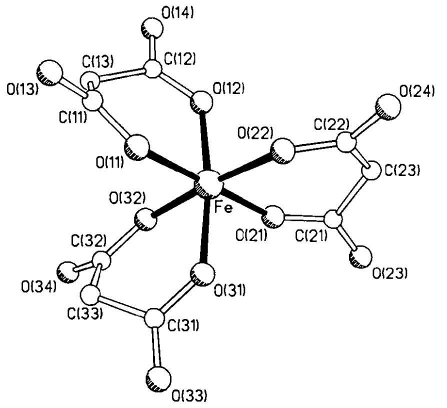

Fig. 1. Structure of the $[Fe(malonate)_3]^{3-}$ anion, viewed along the approximate threefold axis. H atoms are omitted.

anion has approximate D_3 symmetry, as is anticipated for the various classes of compounds for which this is taken as a model.

Each of the three six-membered chelate rings has a boat conformation, the Fe and opposite C atoms both lying on the same side of the mean plane of the other four atoms (Fig. 1). This contrasts with the tris(malonato)manganate(III) ion {studied in $K_3[Mn(malonate)_3].2H_2O$}, for which two rings are boats and the third, lying across a crystallographic twofold rotation axis, has the two O atoms above and below the exact plane of the other four atoms (Lis, Matuszewski & Jeżowska-Trzebiatowska, 1977).

The water molecules are involved in extensive hydrogen bonding with the O atoms of the malonate ligands.

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References

Brown, L. D., Fronczek, F. R., Isied, S. S., Nibert, J. H. & Raymond, K. N. (1976). *J. Am. Chem. Soc.* **98**, 1767–1774.
Callaby, D. R. & Brotto, M. (1970). *J. Photogr. Sci.* **18**, 8–12.
Clegg, W. (1981). *Acta Cryst.* A**37**, 22–28.
Eldick, R. van & van der Berg, J. A. (1970). *J. S. Afr. Chem. Inst.* **23**, 96–104.
Ghosh, J. C. & Mitra, B. N. (1928). *J. Indian Chem. Soc.* **5**, 191–202.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
Isied, S. S., Kuo, G. & Raymond, K. N. (1976). *J. Am. Chem. Soc.* **98**, 1763–1767.
Kosar, J. (1965). In *Light Sensitive Systems*. New York: Wiley–Interscience.
Lis, T., Matuszewski, J. & Jeżowska-Trzebiatowska, B. (1977). *Acta Cryst.* B**33**, 1943–1946.
Powell, A. K. & Ware, M. J. (1984). Personal communication.
Sheldrick, G. M. (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Univ. of Göttingen.

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Structure of Bis[*N*,*N*-bis(2-hydroxyethyl)dithiocarbamato]copper(II), $[Cu(C_5H_{10}NO_2S_2)_2]$

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Abstract. $M_r = 423\cdot5$, triclinic, $P\bar{1}$, $a = 11\cdot946$ (3), $b = 7\cdot826$ (3), $c = 9\cdot789$ (4) Å, $\alpha = 69\cdot65$ (3), $\beta = 83\cdot06$ (3), $\gamma = 81\cdot78$ (3)°, $V = 846\cdot66$ Å^3, $Z = 2$, $D_x = 1\cdot66$ Mg m^{-3}, λ(Mo $K\alpha$) = $0\cdot71069$ Å, $\mu = 1\cdot706$ mm^{-1}, $F(000) = 434$, $T = 293$ K, $R = 0\cdot086$ for 1654 unique observed reflections. The pair of centrosymmetrically related molecules form a dimer. Intradimer short contacts observed [Cu···Cu: 3·451 (2), Cu···S: 2·773 (4) Å] are the shortest reported so far in dimeric Cu^{II} dithiocarbamate complexes. The copper

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atom is four-coordinated by a pair of ligands with an average Cu—S distance of 2·322 (4) Å. The CuS_4 moiety is planar to 0·261 (1) Å.

Introduction. Structure types of Cu^{II} dithiocarbamates $Cu(S_2CN{<}^{R_1}_{R_2})_2$ fall into two categories featuring either monomeric planar or weakly dimeric tetragonal-pyramidal coordination of sulphur atoms around the copper atom. Amongst the dimeric types, the present compound features the strongest dimer interaction as seen from the structural studies. This is expected to influence the magnetic property of the compound. This aspect is being taken up shortly.

Experimental. The title compound was prepared following the method reported by Sejekan & Aravamudan (1978) and recrystallized from methanol. Brownish crystals, 0·075 × 0·125 × 0·525 mm, Enraf–Nonius CAD-4 diffractometer, cell constants from least-squares analysis of 23 high-angle reflections, range of 2θ from 2 to 50° and reflections h: 0 to 14, k: −9 to 9, l: −11 to 11, Lorentz–polarization corrections, but no absorption correction. Insignificant intensity fluctuations in standard reflections $23\bar{2}$ and 531 monitored every hour during data collection; 1751 reflections with $I > 3\sigma(I)$ considered observed. $R_{\rm int} = 0{\cdot}03$ from merging 97 equivalent reflections. Structure determined using *SHELX*76 (Sheldrick, 1976) program and heavy-atom technique. Cromer & Mann (1968), Stewart, Davidson & Simpson (1965) and Cromer & Liberman (1970) were the sources for non-hydrogen and hydrogen atomic scattering factors and non-hydrogen anomalous-dispersion-correction factors respectively. All but two hydrogen atoms fixed geometrically. Final $R = 0{\cdot}086$, $wR = 0{\cdot}092$ with $w = 1{\cdot}00/[\sigma^2(F_o) + 0{\cdot}00015\,|F_o|^2]$, number of parameters refined = 233, non-hydrogen anisotropic, hydrogen isotropic. Function minimized $\sum w|\Delta F|^2$, average shift/e.s.d. = 0·186, maximum shift/e.s.d. = 0·628. Final difference Fourier map featured no peak higher than 1·29 e Å^{-3}.

Discussion. Tables 1 and 2* give the atomic coordinates and their bond parameters. Figs. 1 and 2 depict the molecule and dimer involving the two centrosymmetrically related copper atoms. The pairs of centrosymmetrically related molecules within the unit cell form a dimer, the Cu···Cu distance being 3·451 (2) Å. Each copper atom is four-coordinated by the pair of chelating dtc ligands with an average Cu—S distance of 2·322 (4) Å. The CuS_4 moiety is planar to 0·261 (1) Å. In addition, there is a weak intradimer Cu···S′ interaction [2·773 (4) Å compared to the van der Waals Cu···S = 3·9 Å], with the sulphur atom occupying an apical position. The long Cu···S′ bond is nearly normal to the basal plane. The coordination around Cu can be best described as tetragonal pyramidal, the bite and the non-bite S—S distances being 2·874 (6) and 3·590 (5) Å and bite angle

Table 1. *Fractional coordinates* (× 10^4) *of non-hydrogen atoms and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_{i=1}^{3} U_{ii}.$$

	x	y	z	$U_{\rm eq}$
Cu	4963 (1)	1982 (2)	3499 (1)	38 (<1)
S(1)	4114 (3)	3398 (5)	5155 (4)	42 (2)
S(2)	3448 (3)	284 (5)	4641 (4)	43 (2)
S(3)	5439 (3)	982 (5)	1512 (4)	44 (2)
S(4)	6018 (3)	4203 (5)	1898 (4)	40 (2)
C(1)	6111 (10)	2928 (18)	751 (14)	37 (7)
N(1)	6667 (9)	3371 (15)	−550 (12)	36 (6)
C(2)	7150 (14)	5129 (21)	−1166 (16)	49 (9)
C(3)	6576 (14)	2318 (24)	−1536 (17)	58 (10)
C(4)	8349 (16)	5001 (30)	−705 (28)	86 (14)
C(5)	7354 (15)	538 (28)	−1213 (21)	71 (11)
O(1)	8515 (12)	747 (24)	−1287 (23)	115 (14)
O(2)	9148 (12)	3915 (22)	−1247 (24)	130 (5)
C(6)	3148 (11)	1905 (18)	5513 (14)	39 (5)
N(2)	2197 (10)	1925 (17)	6415 (13)	51 (4)
C(7)*	1157 (12)	971 (15)	6281 (14)	66 (1)
C(8)	2011 (14)	3230 (22)	7243 (18)	55 (9)
C(9)*	1229 (12)	−528 (15)	7679 (14)	67 (1)
C(10)	1524 (15)	5128 (30)	6290 (26)	78 (14)
O(3)	183 (19)	−1462 (27)	7797 (25)	147 (6)
O(4)	368 (18)	5335 (29)	6625 (25)	143 (6)

* Refined isotropically.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Cu—S(1)	2·326 (4)	Cu—S(2)	2·335 (4)
Cu—S(3)	2·320 (5)	Cu—S(4)	2·307 (4)
S(1)—C(6)	1·680 (15)	S(2)—C(6)	1·736 (16)
C(6)—N(2)	1·354 (17)	N(2)—C(7)	1·578 (20)
N(2)—C(8)	1·489 (25)	C(7)—C(9)	1·463 (15)
C(9)—O(3)	1·509 (28)	C(8)—C(10)	1·528 (25)
C(10)—O(4)	1·381 (28)	S(3)—C(1)	1·714 (14)
S(4)—C(1)	1·728 (17)	C(1)—N(1)	1·319 (16)
N(1)—C(3)	1·492 (25)	N(1)—C(2)	1·468 (19)
C(3)—C(5)	1·516 (33)	C(5)—O(1)	1·410 (22)
C(2)—C(4)	1·533 (28)	C(4)—O(2)	1·369 (30)
S(1)—Cu—S(2)	76·5 (2)	S(4)—Cu—S(3)	76·5 (2)
S(1)—Cu—S(4)	102·2 (2)	Cu—S(3)—C(1)	85·4 (5)
S(2)—Cu—S(3)	100·3 (2)	Cu—S(4)—C(1)	85·5 (5)
Cu—S(1)—C(6)	84·7 (6)	S(3)—C(1)—N(1)	123·5 (9)
Cu—S(2)—C(6)	83·2 (6)	S(4)—C(1)—N(1)	123·8 (9)
S(1)—C(6)—S(2)	115·2 (8)	S(3)—C(1)—S(4)	112·6 (8)
S(1)—C(6)—N(2)	123·7 (9)	C(1)—N(1)—C(3)	119·7 (10)
S(2)—C(6)—N(2)	121·1 (9)	C(1)—N(1)—C(2)	120·0 (9)
C(6)—N(2)—C(7)	119·7 (9)	C(3)—N(1)—C(2)	118·7 (10)
C(6)—N(2)—C(8)	119·8 (10)	N(1)—C(3)—C(5)	113·9 (12)
N(2)—C(7)—C(9)	97·0 (9)	N(1)—C(2)—C(4)	112·3 (12)
N(2)—C(8)—C(10)	110·9 (13)	C(3)—C(5)—O(1)	114·4 (14)
C(7)—N(2)—C(8)	118·6 (10)	C(2)—C(4)—O(2)	114·5 (16)
C(8)—C(10)—O(4)	108·8 (16)		
C(7)—C(9)—O(3)	103·3 (11)		

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* Lists of structure factors, anisotropic thermal parameters, hydrogen-atom coordinates and least-squares-planes' parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42138 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

S—Cu—S 76·5 (2)°. The dimer is crystallographically required to possess a centre of symmetry, so that a pair of parallel Cu···S interactions results (Fig. 2).

Similar dimeric structures have been reported in $\mathrm{Cu^{II}}$ bis(dithiocarbamates) in which both R_1 and R_2 are the alkyl substituents, ethyl (compound I) (Bonamico, Dessy, Mugnoli, Vaciago & Zambonelli, 1965), *n*-propyl (Pignedoli & Peyronel, 1962) and *n*-butyl (compound II) (Boyd, Mitra, Raston, Rowbottom & White, 1981). In the half-dimer unit in the present compound (compound III), the copper atom is displaced (as in I and II) out of the plane of the four sulphur atoms by 0·261 (1) Å towards the centrosymmetrically related dimer molecule. This distortion arises due to the fifth Cu···S′ contact. Among the four Cu—S bond lengths, the Cu—S(2) (2·335 Å) involving the apical sulphur to the centrosymmetrically related copper atom is slightly but significantly longer than the mean Cu—S length 2·322 (6) Å (as in I and II) and the Cu—S(4) (2·307 Å) is significantly shorter than the mean length.

Resonance delocalization lends partial double-bond character to the C—N bond and leads to near equalization of lengths of the two C—S bonds in the dtc ligands in their metal complexes. However, in the present compound, resonance delocalization appears to be restricted to one of the ligands, namely the one containing S(3), S(4), C(1) and N(1). In the other ligand, the C(6)—S(1) and C(6)—S(2) distances are quite unequal (1·680, 1·736 Å) and also the C(6)—N(2) distance is much longer (1·354 Å) than observed in ligated dtc groups (1·32 Å). The averages of the N—C, C—C and C—O distances are 1·507 (22), 1·488 (26) and 1·415 (27) Å and are in reasonable agreement with those reported in $[\mathrm{Cu(S_2CNMePh)_2}]$ (Martin, Newman, Robinson & White, 1972), $[\mathrm{Cu\{S_2CN(CH_2)_4\}_2}]$ (Newman, Raston & White, 1973) and $[\mathrm{Cu(S_2CNBu_2)_2}]$ (Boyd *et al.*, 1981). The $\mathrm{S_2CNC_2}$ parts of the ligands are planar [r.m.s. deviation = 0·36 (1) Å]. The two ligand planes intersect at Cu making an angle of 23·5 (2)°. Planarity and bonding parameters around C(1), N(1), C(6) and N(2) indicate conjugation with sp^2 hybridization of their valence orbitals. Compounds (I) and (II) exist as monomers in solution. The oxygen atoms of all the $\mathrm{C_2H_4OH}$ groups are well outside even the weakest bonding coordination to the copper atom.

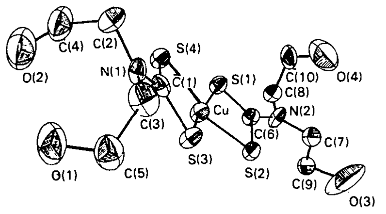

Fig. 1. Perspective view of the molecule.

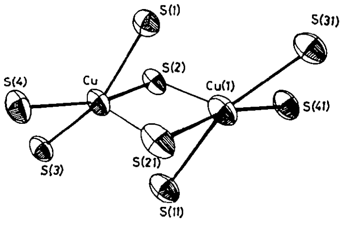

Fig. 2. View of the bridging plane of the two copper atoms and their immediate neighbours.

Table 3. *Comparison of interactions in compounds* (I), (II) *and* (III)

	Compound (I)	Compound (II)	Compound (III) (present study)
Cu···Cu(Å)	3·588	3·785	3·451 (2)
Cu···S(Å)	2·851	2·899 (4)	2·773 (4)
S···S(Å)	3·867	3·888 (4)	3·857 (5)
Cu···S···Cu′ (°)	86·9	92·1	84·5 (2)

There are two short contacts within the dimer, Cu···C(6) [3·43 (1) Å] and S(3)···N(2) [3·69 (1) Å]. There is a short (less than van der Waals) interdimer S···S contact of 3·857 (5) Å shorter than 3·888 (4) Å found in (II). In addition, there is an O(4)···O(2)($\bar{x}$, 1−*y*, 1−*z*) contact of 2·412 (2) Å showing the presence of a hydrogen bond. The position of the involved hydrogen atom could not be located.

Amongst compounds (I), (II) and (III) (Table 3) the present compound (III) has the shortest Cu···Cu, Cu···S (intradimer) and S···S (interdimer) contacts. There is a large variation in the bridging angle Cu···S···Cu′, indicating that the coordination geometry around the copper atom in all these structures is similar, but not identical.

It is interesting to compare the structure of $\mathrm{Ni^{II}}$ and $\mathrm{Cu^{II}}$ complexes of various dithiocarbamates. The $\mathrm{Ni^{II}}$ complexes are all monomeric, diamagnetic and feature planar $\mathrm{NiS_4}$ units, with Ni occupying an inversion centre as reported in $[\mathrm{Ni(S_2CNEt_2)_2}]$ (Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965), $[\mathrm{Ni(S_2CNPr^n_2)_2}]$ (Peyronel & Pignedoli, 1967), $[\mathrm{Ni(S_2CNHMe)_2}]$ (Newman & White, 1972), $[\mathrm{Ni(S_2CNMePh)_2}]$ (Martin *et al.*, 1972) and $[\mathrm{Ni\{S_2CN(C_2H_4OH)_2\}_2}]$ (Ramalingam, Radha, Aravamudan, Mahadevan, Subramanyam & Seshasayee, 1984), with the exception of $[\mathrm{Ni(S_2CNH_2)_2}]$ (Gasparri, Nardelli & Villa, 1967) in which the nickel atom does not occupy the centre of inversion and neither is the $\mathrm{NiS_4}$ group planar. Intermolecular S···C and S···H short contacts influence packing in these monomeric structures. There are no close S···S or metal···S contacts. In $\mathrm{Cu^{II}}$ dtc complexes, with the exception of $[\mathrm{Cu(S_2CNMePh)_2}]$ (Martin *et al.*, 1972), there is a tendency to form dimers in the solid state. The monomeric $[Ni(S_2CNMePh)_2]$ and $[Cu(S_2CNMePh)_2]$ are isostructural. In reported structures such as $[Cu(S_2CNPr^n_2)_2]$ (Pignedoli & Peyronel, 1962), (I), (II) and (III) there is an intermolecular Cu···S contact less than 2·9 Å and dimerization occurs *via* this Cu···S interaction. The bridging S occupies the fifth coordination site of Cu, with the nearly flat molecules approaching each other in a parallel fashion. The formation of such a dimer is prevented in $[Cu(S_2CNMePh)_2]$ by the phenyl rings lying normal to the plane of the molecule.

References

BONAMICO, M., DESSY, G., MARIANI, C., VACIAGO, A. & ZAMBONELLI, L. (1965). *Acta Cryst.* **19**, 619–626.

BONAMICO, M., DESSY, G., MUGNOLI, A., VACIAGO, A. & ZAMBONELLI, L. (1965). *Acta Cryst.* **19**, 886–897.

BOYD, P. W. D., MITRA, S., RASTON, C. L., ROWBOTTOM, G. L. & WHITE, A. H. (1981). *J. Chem. Soc. Dalton. Trans.* pp. 13–22.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

GASPARRI, G. F., NARDELLI, M. & VILLA, A. (1967). *Acta Cryst.* **23**, 384–391.

MARTIN, J. M., NEWMAN, P. W. G., ROBINSON, B. W. & WHITE, A. H. (1972). *J. Chem. Soc. Dalton Trans.* pp. 2233–2238.

NEWMAN, P. W. G., RASTON, C. L. & WHITE, A. H. (1973). *J. Chem. Soc. Dalton Trans.* pp. 1332–1335.

NEWMAN, P. W. G. & WHITE, A. H. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1460–1463.

PEYRONEL, G. & PIGNEDOLI, A. (1967). *Acta Cryst.* **23**, 398–410.

PIGNEDOLI, A. & PEYRONEL, G. (1962). *Gazz. Chim. Ital.* **92**, 745–760.

RAMALINGAM, K., RADHA, K., ARAVAMUDAN, G., MAHADEVAN, C., SUBRAMANYAM, CH. & SESHASAYEE, M. (1984). *Acta Cryst.* C**40**, 1838–1839.

SEJEKAN, B. G. & ARAVAMUDAN, G. (1978). *Monatsh. Chem.* **109**, 165–177.

SHELDRICK, G. M. (1976). *SHELX76*. 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 (*N,N'*-*o*-Phenylenedisalicylideneaminato)nickel(II), $[Ni(C_{20}H_{14}N_2O_2)]$

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Abstract. $M_r = 373$, orthorhombic, $P2_12_12_1$, $a = 5·458\,(1)$, $b = 16·585\,(4)$, $c = 17·287\,(5)$ Å, $V = 1565$ Å^3, $Z = 4$, $D_x = 1·59$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, μ(Mo $K\alpha_1$) = 11·9 cm^{-1}, ($\lambda K\alpha_1 = 0·70926$ Å), $F(000) = 768$, room temperature, final $R = 0·052$ for 1357 unique reflections. The crystal consists of discrete molecules and the central Ni atom has an approximately square-planar coordination geometry [average Ni—N 1·849 (5), Ni—O 1·837 (4) Å, respectively]. The packing is determined solely by van der Waals forces.

Introduction. Ni^{II} exhibits a diversity of stereochemistry in its complexes with Schiff bases (Holm & O'Connor, 1971). The Cu and Pd complexes of *N,N'*-ethylenedisalicylideneamine (H_2salen, $C_{16}H_{16}N_2O_2$) are isostructural, but Ni is not (Shkol'nikova, Yumal', Shugam & Voblikova, 1970). Work on the Cu^{II} (Montgomery & Morosin, 1961), Pd^{II} (Fallon & Galehouse, 1976) and Co^{II} (Pahor, Calligaris, Delise, Dodic, Nardin & Randaccio, 1976) complexes of the title quadridentate ligand show that they are all isostructural. Structural work on the title compound [Ni(salph)] is reported here. The effect of complexation on the interatomic distances in the ligand is also discussed.

Experimental. Single crystals of the complex were obtained by slow evaporation of a solution of the compound in dichloromethane–*n*-butanol. Unit-cell dimensions of a single crystal 0·47 × 0·27 × 0·15 mm obtained from the least-squares refinement of θ values of 25 high-angle reflections. From the systematic absences ($h00$: $h = 2n$; $0k0$: $k = 2n$; $00l$: $l = 2n$) the space group was unambiguously fixed as $P2_12_12_1$. Three-dimensional intensity data collected on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. $\omega/2\theta$ scan mode. 2259 reflections in the range 2° < 2θ < 60° (h 0 to 7, k 0 to 19, l 0 to 22) measured, 1371 of which considered observed [$I > 3\sigma(I)$]. Max. counting time for each reflection 60 s. Standard reflections (358 and $\bar{2}35$) measured periodically, no significant change in intensity. No absorption correction. $R_{\rm int}$ from merging 14

0108-2701/85/081169-03$01.50