Crystal and Molecular Structure of Bis(aminomethanesulphonato)copper(II)

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Crystals of the title compound are monoclinic, $a = 7{\cdot}064$, $b = 7{\cdot}668$, $c = 7{\cdot}256$ all $\pm 0{\cdot}003$ Å, $\gamma = 88{\cdot}81 \pm 0{\cdot}005°$, space group $P2_1/n$, $Z = 2$. The structure was determined from diffractometer data (555 independent reflections) by three-dimensional *X*-ray methods and refined by least squares to *R* 0·053. The crystals are formed from *trans*-bis(aminomethanesulphonato)copper(II) chelates at centres of symmetry, linked into a three-dimensional array by hydrogen bonds and the long copper–sulphonate-oxygen contacts which give copper a distorted octahedral co-ordination-sphere (Cu–O 1·995 and 2·506, Cu–N 1·999 Å).

The crystal and molecular structure of bis(aminomethanesulphonato)copper(II) has been determined in order to compare it with those of other five-membered copper(II) chelate rings.[1-3]

EXPERIMENTAL

Azure blue crystals were prepared by Palmer's method.[4]

Crystal Data.—$C_2H_8CuN_2O_6S_2$, $M = 283{\cdot}8$, Monoclinic, $a = 7{\cdot}064 \pm 0{\cdot}003$, $b = 7{\cdot}668 \pm 0{\cdot}003$, $c = 7{\cdot}256 \pm 0{\cdot}003$ Å, $\gamma = 88{\cdot}81 \pm 0{\cdot}05°$, $U = 284{\cdot}63$ Å^3, $D_m = 2{\cdot}38$, $Z = 2$, $D_c = 2{\cdot}398$ g cm^{-3}. Space group $P2_1/n$ (C^5_{2h}, No. 14, non-standard setting general positions $\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z)$. Cu-$K_\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, μ(Cu-K_α) $= 75{\cdot}4$ cm^{-1}.

Measurements of unit-cell dimensions and *X*-ray intensities of 555 independent reflections were made on a Hilger and Watts four-circle diffractometer. Balanced filters were used at Bragg angles less than 20°. Intensities of reflections were assumed to be non-zero for $I > 3\sigma$. Lorentz, polarisation, and empirical absorption corrections [5] were applied.

Six well resolved, prominent independent maxima of the unsharpened three-dimensional Patterson synthesis were consistent with the presence of two centrosymmetric molecules in the unit cell about the crystallographic symmetry centres at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. The preliminary atomic parameters were refined by five full-matrix least-squares cycles. The first two cycles assumed isotropic and the remaining three anisotropic thermal motion. Refinement converged at *R* 0·053 with the weighting scheme $w = \{1 + [|(F_o - 4{\cdot}2)|/4{\cdot}2]^2\}^{-1}$. Hydrogen atoms could not be located in the final difference synthesis. Observed structure amplitudes and structure factors calculated from the final atomic parameters in Table 1,

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[1] C. K. Prout, R. A. Armstrong, J. R. Carruthers, J. G. Forrest, P. Murray-Rust, and F. J. C. Rossotti, *J. Chem. Soc.* (*A*), 1968, 2791.

[2] C. K. Prout, J. R. Carruthers, and F. J. C. Rossotti, *J. Chem. Soc.* (*A*), 1971, **554**, and references therein.

[3] H. C. Freeman, *Adv. Protein. Chem.*, 1967, **22**, 257.

[4] W. G. Palmer, 'Experimental Inorganic Chemistry,' Cambridge University Press, Cambridge, 1954, p. 141.

[5] A. C. T. North, D. C. Phillips, and M. S. Matthews, *Acta Cryst.*, 1968, **A24**, 351.

TABLE 1

Atomic parameters ($\times 10^4$) with standard deviations in parentheses *

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
Cu(1)	0	0	0	336(8)	291(7)	255(6)	−83(10)	45(9)	−67(11)
S(1)	−2617(2)	1172(2)	2948(2)	300(7)	211(8)	218(7)	−17(10)	33(11)	−49(11)
O(1)	−2560(6)	287(6)	1136(5)	338(19)	344(24)	203(21)	−19(33)	60(34)	−61(34)
O(2)	−4251(6)	2343(5)	3102(7)	343(22)	270(23)	405(25)	−11(42)	101(38)	76(34)
O(3)	−2417(7)	77(6)	4448(6)	480(24)	360(26)	267(21)	17(41)	27(41)	−17(40)
N(1)	991(7)	1482(7)	2035(7)	334(25)	293(27)	284(24)	−11(43)	90(43)	−7(41)
C(1)	−551(8)	2477(8)	2911(9)	310(29)	306(33)	357(32)	23(54)	20(48)	−12(40)

*The temperature factor T is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

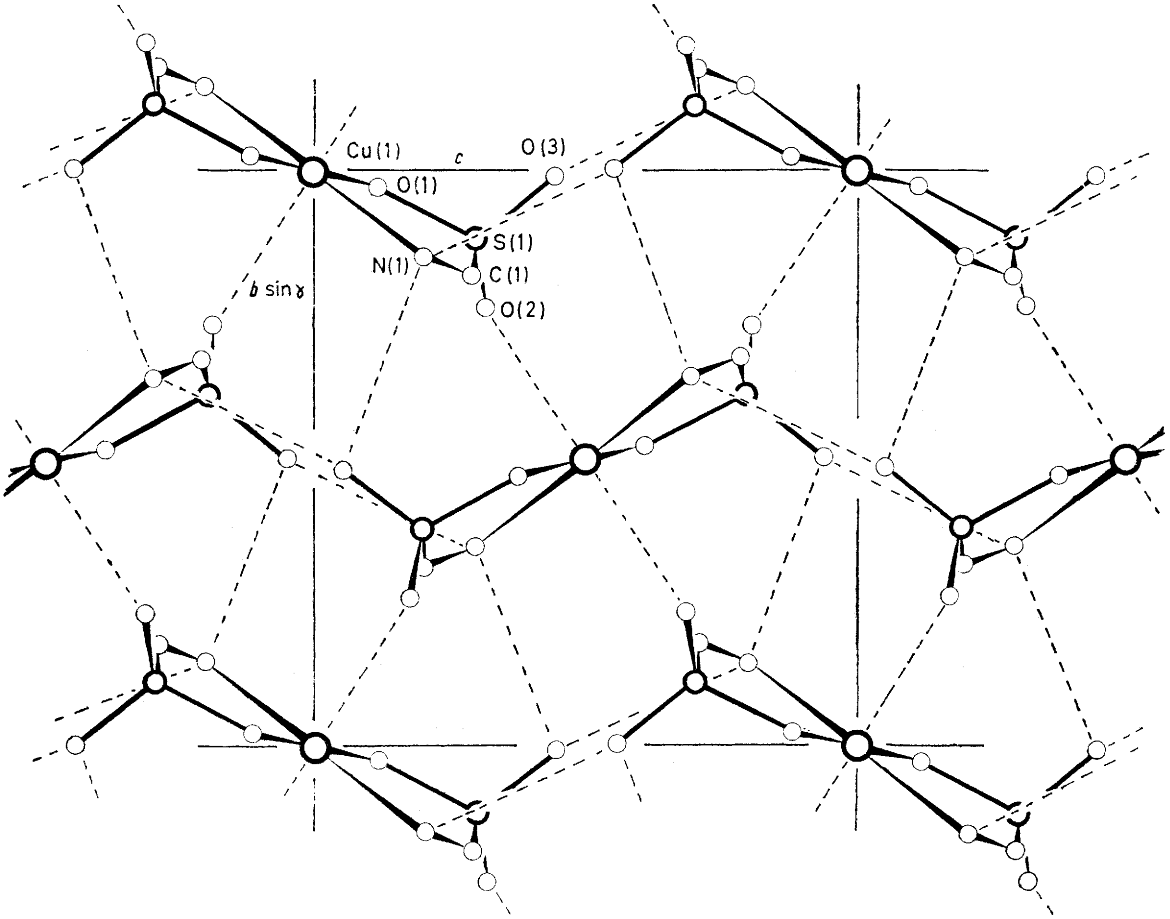

FIGURE 1 Projection of the crystal structure down the a axis

are given in Supplementary Publication * No. SUP 20704 (5 pp., 1 microfiche). Atomic scattering factors were those for neutral atoms from ref. 6 corrected for the real part of the anomalous dispersion. Rollett and Ford's ALGOL system [7] was used for all calculations.

RESULTS AND DISCUSSION

The crystal structure projected down the a axis is shown in Figure 1 and interatomic distances and inter-bond angles in Table 2. The crystals are built up from *trans*-bis(aminomethanesulphonato)copper(II) chelates at the symmetry centres 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ in the unit cell. The copper co-ordination sphere is completed by sulphonate oxygen atoms O(2) of two neighbouring chelates (see Figure 1). In the chelate ring, the copper–nitrogen contact Cu–N(1) (1·999 Å) is similar to that found in aquobis(glycinato)copper(II) [8] but the copper–oxygen contact Cu–O(1) (1·995 Å) is rather longer than the copper–carboxylate-oxygen bond (1·96 Å) in the glycinato-complex and significantly longer than that (1·91 Å) in bis(glycolato)copper(II).[1] The longer Cu–O(1) contact is compatible with the greater acid

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* See note about Supplementary Publications in Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue (items less than 10 pp. are supplied as full size copies).

[6] 'International Tables for X-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962, p. 220.

[7] J. S. Rollett and G. Ford, unpublished work.

[8] H. C. Freeman, M. R. Snow, I. Nitta, and K. Tomita, *Acta Cryst.*, 1964, **17**, 1463.

strength of the sulphonate. The Cu–O(2) bonds (2·506 Å) completing the distorted octahedral co-ordination are not significantly different in length from those found in structurally similar carboxylate complexes.[1-3,8]

Table 2

Distances (Å) and angles (°)

(*a*) Distances

Cu–O(1)	1·995(2)	S(1)–O(2)	1·452(3)
Cu–O(2$^{\text{I}}$)	2·506(2)	S(1)–O(3)	1·455(3)
Cu–N(1)	1·999(2)	S(1)–C(1)	1·787(4)
O(1)–S(1)	1·480(3)	C(1)–N(1)	1·462(4)

(*b*) Angles

N(1)–Cu–O(1)	87·7(1)	O(1)–S(1)–C(1)	103·2(2)
N(1)–Cu–O(2$^{\text{I}}$)	89·2(1)	O(2)–S(1)–O(3)	114·5(2)
O(1)–Cu–O(2$^{\text{I}}$)	92·2(1)	O(2)–S(1)–C(1)	107·6(2)
Cu–O(1)–S(1)	115·7(2)	O(3)–S(1)–C(1)	108·1(2)
O(1)–S(1)–O(2)	111·5(2)	S(1)–C(1)–N(1)	108·8(3)
O(1)–S(1)–O(3)	111·2(2)	C(1)–N(1)–Cu	110·6(4)

(*c*) Hydrogen bonded contacts

N(1) · · · O(3$^{\text{II}}$)	2·94	N(1) · · · O(3$^{\text{III}}$)	3·08

Roman numerals as superscripts refer to the following equivalent positions:

I $\frac{1}{2} + x, y - \frac{1}{2}, \frac{1}{2} - z$ III $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$
II $\bar{x}, \bar{y}, 1 - z$

Within the ligand, the bond lengths agree well with accepted values.[9] However, the S–O(1) bond (1·480 Å) is longer than the S–O(2) and S–O(3) bonds (1·455 Å) which are equivalent. The elongation of this bond may reflect the partial covalent nature of the Cu–O(1) bond. The longer Cu–O(2) bond, which produces no perturbation of the sulphonate, most probably indicates an ion–dipole interaction.

Whereas the immediate CuO_2N_2 co-ordination sphere is strictly planar by symmetry, the chelate rings are grossly non-planar with a torsion angle O(1)–S(1)–C(1)–N(1) of 39° (Figure 2). By contrast, the glycolate ring is planar and in the glycinate the analogous torsional angles are only 5 and 8° for the two independent chelate rings. The large torsional angle in the sulphonate is most probably a function of the repulsion between the sulphonate oxygen atoms and the adjacent methylene hydrogen atoms. The ideal torsion angle to minimise such hydrogen–oxygen repulsions would be 60° in the sulphonate and 0° in the glycinate and glycolate. The full 60° torsion angle in the sulphonate would bring the amino-hydrogen atoms into conflict with O(2) if they, in their turn, are to avoid the methylene hydrogen atoms. The observed conformation appears therefore to involve a compromise minimisation of hydrogen atom repulsions and not to be a function of the copper co-ordination stereochemistry.

The bite of the aminomethanesulphonate ligand would be expected to be larger than those of the glycinate and glycolate ligands because the carbon–sulphur and sulphur–oxygen bonds are sufficiently longer than the corresponding bonds in the other two ligands to compensate for the smaller angle at the sulphur atom.

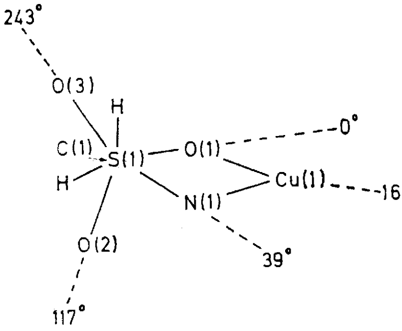

Figure 2 Torsion angles about the C(1)–S(1) bond

This hypothetical bite is increased, on the one hand, as a consequence of the large torsion angle and decreased, on the other, as the bond angles at sulphur and carbon within the chelate ring are less (103·2 and 108·8°) than the expected values (109 and 113°). As a result of these angular distortions, a ligand is produced with a bite of 2·77 Å, only a little larger than those of the 2-aminocarboxylates [3] (2·65—2·70 Å) and the 2-hydroxycarboxylates (2·55—2·65 Å).

In the crystal structure, the chelates are linked by the long Cu · · · O(2) contacts to form sheets parallel to the (101) crystal plane. The nitrogen atom N(1) forms two hydrogen bonds to oxygen atoms O(3) of two different sulphonate ligands (see Figure 1 and Table 2). The hydrogen bond N(1) · · · O(3$^{\text{II}}$) (2·94 Å), links the complexes in chains parallel to the *c* axis and the hydrogen bond N(1) · · · O(3$^{\text{III}}$) (3·08 Å) links them into sheets parallel to the ($\bar{1}$01) crystal plane. The chelates are linked by weak interactions into a three-dimensional network. The crystal structure is closely analogous to that of the anhydrous copper glycolate.[1]

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[9] *Chem. Soc. Special Publ.*, No. 11, 1958, and No. 18, 1965.