Crystal Structures of Thiocyanate Polyamine Copper(II) Complexes. Part IV.[1] Di-μ-thiocyanato-bis[di-(2-aminoethyl)amine]dicopper(II) Diperchlorate

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

Crystals of the title compound are triclinic, space group $P\bar{1}$, with $Z = 2$ (*i.e.* 1 dimer) in a unit cell of dimensions $a = 11{\cdot}81(2)$, $b = 7{\cdot}48(2)$, $c = 7{\cdot}48(2)$ Å, $\alpha = 70{\cdot}9(3)$, $\beta = 89{\cdot}7(3)$, $\gamma = 105{\cdot}4(3)°$. The structure was solved from diffractometer data by Patterson and Fourier methods and refined by block-diagonal least-squares methods to R 0·044 for 1564 observed reflections. The co-ordination polyhedron of the copper(II) ion may be considered as a tetragonally distorted octahedron, with the base formed by amine (mean Cu–N 2·01 Å) and thiocyanate nitrogen (Cu–N 1·95 Å) atoms, and apical positions occupied by the sulphur (Cu–S 2·76 Å) of the bridging thiocyanate and a long contact by one perchlorate oxygen atom (Cu–O 2·90 Å); if only the five nearest contacts are considered, the co-ordination is square pyramidal.

IN this paper we report details of the structure analysis of [Cu(den)(SCN)][ClO$_4$]$_2$ [den = di-(2-aminoethyl)-amine].

EXPERIMENTAL

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

Crystal Data.—$C_5H_{13}ClCuN_4O_4S$, $M = 324{\cdot}22$, Triclinic, $a = 11{\cdot}81(2)$, $b = 7{\cdot}48(2)$, $c = 7{\cdot}48(2)$ Å, $\alpha = 70{\cdot}9(3)$, $\beta = 89{\cdot}7(3)$, $\gamma = 105{\cdot}4(3)°$, $U = 605{\cdot}43$ Å^3, D_m (picnometric) 1·77 g cm^{-3}, $Z = 2$, $D_c = 1{\cdot}787$ g cm^{-3}, $F(000) = 660$. Space group $P\bar{1}$ from structure analysis. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 22·7 cm^{-1}.

Unit-cell parameters and their estimated standard deviations were determined from a least-squares fit to 23 values of θ, χ, ϕ accurately measured by use of a very narrow counter aperture.

Intensity Measurements.—A crystal of dimension *ca.* 0·10 × 0·18 × 0·30 mm was mounted on a Siemens automatic single-crystal AED diffractometer, equipped with a scintillation counter and pulse-height analyser, with the c axis (the diagonal of the largest crystal face) nearly coincident with the polar ϕ axis of the goniostat. Intensity data were collected with zirconium-filtered Mo-K_α radiation. The procedure was similar to that previously described.[3] The ω-scan technique was used, each reflection being scanned twice at 2·5° min^{-1} over a range empirically fixed from −0·70 to 0·70° from calculated 2θ values; 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 2054 independent intensities up to $2\theta \leqslant 50°$ were recorded. The intensities of three standard reflections, measured every 200 reflections, remained essentially constant throughout. The intensities were assigned standard deviations equal to $\sqrt{N_T}$, where N_T = peak + background counts; 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; 148 having $I < 3\sigma(I)$ were not used in the analysis.

Solution and Refinement of the Structure.—The presence of two molecules in a triclinic unit cell suggested $P\bar{1}$ as the most probable space group; this was confirmed by structure analysis. The co-ordinates of the copper, sulphur, and chlorine atoms were derived from a three-dimensional Patterson synthesis and a successive three-dimensional Fourier map gave the positions of all non-hydrogen atoms; positional parameters were first refined by a further three-dimensional Fourier. R, with an overall isotropic thermal parameter of 2·5 Å^2 derived by a Wilson plot, was 0·22 for 1906 observed reflections. Both positional and thermal parameters were then refined by the block-diagonal least-squares method using the program written by Shiono for the IBM 1130 computer; the quantity minimized was $\Sigma w(\Delta F)^2$, where $w = 4F_o^2/[\sigma^2(F_o^2) + (0{\cdot}12F_o^2)^2]$.[4] Three cycles reduced R to 0·16. Hydrogen atoms were then introduced at calculated positions at the end of every two cycles, but both positional and isotropic thermal parameters (B 4·5 Å^2) were held fixed throughout refinement. With two further cycles, where reflections with $\sin\theta < 0{\cdot}2$ were omitted because of computing time allocation on the IBM 1130, R was reduced to 0·12. After one cycle, where the thermal parameters of non-hydrogen atoms were refined anisotropically, R dropped to 0·07. Refinement was terminated after five further cycles, when atomic parameter shifts were all $<\sigma$. The final R and $R'\{R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$ for the 1564 refined reflections were 0·044 and 0·060.

The value of the goodness of fit, S, was 1·8 $\{S = [\Sigma w(\Delta F)^2/(n - m)]^{\frac{1}{2}}$, where n is the number of ΔF values, and m the number of variables$\}$. The final R for the 2054 measured reflections was 0·063.

The atomic scattering factors were taken from ref. 5 for non-hydrogen atoms and from ref. 6 for hydrogen. Final atomic parameters with estimated standard deviations are given in the Table. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20785 (12 pp., 1 microfiche).*

DISCUSSION

The crystal structure consists of perchlorate groups and of centrosymmetric dimeric units of [Cu(den)NCS]$^+$, with Cu · · · Cu 5·51 Å.

---

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

[1] Part III, M. Cannas, G. Carta, and G. Marongiu, preceding paper.

[2] A. Cristini and G. Ponticelli, *J. Inorg. Nuclear Chem.*, 1973, **25**, 2691.

[3] Part II, M. Cannas, G. Carta, and G. Marongiu, *J.C.S. Dalton*, 1974, 550.

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

[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.

A perspective view of the molecular structure is shown in Figure 1, together with bond distances and angles. The copper ion is in a tetragonally distorted octahedral environment of the type 4 + 1 + 1, with four nitrogen atoms (from amine and thiocyanate) in an approximately square-planar configuration and the sulphur atom of the bridging thiocyanate and one oxygen atom O(4) of perchlorate in the tetragonal positions. The Cu–O(4) distance (2·90 Å) is *ca.* 0·2 Å longer than the values generally found in 4 + 1 + 1 co-ordination polyhedrons of copper(II) [7] so that if only the five closest neighbours are considered, the co-ordination geometry is square-pyramidal. The copper ion is slightly inside the pyramid, 0·17 Å from the least-squares basal plane of equation $-1{\cdot}099X - 1{\cdot}524Y + 6{\cdot}192Z = -1{\cdot}716$ (referred to the direct cell); nitrogen atoms are alternately below and above this plane: N(1) 0·10, N(2) −0·10, N(3) 0·11, and N(4) −0·10 Å. As in Cu(den)$(NCS)_2$, the basal Cu–N(NCS) bond value is significantly shorter than the mean Cu–N(amine) distance.

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	1706(1)	−368(1)	7703(1)	62(1)	140(2)	135(2)	43(1)	−10(1)	−54(1)
Cl	3036(2)	3491(3)	2564(3)	116(2)	161(4)	135(4)	66(2)	−4(2)	−39(3)
S	−1222(2)	2606(3)	8440(3)	83(2)	213(5)	143(4)	82(2)	7(2)	−11(3)
O(1)	3405(15)	4755(19)	3641(19)	262(17)	346(30)	363(30)	15(17)	−14(18)	−185(25)
O(2)	2743(17)	4499(22)	805(13)	316(24)	516(43)	203(19)	293(28)	−29(16)	−9(22)
O(3)	3825(25)	2541(39)	2336(21)	455(35)	1100(90)	374(34)	611(53)	−48(26)	−153(42)
O(4)	2046(17)	2048(30)	3727(23)	209(18)	632(59)	308(34)	−54(26)	9(19)	−24(33)
N(1)	435(7)	854(11)	7653(10)	82(6)	244(18)	148(14)	80(9)	−2(7)	−51(12)
N(2)	846(7)	−2406(11)	6600(10)	89(7)	213(16)	179(15)	48(8)	−39(8)	−75(12)
N(3)	3070(6)	−1467(9)	7578(9)	91(5)	154(14)	108(12)	54(7)	−4(6)	−32(10)
N(4)	2949(7)	1907(11)	8033(11)	100(6)	158(16)	181(15)	36(8)	−5(7)	−77(12)
C(1)	−254(7)	1570(12)	8018(10)	67(6)	156(16)	107(14)	49(8)	−6(7)	−19(12)
C(2)	1591(9)	−3722(13)	6591(13)	118(8)	163(17)	178(18)	45(9)	−15(9)	−72(14)
C(3)	2859(9)	−2524(13)	6203(13)	117(8)	170(18)	170(18)	59(10)	13(9)	−66(14)
C(4)	4174(7)	143(14)	7199(13)	61(6)	222(22)	228(19)	42(9)	3(8)	−79(16)
C(5)	4058(8)	1328(16)	8424(16)	72(7)	279(23)	284(24)	32(10)	−38(10)	−152(19)

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

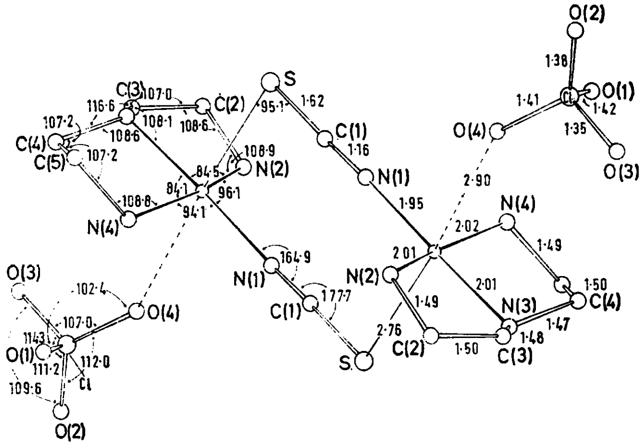

FIGURE 1 Bond distances and angles. Calculated standard deviations are: 0·01 Å and 0·04° for bond distances and angles involving the Cu and S atoms in the co-ordination polyedron, 0·015 Å and 0·8° for those in the ligands, and 0·2 Å and 1·5° for those in the perchlorate group. Non-quoted bond angles (deg.) are: S–Cu–N(1) 94·9, S–Cu–N(2) 99·2, S–Cu–N(3) 89·1, and S–Cu–N(4) 96·1

The eight-membered ring formed by the two copper atoms and by the two bridging thiocyanates is only approximately planar, with the copper atoms displaced 0·25 Å above and below the plane determined by the two coplanar thiocyanate groups. This ring is also present in the structures of other copper compounds: $Cu_2(NCS)_3(NH_3)_3$,[8] Cu(en)$(NCS)_2$ (en = ethylenediamine),[9] [Cu(NCS)$(PMePh_2)_2]_2$,[10] Cu$(py)_2(NCS)_2$ (py = pyridine),[11] and in the α- and β-forms of $Pt_2Cl_2(PPr^n{}_3)_2(SCN)_2$.[12] The distances of the copper atoms from the planes through the thiocyanate groups are ±0·56, ±0·37, and ±0·29 Å in the first three compounds,[8-10] while in the last two [11,12] the metal atoms lie on the plane. Gregory *et al.*[12] suggested that the planar configuration is the one which involves least steric strain, which, in their opinion,

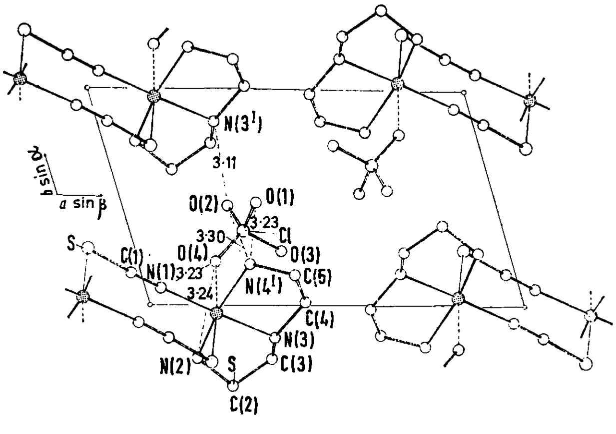

FIGURE 2 Projection of the crystal structure along the *c* axis, showing the shortest intermolecular contacts; N(3^I) and N(4^I) are at − 1 + *z*

---

[7] M. Martinez-Ripoll and S. Garcia-Blanco, *Rev. Real Acad. Cienc. Exat.*, 1971, LXV, 533.

[8] J. Garay, *Inorg. Chem.*, 1969, **8**, 304.

[9] J. Garay, M. Dunaj-Jurco, and O. Lindgren, *Coll. Czech. Chem. Comm.*, 1971, **38**, 3863.

[10] A. P. Gaughan, R. F. Ziolo, and Z. Dori, *Inorg. Chim. Acta*, 1970, **4**, 640.

[11] M. A. Porai-Koshits and G. N. Tishchenko, *Sov. Phys. Cryst.*, 1959, **4**, 216.

[12] U. A. Gregory, J. A. J. Jarvis, B. T. Kilbaun, and P. G. Owston, *J. Chem. Soc.* (*A*), 1970, 2270.

appears as a deviation of 25° at the Pt–N–C angles. We believe rather that the deviation of this angle from 180° is due to partial sp^2 character in the nitrogen atoms.[1] The metal atoms must lie on the plane defined by the two linear and centrosymmetrically related thiocyanate groups only if M–N–C is 180°. Non-linearity, due to partial sp^2 character, may, but need not, lead to departure from coplanarity in the eight-membered ring.

The values of bond distances and angles in the ligands are in the expected range. The five-membered amine rings adopt a kk′ configuration, according to the Corey and Bailar notation [13] and are *gauche* unsymmetrical, as shown by the deviations of carbon atoms from the pertinent Cu,N,N planes: C(2) −0·20, C(3) 0·48, C(4) 0·41, C(5) −0·30 Å.

The molecular packing with short intermolecular distances is shown in Figure 2. The perchlorate ions link the dimers along the *b* axis through contacts, which could be considered as weak hydrogen bonds.

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

[3/618 *Received, 26th March,* 1973]

---

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