Crystal Structures of Thiocyanate Polyaminecopper(II) Complexes. Part I. Bis(ethylenediamine)copper(II) Thiocyanate Perchlorate

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Crystals of the title compound are orthorhombic, space group *Pnam*, with $Z = 4$ in a unit cell of dimensions $a = 15{\cdot}60(3)$, $b = 7{\cdot}62(2)$, and $c = 10{\cdot}82(3)$ Å. The structure was solved by Patterson and Fourier methods and refined by block-diagonal least-squares to R 0·083 for 1090 observed reflections measured photographically.

The copper ion is in a tetragonally distorted octahedral environment with four nitrogen atoms from ethylenediamine in an approximately square-planar configuration (Cu–N 2·02 Å) and the nitrogen atom from the thiocyanate group in the tetragonal positions (Cu–N 2·73 Å).

In a preliminary communication[1] we showed that substitution of one thiocyanate ligand by perchlorate in $\mathrm{Cu(en)_2(SCN)_2}$ (en = ethylenediamine) leads to a different orientation of the remaining thiocyanate in the co-ordination polyhedron of copper. We now report the details of the structure analysis.

EXPERIMENTAL

Violet crystals, suitable for *X*-ray analysis, were obtained by evaporation of a concentrated methyl alcohol solution of the complex, with a few drops of water added. Unit-cell dimensions were determined from zero-level Weissenberg photographs taken around [010] and [001].

Crystal Data.—$\mathrm{C_5H_{16}ClCuN_5SO_4}$, $M = 341{\cdot}3$, Orthorhombic, $a = 15{\cdot}60(3)$, $b = 7{\cdot}63(2)$, $c = 10{\cdot}82(3)$ Å, $U =$

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

1267·9 Å^3, D_m (picnometric) $= 1·74 \pm 0·02$, $Z = 4$, $D_c = 1·76$. Cu-K_α radiation, $\lambda = 1·5418$ Å; μ(Cu-K_α) $= 60·20$ cm^{-1}. Space group *Pnam* (No. 62) or $Pna2_1$ (No. 33) from systematic absences: $0kl$ for $k + 1 = 2n + 1$; $h0l$ for $h = 2n + 1$; shown to be the former by the subsequent successful structure analysis.

Intensities for $h0$—$5l$ and $hk0$—2 reflections were collected on an integrating Weissenberg camera from two crystals mounted along b (cross-section $0·12 \times 0·25$ mm^2) and c (cross-section $0·06 \times 0·23$ mm^2) respectively and determined photometrically with the aid of a microdensitometer. A total of 1264 reflections were measured; after correction for Lorentz and polarization factors, they were placed on the same relative scale by the least-squares procedure of Rae [2] and reduced to a set of 968 observed independent reflections. The weakest reflections (150) were visually estimated with the aid of a calibrated scale. Unobserved reflections (181) were given an intensity value equal to $I_{\text{min.}}/2$, where $I_{\text{min.}}$ is the minimum intensity determined in the relevant Weissenberg layer. The atomic scattering factors were taken from ref. 3 for copper, sulphur, chlorine, oxygen, nitrogen, and carbon and from ref. 4 for hydrogen.

TABLE 1

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

Atom	X/a	Y/b	Z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	5000	5000	5000	23(1)	103(5)	83(2)	−4(1)	0(1)	0(3)
Cl	3341(2)	802(6)	2500	15(1)	75(8)	43(3)	−9(2)	*	*
S	4031(4)	1438(9)	7500	42(2)	149(13)	110(6)	7(4)	*	*
O(1)	2637(9)	−413(21)	2500	28(6)	146(29)	123(18)	−37(11)	*	*
O(2)	3032(10)	2591(20)	2500	43(6)	70(25)	86(13)	12(10)	*	*
O(3)	3853(8)	542(17)	1420(10)	47(5)	208(26)	77(9)	2(10)	29(6)	−25(14)
N(1)	4608(7)	7471(15)	5298(9)	21(4)	85(18)	52(8)	−3(6)	−3(4)	−1(12)
N(2)	3727(6)	4475(17)	4843(10)	20(3)	106(21)	64(9)	−10(8)	−2(4)	−18(12)
N(3)	4991(11)	4476(31)	7500	36(8)	174(41)	58(14)	−33(13)	*	*
C(1)	3687(8)	7466(21)	5573(13)	26(4)	121(29)	60(10)	1(9)	7(6)	5(16)
C(2)	3269(8)	6143(20)	4689(14)	17(4)	117(27)	78(11)	9(8)	−6(5)	4(16)
C(3)	4595(12)	3228(34)	7500	35(7)	179(54)	37(12)	24(16)	*	*

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

Structure Determination and Refinement.—With $Z = 4$ the non-centrosymmetric space group $Pna2_1$ imposes no symmetry restrictions on the molecule, whereas in the centrosymmetic space group *Pnam* the Cu atoms are required to occupy special positions with point symmetry m or $\bar{1}$ and the thiocyanate and perchlorate ions must lie on mirror planes since they cannot possess symmetry $\bar{1}$. Although the three-dimensional Patterson synthesis indicated that the heavy atoms were very close to special positions, preliminary calculations were performed in the non-centrosymmetic $Pna2_1$. All the non-hydrogen atoms were located in a three-dimensional Fourier synthesis and two full-matrix least-squares cycles were performed with unit weights assigned to all observed reflections. The function minimized was $\Sigma w(kF_o - F_c)^2$. Although R was reduced to 0·15, the correlation matrix showed large off-diagonal terms between corresponding parameters of atoms which are independent in $Pna2_1$, but symmetry-related in *Pnam*; the most striking effect of the refinement was that the isotropic thermal parameter shifts for these couples of atoms were opposite; if for one atom the B value became low or negative, for the other it jumped to a value close to 10 Å^2; moreover, the positional parameter shifts were such that chemically equivalent bond lengths became rather different (Cu–N, 1·99 and 2·07 Å; C–C, 1·50 and 1·60 Å). Refinement was therefore completed in space group *Pnam*. Three full-matrix least-squares cycles with isotropic temperature factors and unit weights reduced R to 0·13 for the 968 photometrically observed reflections; at this point all the observed reflections, excluding 28 very strong ones, apparently affected by systematic errors ($F_o \ll F_c$), were included in the refinement which proceeded by the block-diagonal least-squares method, with unit weights and anisotropic temperature factors; the hydrogen atoms were also introduced and held fixed at the calculated positions with a B value of 4·0 Å^2. After two cycles R was 0·086 for 1090 observed reflections and refinement was terminated after two more cycles with weights equal to $1/(A + BF_o)^2$, with $A = 0·8$ and $B = 0·043$, determined by plotting mean $|\Delta F|$ *vs.* mean $|F_o|$ for groups of reflections of similar magnitudes.[5] The final R and R' values ($R' = [\Sigma w\Delta F^2/\Sigma wF_o^2]^{\frac{1}{2}}$), were 0·083 and 0·117 respectively. The value of the goodness of fit S was 1·5 ($S = [\Sigma(W\Delta^2)/(m - n)]^{\frac{1}{2}}$, where m is the number of Δ values, and n the number of variables). R for the 1299 observed and unobserved reflections was 0·113. The final atomic parameters with estimated standard deviations are given in Table 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20534 (8 pp., 1 microfiche).*

DISCUSSION

Figure 1 shows the co-ordination polyhedron together with relevant bond distances and angles. The copper ion is in a tetragonally distorted octahedral environment with four nitrogen atoms, from ethylenediamine molecules, in an approximately square-planar configuration, and the nitrogen atom from the thiocyanate group in the tetragonal positions; thiocyanate thus forms a bridging unit between two $[Cu(en)_2]^{2+}$ cations, and hence gives rise to an infinite chain structure.

A tetragonal environment is quite common in $[Cu(en)_2]X_2$ complexes and the regular presence of long apical bond distances was used to introduce the concept

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* For details see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[2] A. D. Rae, *Acta Cryst.*, 1965, **19**, 683.

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

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

[5] G. H. Stout and L. H. Jensen, '*X*-Ray Structure Determination; A Practical Guide,' MacMillan, New York, 1968, p. 455.

of semi-co-ordination.[6] In $[Cu(en)_2](SCN)(ClO_4)$ the ratio T ($= R_s/R_L = 2{\cdot}02/2{\cdot}73$) is 0·74, which is very close to the limiting value accepted in considering the apical bonds as semi-co-ordinate. Unfortunately, none of the available experimental data gives, in our opinion, definite information about electronic interaction between the anion and the cation. In fact, the Cu–N distance is equal to the sum of the square $d(sp^2)$ radius for copper(II) (1·30 Å) and of the van der Waals radius for nitrogen (1·50 Å);[7] the characteristic thiocyanate frequencies in the i.r. spectra of a polycrystalline sample (ν_1 2025 and 2085, ν_2 490, and ν_3 758 cm^{-1}) are close to those of the free ion and the electronic band maximum at 18·5 kK is slightly on the low side for strictly square-coplanar stereochemistry. If, on the other hand, thiocyanate were to be considered as weakly bonded, the structure of $[Cu(en)_2](SCN)(ClO_4)$ would be an uncommon example of thiocyanate bridged through the nitrogen atom.

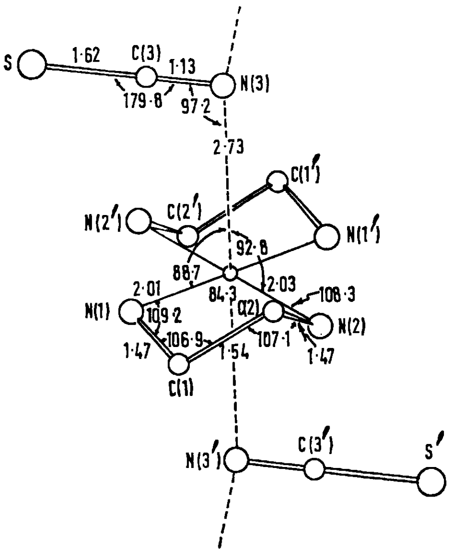

FIGURE 1 Bond distances and angles in the $Cu(en)_2NCS$ group. Standard deviations are 0·01 Å and 0·5° for bonds and angles involving the copper atom, and 0·02 Å and 0·8° for those in the ligands

Bond lengths and angles within the ligand are in accord with previously reported values.[8-10] Unlike the unsymmetrical *gauche* form observed in the other copper ethylenediamine complexes,[8,9] the conformation of chelate rings in this compound is *gauche* symmetrical, with atoms C(1) and C(2) 0·36 Å respectively below and above the co-ordination plane; the dihedral angle between N(1),C(1),C(2) and N(2),C(2),C(1) is 54°. This different conformation does not effect, as shown by Gollogly and Hawkins,[11] the minimum of both torsional and bending energy of the ring; these authors have, in fact, shown by conformation analysis on ethylenediamine cobalt(III) complexes that minimum-energy values can be reached both with symmetrical and unsymmetrical forms.

The crystal structure, whose projection along the *b* axis is shown in Figure 2, can be described in terms of successive layers of cations and anions parallel to the plane (001); $[Cu(en)_2]^{2+}$ units have crystallographic symmetry $\bar{1}$, with the Cu atoms at centres of symmetry on the planes $z = 0$ and $\frac{1}{2}$, while thiocyanate and perchlorate ions lie on mirror planes at $z = \frac{1}{4}$ and $\frac{3}{4}$. The value of the Cu–N–C(NCS) angle (97°) is therefore to be ascribed to the molecular packing in the crystal, and is not unexpected, especially as values found for this angle in other compounds with a long Cu ··· N(NCS) interaction, cover a wide range: 128·6° in bis-(*NN'*-dimethylethylenediamine)copper(II) thiocyanate[12] and 140° in *trans*-bis(ethylenediamine)bis(isothiocyanate)-nickel(II).[10] The Cu–NCS group is, on the other hand, approximately linear whenever a Cu–N covalent bond is present. The molecular packing is quite close, as can also be deduced by the density value; the shortest intermolecular contacts (Figure 2) are between perchlorate, and the ethylenediamine amino-groups. The calculated

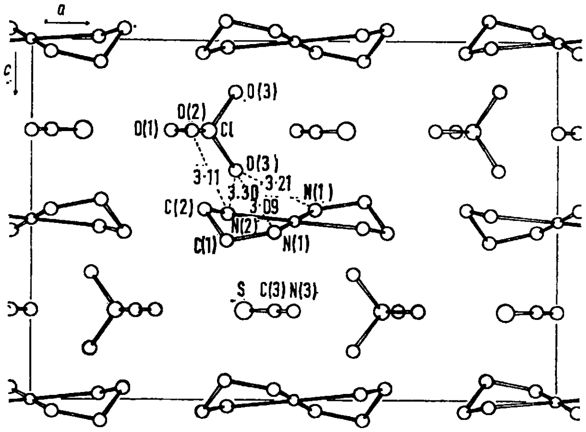

FIGURE 2 Projection of the crystal structure along *b* axis

TABLE 2

Bond distances (Å) and angles (°) for the perchlorate groups

(*a*) Distances			
Cl–O(1)	1·44(2)	Cl–O(3)	1·43(2)
Cl–O(2)	1·45(2)		
(*b*) Angles			
O(1)–Cl–O(2)	110·7(8)	O(2)–Cl–O(3)	108·5(6)
O(1)–Cl–O(3)	109·8(6)	O(2)–Cl–O(3')	108·5(4)
O(1)–Cl–O(3')	109·8(4)	O(3)–Cl–O(3')	109·6(5)

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[6] I. M. Procter, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc.* (*A*), 1968, 1678.

[7] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn. Cornell University Press, Ithaca, New York, 1960, pp. 252, 260.

[8] B. W. Brown and E. C. Lingafelter, *Acta Cryst.*, 1964, **17**, 254, and references therein.

[9] A. Pajunen, *Suomen Kemi.*, 1967, **40**, 32, and references therein.

[10] B. W. Brown and E. C. Lingafelter, *Acta Cryst.*, 1963, **16**, 753.

[11] J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 1969, **8**, 1168.

[12] J. Korvenranta and A. Pajunen, *Suomen Kem.*, 1970, *B*, **43**, 119.

positions for one hydrogen bonded to N(1) and for one bonded to N(2) happen to be approximately in the directions N(1) · · · O(3) and N(2) · · · O(2) respectively, which support the presence of hydrogen bonding. Bond distances and angles for the perchlorate ion are given in Table 2.

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