

(Lumme, Lindroos & Lindell, 1988), where the equatorial plane consists of three O atoms, and one of the Cu—O bonds is distinctly longer. The asymmetry of the equatorial plane is due to the steric effect of the large quinoxaline molecules.

The title compound has an infinite double-chain structure in which quinoxaline molecules form bridges between Cu atoms along the *b* axis. Two such chains are linked together with two Cl atoms, so that the distance between the Cu atoms in different chains is 3.580 (1) Å (Fig. 2). The Cu—Cu distance is similar to dimeric chloro-bridged structures (Marsh, Hatfield & Hodgson, 1982; Klein, Stevens, O'Connor, Majeste & Trefonas, 1983). Two hydrogen bonds connect the double chains to each other in the direction of the *a* and *c* axes, and there is a further hydrogen bond in the direction of the chain.

The aromatic ring of the quinoxaline molecule is planar, the maximum deviation from the least-squares plane being 0.008 (3) Å for C(3). The heterocyclic ring exhibits a slight boat conformation with the N atoms  $-0.026$  (2) Å from the least-squares plane. The C atoms are coplanar [deviations 0.013 (2) and 0.012 (2) Å for C(1) and C(4) respectively]. The aromatic and heterocyclic rings are slightly tilted toward each other, so that the quinoxaline molecule has an open-book form. The dihedral angle is 4.9 (5)°. The bond lengths and angles in the quinoxaline molecule are similar to those measured in other structures (Lumme, Lindroos & Lindell,

1987, 1988; Padmaja, Ramakumar & Viswamitra, 1987; Lipkowski, Andreetti & Sgarabotto, 1977).

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## Structure of Bis(3,4-hexanedione dioximato)bis(thiourea)copper(II)

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**Abstract.**  $[\text{Cu}(\text{C}_6\text{H}_{11}\text{N}_2\text{O}_2)_2(\text{CH}_4\text{N}_2\text{S})_2]$ ,  $M_r = 502.11$ , monoclinic,  $C2/c$ ,  $a = 15.065$  (4),  $b = 10.216$  (3),  $c = 15.513$  (4) Å,  $\beta = 103.86$  (2)°,  $V = 2318.0$  (11) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.43$ ,  $D_x = 1.44$  g cm<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha) = 1.54178$  Å,  $\mu = 32.77$  cm<sup>-1</sup>,  $F(000) = 1052$ , room temperature,  $R = 0.034$ ,  $wR = 0.037$  for 985 reflections with  $I \geq 3\sigma(I)$ . The structure consists of centro-

symmetric monomeric molecules  $[\text{Cu}(\text{hd})_2(\text{tu})_2]$  (hd = 3,4-hexanedione dioximate anion, tu = thiourea). The coordination polyhedron of copper(II) is a square bipyramid with four dioximate N atoms in the equatorial plane and two thiourea S atoms in axial positions, in contrast with the pentacoordinate copper dioximate complexes reported so far.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ ) for non-H atoms, with e.s.d.'s in parentheses

	x	y	z	$U_{\text{eq}}^*$
Cu	2500	7500	0	530 (5)
S	2517 (1)	0365 (1)	0188 (1)	583 (5)
N(1)	3246 (3)	7657 (3)	9136 (2)	375 (14)
N(2)	1285 (2)	7668 (3)	9211 (2)	375 (14)
N(3)	2875 (3)	2229 (4)	1384 (4)	478 (14)
N(4)	2679 (4)	0240 (5)	1914 (3)	593 (19)
O(1)	2137 (2)	7305 (3)	1745 (2)	442 (11)
O(2)	1111 (3)	7749 (3)	8296 (2)	500 (13)
C(1)	0610 (3)	7552 (3)	9570 (3)	358 (18)
C(2)	9643 (4)	7461 (15)	9052 (4)	518 (21)
C(3)	9392 (5)	6047 (7)	8803 (5)	743 (27)
C(4)	4119 (3)	7551 (3)	9449 (3)	359 (18)
C(5)	4787 (4)	7441 (4)	8883 (4)	505 (21)
C(6)	4990 (5)	6019 (6)	8729 (5)	704 (27)
C(9)	2699 (3)	0968 (4)	1225 (2)	585 (6)

$$*U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

Table 2. Selected interatomic distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ ), with e.s.d.'s in parentheses

Cu—N(1)	1.951 (1)	N(1)—Cu—N(2)	99.8 (1)
Cu—N(2)	1.950 (1)	Cu—N(1)—O(1)	121.4 (1)
N(1)—O(1)	1.351 (2)	Cu—N(1)—C(4)	115.9 (1)
N(2)—O(2)	1.382 (1)	Cu—N(2)—O(2)	124.6 (1)
N(1)—C(4)	1.293 (1)	Cu—N(2)—C(1)	116.4 (1)
N(2)—C(1)	1.277 (1)		
C(1)—C(4)	1.482 (1)		
C(1)—C(2)	1.489 (1)	N(2)—C(1)—C(2)	123.3 (1)
C(2)—C(3)	1.519 (1)	N(1)—C(4)—C(5)	123.6 (1)
C(4)—C(5)	1.491 (1)	C(1)—C(2)—C(3)	110.4 (1)
C(5)—C(6)	1.514 (1)	N(1)—C(4)—C(5)	123.7 (1)
Cu—S	2.941 (1)		
S—C(9)	1.682 (1)	C(4)—C(5)—C(6)	110.8 (1)
C(9)—N(3)	1.326 (1)	Cu—S—C(9)	117.1 (1)
C(9)—N(4)	1.308 (1)	N(3)—C(9)—N(4)	116.3 (1)

**Introduction.** In our investigation of the stabilizing influence of dioxime ligands on copper(II) relative to copper(I) in the presence of reducing ligands, several complexes of composition  $[\text{Cu}(\text{dioximate})_2L_n]$  ( $L =$  thiourea or its methyl derivatives,  $n = 1, 2$ ) have been prepared. Magnetic and ESR measurements confirmed the presence of copper in oxidation state II, and electronic and IR spectra indicated chelate bonding of dioximate ligands. In order to clarify the bonding mode of the thiourea ligands, the crystal structure determination of the title compound was undertaken.

**Experimental.** The  $[\text{Cu}(\text{hd})_2(\text{tu})_2]$  complex was prepared by reaction of stoichiometric amounts of  $\text{Cu}(\text{hd})_2$  and thiourea in carbon tetrachloride-ethanol at room temperature. Cooling the reaction mixture to 263 K yielded the product as crystals of satisfactory quality. Prism-shaped crystal, dark brown colour,  $0.4 \times 0.3 \times 0.2$  mm;  $D_m$  measured by flotation; cell parameters refined on Syntex  $P2_1$  four-circle diffractometer with graphite-monochromated Cu  $K\alpha$  radiation by least squares from 15 reflections

with  $11.4 \leq \theta \leq 29.2^\circ$ . Absorption and extinction ignored;  $0 \leq 2\theta \leq 100^\circ$ ;  $hkl$  range 0, 0, -15 to 15, 11, 15. Two standard reflections, checked after every 98 measurements, decreased in intensity by 15% during the course of the experiment, 985 independent reflections with  $I \geq 3\sigma(I)$  (392 unobserved reflections),  $\omega/2\theta$  scans. Cu position from Patterson function; other non-H atoms from Fourier syntheses; H atoms from difference syntheses. Anisotropic full-matrix refinement for non-H atoms based on  $F$  (isotropic refinement for H atoms).  $R = 0.034$ ,  $wR = 0.037$ ,  $w = k/[\sigma^2(F_o) + g(F_o)^2]$  ( $k = 1.0000$ ,  $g = 0.0047$ );  $(\Delta/\sigma)_{\text{max}}$  in final least-squares cycle 0.50; max. and min. values of residual  $\Delta\rho = 0.20$  and  $-0.39 \text{ e \AA}^{-3}$ . Calculations performed with SHELX76 program system (Sheldrick, 1976); scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Atomic coordinates are listed in Table 1. Table 2 gives the bond distances and angles.\* The crystal structure consists of monomeric centrosymmetric molecules  $[\text{Cu}(\text{hd})_2(\text{tu})_2]$  with a  $\text{CuN}_4\text{S}_2$  chromophore (Fig. 1). The molecules are hydrogen bonded into layers parallel to (100). The coordination polyhedron of the  $\text{Cu}^{\text{II}}$  atom is a square bipyramid with dioximate N atoms in the equatorial plane and thiourea S atoms in axial positions. The average Cu—N distance [1.950 (1)  $\text{\AA}$ ] agrees well with the value found in pentacoordinate copper(II) dioximate complexes {1.956 (1), 1.944 (3) and 1.952 (4)  $\text{\AA}$  for

\* 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 52986 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

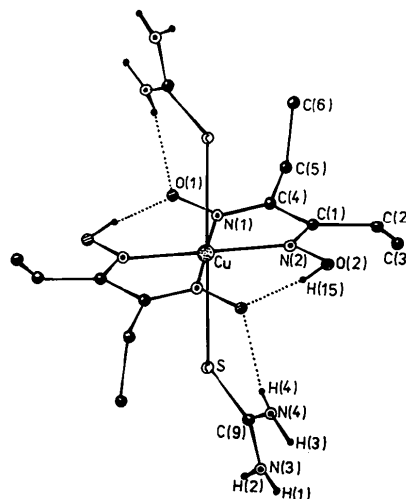


Fig. 1. Molecular structure of  $[\text{Cu}(\text{hd})_2(\text{tu})_2]$ .

[Cu(Hdmg)<sub>2</sub>(im)] (Morehouse, Polychronopoulou & Williams, 1980), [Cu(Hdpg)<sub>2</sub>(H<sub>2</sub>O)] (Falk, Ivanova, Roos & Vännard, 1970) (Hdmg – dimethylglyoximate, im – imidazole, Hdpg – dipropylglyoximate) and [Cu<sub>2</sub>(Hdmg)<sub>4</sub>] (Vaciego & Zambonelli, 1970)}.

The Cu—S distance of 2.941 (1) Å is similar to that found in the complex [Cu(pic)<sub>2</sub>(tu)<sub>2</sub>] [2.943 (1) Å, pic – picolate] (Ferrari, Capacchi, Fava, Montenero & Nardelli, 1972) where the thiourea molecules are oriented almost parallel to the equatorial plane, in contrast with the present complex where the angle between the equatorial and thiourea planes is 81.3°.

The intramolecular O—H—O hydrogen bonds bridging the dioxime ligands are asymmetric [O(1)···O(2) = 2.656 (6), O(2)—H(15) = 0.79 (8), O(1)···H(15) = 1.87 (8) Å]. The O(1) atom is also involved both in a second intramolecular hydrogen bond [O(1)···N(2) = 3.089 (5) Å] and in two intermolecular hydrogen bonds with thiourea ligands.

Hexacoordination has not previously been structurally confirmed for copper dioximate complexes, although it has been assumed for a water adduct (Falk, Ivanova, Roos & Vännard, 1970); otherwise only pentacoordinate complexes have been reported. The complex [Cu(hd)<sub>2</sub>(tu)<sub>2</sub>] thus represents a new structural type among compounds of this class.

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## Structure of Two Crystalline Forms of $\mu$ -(1,2-Phenylenediaminato-*N,N,N',N'*)-bis[dicarbonyl(triphenylphosphine)ruthenium(I)](*Ru—Ru*) [ $\{\text{Ru}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\}_2$ ]- $\{\mu$ -1,2- $\text{C}_6\text{H}_4(\text{NH})_2$ }]

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**Abstract.**  $\{\{\text{Ru}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\}_2\{\mu$ -1,2- $\text{C}_6\text{H}_4(\text{NH})_2\}\}_2$ - $\frac{2}{3}\text{C}_7\text{H}_8$  (*A*),  $\text{C}_{46}\text{H}_{36}\text{N}_2\text{O}_4\text{P}_2\text{Ru}_2\frac{2}{3}\text{C}_7\text{H}_8$ ,  $M_r = 1006.3$ , monoclinic,  $P2_1/c$ ,  $a = 10.040$  (4),  $b = 17.802$  (2),  $c = 27.279$  (9) Å,  $\beta = 98.26$  (3)°,  $V = 4825$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.39$  g cm<sup>-3</sup>, Mo  $K\alpha$  radiation (graphite crystal monochromator,  $\lambda = 0.71073$  Å),  $\mu(\text{Mo } K\alpha) = 7.21$  cm<sup>-1</sup>,  $F(000) = 2037$ ,  $T = 293$  K. Final conventional  $R$  factor = 0.049 for 3908 'observed' reflections and 512 variables.  $\{\{\text{Ru}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\}_2$ - $\{\mu$ -1,2- $\text{C}_6\text{H}_4(\text{NH})_2\}\}_2\cdot\text{C}_9\text{H}_{12}$  (*B*),  $\text{C}_{46}\text{H}_{36}\text{N}_2\text{O}_4\text{P}_2\text{Ru}_2\cdot\text{C}_9\text{H}_{12}$ ,  $M_r = 1065.1$ , monoclinic,  $P2_1/m$ ,  $a = 9.9994$  (1),  $b = 25.477$  (2),  $c = 10.515$  (2) Å,  $\beta =$

114.51 (1)°,  $V = 2437.4$  (5) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.45$  g cm<sup>-3</sup>, Mo  $K\alpha$  radiation (graphite crystal monochromator,  $\lambda = 0.71073$  Å),  $\mu(\text{Mo } K\alpha) = 7.17$  cm<sup>-1</sup>,  $F(000) = 1084$ ,  $T = 293$  K. Final conventional  $R$  factor = 0.036 for 5414 'observed' reflections and 332 variables. The above structures correspond to two different crystalline forms (depending on the solvent) adopted by the compound previously formulated as  $[\text{Ru}_2\{\mu$ -1,2- $\text{C}_6\text{H}_4(\text{NH})_2\}(\text{CO})_2(\text{PPh}_3)_2]$  (*C*). The asymmetric unit contents are an entire formula unit in structure (*A*) and a half formula unit in structure (*B*). The Ru—Ru lengths found in both cases are equal and significantly short (2.56 Å).

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