Crystal Structures of Thiocyanate Polyamine Copper(II) Complexes. Part III.† [Di-(2-aminoethyl)amine]di-isothiocyanatocopper(II)

By **Mario Cannas,* Gino Carta,** and **Giaime Marongiu,** Istituto Chimico, Università di Cagliari, 09100 Cagliari, Italy

Crystals of the title compound are monoclinic, space group $P2_1/n$ with $Z = 4$ in a unit cell of dimensions a = 11·24(2), b = 14·02(2), c = 7·32(2) Å, β = 97·5(3)°. The structure was solved from diffractometer data by Patterson and Fourier methods and refined by block-diagonal least-squares methods to R 0·053 for 1472 reflections. The co-ordination polyhedron of the copper(II) ion is a tetragonal pyramid with the basal plane occupied by the amine (mean Cu–N 2·02 Å) and thiocyanate nitrogen (Cu–N 1·97 Å) atoms; the apical position is filled by the nitrogen atom of the second thiocyanate (Cu–N 2·26 Å).

WE have previously shown[1] that replacement of a thiocyanate ligand by perchlorate in compounds of the type $CuL(SCN)_2$ (L = polyamine) leads to a different bonding mode of the remaining thiocyanate. We have now examined the compounds where L = den = di-(2-aminoethyl)amine and report details of the structure analysis of $Cu(den)(SCN)_2$.

EXPERIMENTAL

The compound was prepared according to the method of ref. 2, as blue prismatic crystals by evaporation of a concentrated methyl alcohol solution which contained a few drops of water.

Crystal Data.—$C_6H_{13}N_5CuS_2$, M = 282·90, Monoclinic, a = 11·24(2), b = 14·02(2), c = 7·32(2) Å, β = 97·5(3)°, U = 1144 Å^3, D_m(picnometric) 1·63 g cm^{-3}, Z = 4, D_c = 1·64 g cm^{-3}, $F(000)$ = 580. Space group $P2_1/n$ from systematic absences: $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$. Mo-K_α radiation, λ = 0·7107 Å for intensity measurements; μ(Mo-K_α) = 22·86 cm^{-1}. Unit-cell parameters and their estimated standard deviations were determined from a least-squares fit for 15 values of θ, χ, ϕ accurately measured by use of a very narrow counter aperture.

Intensity Measurements.—A crystal of dimensions *ca.* 0·12 × 0·18 × 0·35 mm was mounted on a SIEMENS automatic single-crystal AED diffractometer equipped with a scintillation counter and pulse-height analyzer, with the c axis (the longest dimension of the crystal) nearly coincident with the polar ϕ axis of the goniostat. Intensity data were collected by use of zirconium-filtered Mo-K_α radiation, as described in the preceding paper.[3] The ω-scan technique was used; each reflection was scanned twice at a rate of 2·5° min^{-1} over a range empirically fixed from −0·60 to 0·80° from the 2θ value calculated for a wavelength of 0·7107 Å; at each end of the scan, stationary-crystal–stationary-counter background counts were taken for a time equal to the scan time.

A total of 1764 independent intensities up to $2\theta < 50°$ were recorded; the intensities of three standard reflections, measured every 200 reflections, remained essentially constant throughout data collection.

The intensities were assigned standard deviations according to standard statistics; the values of I and $\sigma(I)$ extrapolated to an unit scan time were corrected for Lorentz-polarization effects. No absorption or extinction corrections were applied to the reflections; 265 were having $I < 3\sigma(I)$ were not used in the analysis.

Solution and Refinement of the Structure.—The positions of the copper and sulphur atoms were derived from a three-dimensional Patterson synthesis. The carbon and nitrogen atoms were located from two successive three-dimensional electron-density maps. A structure-factor calculation with an overall isotropic temperature factor of 3·5 Å^2, as derived from a Wilson plot, gave R 0·21 for 1499 observed reflections. The co-ordinates and the isotropic temperature factors of the non-hydrogen atoms were refined by the block-diagonal matrix least-squares method. Since computing time on the IBM 1130 of our University was very tight, refinement was carried out on 1306 reflections with $\sin\theta >$ 0·2, the quantity minimized being $\Sigma w(F_o - F_c)^2$, where $w = 4F_o^2/[\sigma^2(F_o^2) + (0{\cdot}12F_o^2)^2]$ (ref. 4); convergence was reached after five cycles at R = 0·14. At this stage hydrogen atoms were introduced at calculated positions and given an isotropic B value of 4·5 Å^2, but their parameters were held

---

† Part II, ref. 3.

[1] M. Cannas, G. Carta, and G. Marongiu, *Chem. Comm.*, 1971, 673, 1462.

[2] A. Cristini and G. Ponticelli, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2691.

[3] Part II, M. Cannas, G. Carta, and G. Marongiu, preceding paper.

[4] D. F. Grant and R. C. G. Killean, *Acta Cryst.*, 1969, **B25**, 374.

fixed in the next cycles, where anisotropic thermal parameters were assigned to the other atoms. Seven successive cycles reduced R to 0·06. At this stage all observed reflections, except 27, which were apparently affected by some accidental error, were included in the last two cycles; at the end of the second, most of the parameter shifts were $<\sigma$ and refinement was terminated.

The final R and R' values ($R' = [\Sigma w(\Delta F)^2/\Sigma w F_o{}^2]^{\frac{1}{2}}$) for the 1472 refined reflections were 0·053 and 0·079. The value of goodness of fit, S, was 1·3 $\{S = [\Sigma w(\Delta F)^2/(m - n)]^{\frac{1}{2}}$, where m is the number of observations and n the number of variables$\}$. The final R for the 1764 measured reflections was 0·070.

Positional and anisotropic thermal parameters * ($\times 10^4$), with estimated standard deviations in parentheses

	X/a	Y/b	Z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	3098(1)	5236(1)	4448(2)	74(1)	41(1)	150(3)	−8(1)	41(1)	−1(1)
S(1)	5567(3)	6703(3)	565(5)	105(3)	69(2)	204(7)	−13(2)	77(4)	5(3)
S(2)	−112(3)	6855(3)	224(5)	103(3)	75(2)	232(8)	38(2)	25(4)	33(4)
N(1)	4345(10)	5752(9)	3076(15)	98(10)	68(7)	214(26)	−19(7)	74(13)	−11(11)
N(2)	3195(13)	6264(8)	6404(18)	174(16)	59(7)	287(30)	−43(8)	90(18)	−41(11)
N(3)	2148(11)	4571(8)	6181(15)	114(11)	59(7)	168(21)	−28(7)	64(12)	−16(10)
N(4)	2894(11)	3983(9)	3052(17)	113(11)	62(7)	237(27)	−13(7)	78(14)	−37(11)
N(5)	1490(12)	5913(10)	2774(17)	120(14)	76(8)	247(28)	24(8)	−17(16)	28(12)
C(1)	4837(10)	6149(7)	2002(15)	60(9)	39(6)	191(22)	2(5)	12(11)	−9(9)
C(2)	2530(13)	6018(10)	7848(19)	122(14)	62(8)	181(31)	−25(8)	61(17)	−52(12)
C(3)	1760(20)	5202(12)	7432(29)	201(25)	82(10)	405(52)	−54(13)	237(32)	−82(19)
C(4)	1582(18)	3766(12)	5368(24)	171(23)	59(9)	348(44)	−58(11)	163(27)	−58(15)
C(5)	2207(13)	3312(9)	3992(20)	112(13)	51(7)	212(31)	−17(8)	19(16)	−25(12)
C(6)	813(12)	6297(8)	1743(18)	86(11)	38(6)	168(26)	6(6)	26(13)	8(10)

* The temperature factor is of the form: $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

All least-squares refinements were performed by the program written by R. Shiono for the IBM 1130 computer. Atomic scattering factors were taken from ref. 5 for copper, sulphur, nitrogen, and carbon, and from ref. 6 for hydrogen.

Final atomic parameters with their estimated standard deviations are given in the Table. Observed and calculated structure factors are listed in Supplementary Publication, No. SUP 20784 (10 pp., 1 microfiche).*

DISCUSSION

The crystal structure consists of $Cu(den)(NCS)_2$ molecules. The co-ordination polyhedron around the copper atom is a square pyramid with the three amine and one thiocyanate nitrogen atoms in an almost square planar configuration and the nitrogen atom from the second thiocyanate on the apical position (Figure 1): the nearest neighbour of the copper atom on the opposite side of the pyramid is N(1), from the centrosymmetry-related cation, at 3·48 Å.

The copper atom is displaced −0·17 Å from the least-squares basal plane of equation $7{\cdot}967x - 6{\cdot}024y + 3{\cdot}386z = 0{\cdot}992$ (referred to the direct cell); the nitrogen atoms are alternately above and below the plane: N(1) 0·05, N(2) −0·05, N(3) 0·06, and N(4) −0·05 Å.

Cu–N(amine) bond distances are not significantly different, and their mean value, 2·02 Å, is comparable with literature values.[7] However, the Cu–N(NCS) bond distance is significantly shorter (1·97 Å); the difference in the values of the Cu–N bond lengths is probably the result of the different hybridization of nitrogen atoms in the amine (sp^3) and in the thiocyanate (sp), which leads to values of 0·70 and 0·64 Å for the covalent bond radii of nitrogen.[8]

The apical Cu–N(NCS) bond length is 0·30 Å longer than the basal one, as is usually found for apical bonds in square-pyramidal copper(II) complexes.[9] Recently it has been suggested on the basis of i.r. studies[10] that only one of the two thiocyanate groups would be bonded. On the basis of our results the i.r. bands of the supposed non-bonded SCN group must be attributed to the apical weakly bonded substituent. The values of bond distances and angles in the thiocyanate groups are comparable with those found for this ion, whether co-ordinated or not, and correspond to a partial sp^2 hybridization of

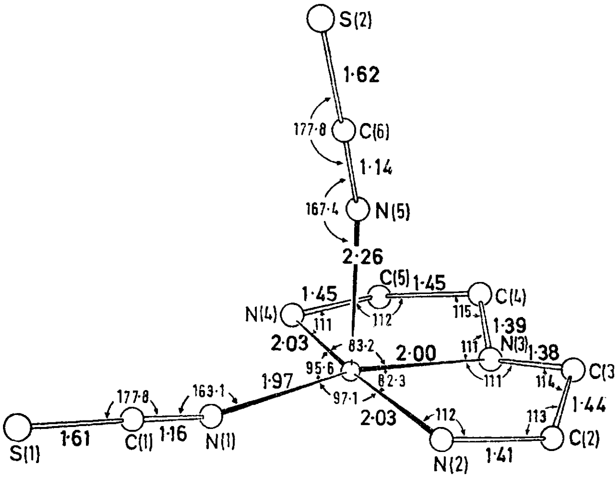

FIGURE 1 Bond distances and angles. Calculated standard deviations are 0·013 Å for Cu–N and S–C bond lengths, 0·6° for N–Cu–N angles and for those involving thiocyanate groups, and 0·025 Å and 1·5° for bond lengths and angles in the amine. Non-quoted bond angles (deg.) are: N(5)–Cu–N(1) 98·1, N(5)–Cu–N(2) 92·9, N(5)–Cu–N(3) 94·9, N(5)–Cu–N(4) 93·5, and C(3)–N(3)–C(4) 129·4

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[5] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[6] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[7] F. S. Stephens, *J. Chem. Soc. (A)*, 1969, 2493.

[8] U. A. Gregory, J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *J. Chem. Soc. (A)*, 1970, 2770.

[9] B. J. Hathaway and B. E. Billing, *Co-ordination Chem. Rev.*, 1970, **5**, 143.

[10] M. J. Bew, B. J. Hathaway, and R. J. Faraday, *J.C.S. Dalton*, 1972, 1229.

nitrogen and sulphur atoms;[11] accordingly, the deviation of the Cu–N–C angle from the value of 180° expected for an *sp* nitrogen hybridization, is also explained.

The deviations from the expected values for the C–C and C–N bond distances in the ligand are most likely a consequence of the high thermal motion of some atoms and no significance should be attached to them. The geometrical feature of the ligand is the one found in similar structures: the five-membered chelate rings are gauche unsymmetrical and adopt a *kk'* configuration;[12] deviations of C(2), C(3), C(4) and C(5) from the relevant N–Cu–N plane are –0·07, –0·38, 0·00, and –0·36 Å.

The projection of the crystal structure along the *c* axis is shown in Figure 2. Molecules around centres of symmetry at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ face each other through the basal plane of the pyramid with a Cu ··· Cu 4·30 Å; they form a close S(1) ··· N(4) contact at 3·48 Å, and S(1) lies 2·7—2·8 Å from the calculated positions of two hydrogen atoms bonded to N(3) and N(4). One more close contact is between the sulphur atom of the apical thiocyanate S(2) and nitrogen N(2) of molecules related by glide planes (3·59 Å); the distances between S(2) and the calculated positions of hydrogen atoms bonded to N(2) are *ca.* 3·1 Å. In both cases the sulphur atoms and the hydrogen atom calculated positions form a geometry similar to that found in bifurcated hydrogen bonding.

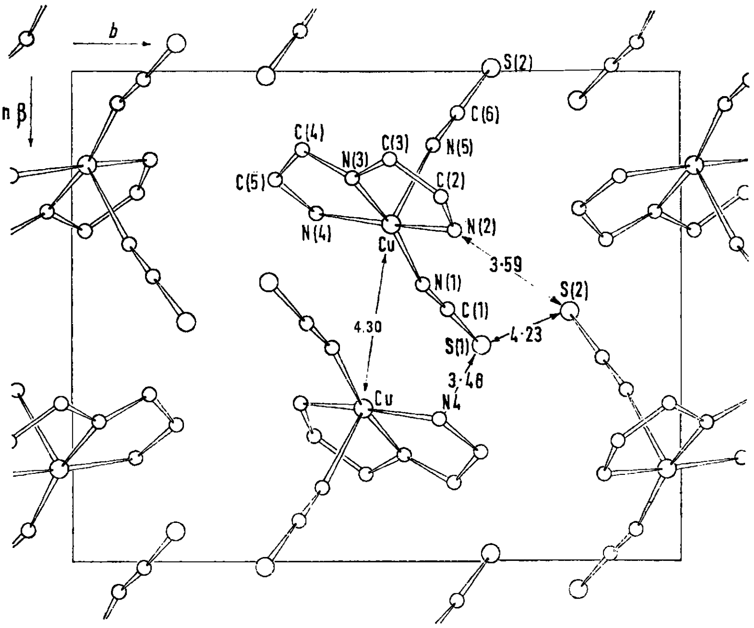

FIGURE 2 Projection of the crystal structure along the *c* axis. The shortest intermolecular contacts are shown

All other close distances again involve sulphur atoms, which play a predominant role in the molecular packing, and also determine the value of the shortest crystallographic axis. Its value (7·4 Å) is in fact very close to four times the van der Waals radius of the sulphur atom, two of which happen to be almost overlapped along the *c* direction.

This work was supported by the Italian C.N.R. Computations were performed on the IBM 1130 of the Centro di Calcolo, Cagliari University.

[3/617 *Received, 26th March,* 1973]

---

[11] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 3rd ed., 1960, p. 273.

[12] E. J. Corey and J. C. Bailey, *J. Amer. Chem. Soc.*, 1959, **81**, 2620.