430 (5)	0·0455 (9)	0·2470 (10)	5·77 (30)
S(1)	0·2613 (2)	−0·1016 (2)	0·5855 (2)	4·35 (6)
C(9)	0·2750 (5)	−0·0783 (7)	0·7782 (8)	3·77 (21)
N(5)	0·2718 (5)	0·0278 (7)	0·8375 (7)	5·16 (23)
N(6)	0·2888 (5)	−0·1674 (7)	0·8717 (8)	5·71 (22)

$$*B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Cu(1)—N(1)	1·946 (3)	N(1)—Cu(1)—N(2)	79·7 (1)
Cu(1)—N(2)	1·956 (3)	N(1)—Cu(1)—N(3)	96·5 (1)
Cu(1)—N(3)	1·951 (3)	N(1)—Cu(1)—N(4)	156·8 (1)
Cu(1)—N(4)	1·954 (3)	N(2)—Cu(1)—N(3)	163·6 (1)
Cu(1)—S(1)	2·484 (1)	N(2)—Cu(1)—N(4)	97·9 (1)
N(1)—O(1)	1·377 (4)	N(3)—Cu(1)—N(4)	79·2 (1)
N(2)—O(2)	1·354 (4)	S(1)—Cu(1)—N(1)	106·9 (1)
N(3)—O(3)	1·357 (4)	S(1)—Cu(1)—N(2)	94·4 (1)
N(4)—O(4)	1·388 (4)	S(1)—Cu(1)—N(3)	102·0 (1)
N(1)—C(1)	1·294 (5)	S(1)—Cu(1)—N(4)	96·3 (1)
C(1)—C(2)	1·481 (5)	Cu(1)—N(1)—C(1)	117·3 (3)
C(2)—N(2)	1·292 (5)	Cu(1)—N(1)—O(1)	123·0 (2)
C(1)—C(3)	1·476 (6)	Cu(1)—N(2)—C(2)	116·2 (2)
C(2)—C(4)	1·487 (5)	Cu(1)—N(2)—O(2)	121·1 (2)
N(3)—C(5)	1·292 (5)	N(1)—C(1)—C(2)	112·4 (3)
C(5)—C(6)	1·493 (6)	N(2)—C(2)—C(1)	114·1 (3)
C(6)—N(4)	1·269 (5)	Cu(1)—N(3)—C(5)	117·5 (3)
C(5)—C(7)	1·464 (6)	Cu(1)—N(3)—O(3)	121·1 (3)
C(6)—C(8)	1·502 (6)	Cu(1)—N(4)—C(6)	117·2 (3)
S(1)—C(9)	1·702 (4)	Cu(1)—N(4)—O(4)	124·4 (2)
C(9)—N(5)	1·345 (5)	N(3)—C(5)—C(6)	111·9 (3)
C(9)—N(6)	1·314 (5)	N(4)—C(6)—C(5)	113·9 (4)
O(1)···O(3)	2·525 (9)	Cu(1)—S(1)—C(9)	117·6 (2)
O(2)···O(4)	2·641 (9)	S(1)—C(9)—N(5)	122·3 (3)
		S(1)—C(9)—N(6)	118·5 (3)
		N(5)—C(9)—N(6)	119·1 (4)

dimethylglyoxime moiety. The O(3) atom is further involved in an intramolecular hydrogen bond with the thiourea ligand [O(3)···N(5) 3·148 (9) Å].

The Cu atom is displaced by 0·334 (1) Å from the basal plane towards the S atom at the apex. This value is comparable with those of 0·273–0·353 Å found in the above cited five-coordinate dioximato–copper(II) complexes. The Cu(1)—S(1) bond length [2·484 (1) Å] is longer than those in trigonal bipyramidal thiourea–copper(II) complexes where the S atom of thiourea occupies a coordination site in the trigonal plane; for example Cu—S bond lengths of 2·404, 2·369 and 2·344 Å are found in $[Cu(phen)_2(tu)](ClO_4)_2.2H_2O$ (Ferrari, Fava & Montenero, 1975), $[Cu(bpy)_2(tu)](ClO_4)_2$ and $[Cu(ptd)(tu)](ClO_4)_2$ [ptd = *N*,*N*′-di(2-pyridylmethylene)tetramethylenediamine] (Ferrari, Corradi, Fava, Palmieri, Nardelli & Pelizzi, 1973), respectively. The Cu(1)—S(1) bond is also much longer than the Cu—S distance of 2·273 Å involving the thiourea ligand in the basal plane of the dimeric square pyramidal [Cu(salalgly)(tu)] (H_2salalgly = *N*-salicylideneglycine) complex (Pavelčík, Krätsmár-Šmogrovič, Švajlenová & Majer, 1981).

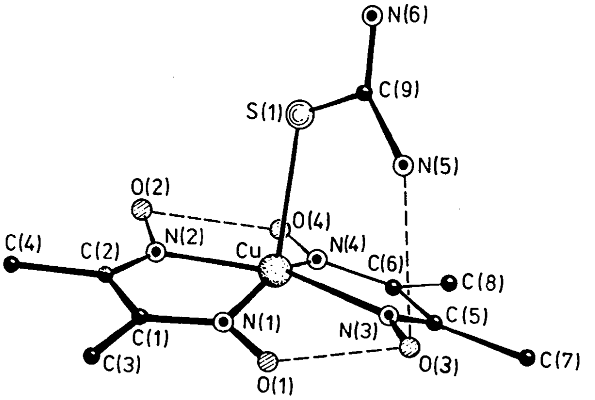

Fig. 1. The structure of $[Cu(Hdmg)_2(tu)]$.

The Cu(1)—S(1)—C(9) angle [117·6 (2)°] is the largest, whereas the dihedral angle between the thiourea molecule and CuSC planes (2·68°) is the smallest so far found for thiourea–copper(II) complexes (Valigura, Ondrejovič & Krätsmar-Šmogrovič, 1987).

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