Crystal Structures of Thiocyanate Polyamine Copper(II) Complexes. Part II.† Bis-(1,3-diaminopropane)isothiocyanatocopper(II) Perchlorate

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Crystals of the title compound are hexagonal, space group $P6_3$, with $Z = 6$ in a unit cell of dimensions $a = b = 13{\cdot}75(2)$, $c = 14{\cdot}55(2)$ Å. The structure was solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares techniques to R 0·064 for 1206 observed reflections. The co-ordination polyhedron of the copper(II) ion is a distorted trigonal bipyramid, the co-ordination sites being occupied by amino and thiocyanate nitrogen atoms, with Cu–N(axl) 2·01, Cu–N(eq) 2·10, and Cu–N(NCS) 2·11 Å.

In a preliminary communication[1] we showed that replacement of one thiocyanate ligand with perchlorate in $Cu(tn)_2(SCN)_2$ (tn = $NH_2{\cdot}[CH_2]_3{\cdot}NH_2$) leads to a change of the co-ordination polyhedron of copper(II) from elongated octahedral to trigonal bipyramidal; in the first case the thiocyanate faces the basal plane with the sulphur atoms 3·15 Å from the copper ion, and in the second it is N-bonded on the basal plane of the bipyramid. We now report the details of the structure analysis carried out on diffractometric data newly collected.

Positional and anisotropic thermal parameters * (× 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	3335(1)	3114(1)	5000(0)	66(1)	63(1)	50(1)	31(1)	−1(1)	−7(2)
Cl(1) ‡	0(0)	0(0)	3894(4)	81(2)	81(0)	45(3)	41(0)		
Cl(2) ‡	3333(0)	6666(0)	1327(6)	85(3)	85(0)	86(4)	43(0)		
Cl(3) ‡	3333(0)	6666(0)	6034(5)	114(4)	114(0)	75(4)	57(0)		
S(1)	3384(2)	−419(2)	5018(5)	79(3)	65(3)	112(2)	41(2)	0(3)	4(4)
O(11) ‡	0(0)	0(0)	4874(14)	113(10)	113(0)	60(13)	57(0)		
O(21)	711(11)	1134(11)	3587(10)	133(15)	103(14)	113(10)	3(13)	−3(11)	33(10)
O(12) ‡	3333(0)	6666(0)	207(33)	168(12)	168(0)	210(22)	84(0)		
O(22)	3533(19)	5823(16)	1480(16)	223(14)	172(14)	187(10)	133(12)	9(10)	21(10)
O(13) ‡	3333(0)	6666(0)	4854(47)	317(13)	317(0)	144(18)	159(0)		
O(23)	3224(14)	5669(16)	6259(15)	152(13)	191(13)	171(9)	88(11)	−19(9)	−11(9)
N(1)	3257(9)	1538(9)	4970(14)	97(9)	76(10)	112(7)	42(8)	12(11)	13(12)
N(2)	2719(10)	3543(14)	3843(8)	84(12)	213(13)	68(9)	95(11)	16(10)	51(9)
N(3)	4892(8)	3833(9)	4425(9)	53(9)	77(9)	91(7)	20(7)	11(6)	−10(6)
N(4)	4073(10)	3925(9)	6237(7)	110(10)	78(10)	54(7)	23(9)	2(7)	12(8)
N(5)	1816(8)	2405(10)	5594(8)	66(9)	109(9)	63(6)	35(7)	8(7)	10(6)
C(1)	3325(8)	723(8)	4984(11)	65(8)	62(8)	65(6)	29(7)	20(10)	5(11)
C(2)	4942(12)	3564(14)	3445(11)	87(14)	110(14)	78(10)	34(12)	9(10)	−10(10)
C(3)	4321(19)	3854(16)	2792(14)	146(28)	128(26)	91(18)	40(24)	22(19)	43(19)
C(4)	3049(20)	3186(18)	2926(11)	153(22)	157(22)	41(15)	68(18)	−2(16)	6(13)
C(5)	3786(23)	3245(19)	7111(17)	136(18)	147(19)	96(12)	60(17)	−18(15)	25(12)
C(6)	2421(14)	2819(14)	7239(11)	78(18)	94(16)	55(11)	−12(15)	27(13)	21(11)
C(7)	1694(11)	1872(12)	6523(7)	89(13)	111(13)	25(9)	15(11)	11(9)	18(9)

* The temperature factor is of the form: $\exp-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$. † Where no value of β_{12} or β_{13} is quoted, it was set to zero for symmetry restrictions. ‡ These atoms lie on a symmetry axis and have an occupancy factor of 1/3.

EXPERIMENTAL

The compound was obtained by adding a solution of $AgClO_4$ to a hot aqueous solution of the stoicheiometric quantity of $Cu(tn)_2(SCN)_2$. Deep blue prismatic crystals, suitable for X-ray analysis, were obtained by evaporation of a concentrated methyl alcohol solution which contained a few drops of water.

Crystal Data.—$C_7H_{20}ClCuN_5O_4S$, $M = 369{\cdot}37$, Hexagonal, $a = b = 13{\cdot}75(2)$, $c = 14{\cdot}55(2)$ Å, $U = 2382{\cdot}23$ Å^3, D_m (picnometric) 1·56 g cm^{-3}, $Z = 6$, $D_c = 1{\cdot}544$ g cm^{-3}, $F(000) = 1044$. Space group $P6_3$ from systematic absences: $00l$ when $l = 2n + 1$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å for intensity measurements; μ(Mo-K_α) = 17·60 cm^{-1}. Unit-cell parameters and their estimated standard deviations were determined from a least-squares fit for 16 values of

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† Part I, M. Cannas, G. Carta, and G. Marongiu, *J.C.S. Dalton*, 1973, 251.

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

θ, χ, φ accurately measured by use of a very narrow counter aperture.

Intensity Measurements.—A crystal of dimensions 0·20 × 0·30 × 0·40 mm was mounted on a Siemens automatic single-crystal AED diffractometer, with the *c* axis (the 0·40 mm 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.

The setting angles, θ, χ, and φ of the reflections used for cell dimensions determination formed the basis for least-squares refinement of orientation. The setting angles for the reflections were then generated and arranged so as to minimize slewing time.

The moving-crystal–moving-counter (θ—2θ) technique was employed with a scintillation counter and pulse-height analyser. The take-off angle was 4·5 Å; the receiving aperture (2·0 mm in diameter) was set 6·0 cm from the crystal. Each reflection was scanned twice at a constant scan rate of 2·5° min^{-1}; the scan range was empirically fixed from −0·65° to 0·80° from the 2θ value calculated for a wavelength of 0·7107 Å, for all reflections. 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 1532 independent intensities up to $2\theta < 50°$ were recorded. The intensities of three standard reflections, measured after every 200 reflections, remained essentially constant throughout, showing only the deviations from the mean predicted from counting statistics. The intensities were assigned standard deviations according to the formula $\sigma^2(I) = P + B + (pI)^2$ where P is the total integrated peak-count obtained in the two scans, B is the total background count, and $I = P - B$; p was selected to be 0·06. The values of I and $\sigma(I)$, extrapolated to a unit scan time, were corrected for Lorentz-polarization effects. No absorption or extinction corrections were applied. Of the 1532 reflections, 318 had $I < 3\sigma(I)$ and were not used in the analysis.

Solution and Refinement of the Structure.—The structure was solved by Patterson and Fourier methods and refined by successive three-dimensional Fourier syntheses to R 0·15 using 876 preliminary photographic data. The positional parameters of non-hydrogen atoms, obtained by a three-dimensional Fourier synthesis calculated at this stage with diffractometric data, were refined by full-matrix least-squares methods, applying isotropic thermal parameters. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2$. Convergence was reached after three cycles at R 0·105 for the 1214 observed reflections used throughout refinement. The high values for the isotropic thermal parameters of the perchlorate oxygen atoms suggested the possibility of disorder for these atoms; a three-dimensional Fourier synthesis, calculated by omitting their contribution, showed distinct but remarkably smeared peaks as a consequence of highly anisotropic thermal motion. Refinement was terminated after two more cycles, where all atoms were given anisotropic thermal parameters; the hydrogen atoms were introduced at calculated positions and given an isotropic thermal parameter equal to 6·0 Å^2; eight reflections, apparently affected by accidental error, were excluded.

The final R and R' values ($R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}$ were 0·064 and 0·086 respectively for 1206 reflections. The value of the goodness of fit, S, was 2·67 ($S = [\Sigma w\Delta^2/(m-n)]^{\frac{1}{2}}$), where m is the number of Δ values and n the number of variables. The final R for 1532 measured reflections was 0·081.

All least-squares refinements were performed with an ORFLS program adapted to the IBM 360/67 of the CNUCE, Pisa.[2] Atomic scattering factors were interpolated from the values given in ref. 3. Final atomic parameters, with estimated standard deviations, are given in the Table. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20783 (9 pp.).*

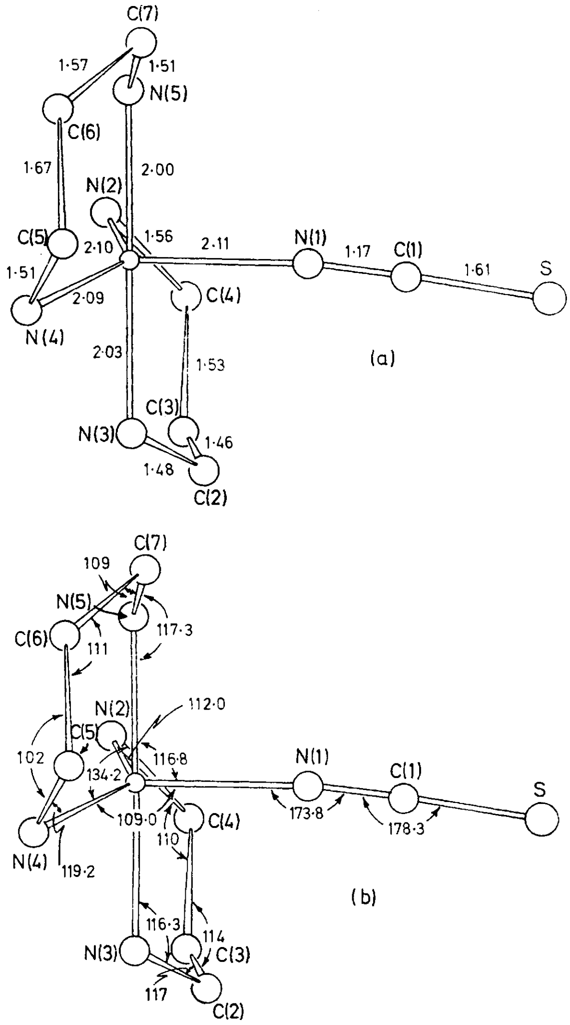

FIGURE 1 Bond distances (a) and angles (b) in the cation. Calculated standard deviations are 0·012 Å and 0·7° for bonds and angles involving the copper atom, 0·03 Å and 2° for those in the ligands. Non-quoted bond angles (deg.) are: N(5)–Cu–N(1) 90·2, N(5)–Cu–N(2) 90·8, N(5)–Cu–N(4) 89·9, N(3)–Cu–N(1) 89·5, N(3)–Cu–N(2) 90·5, N(3)–Cu–N(4) 89·0, and N(3)–Cu–N(5) 178·7

DISCUSSION

The co-ordination polyhedron with the values of bond distances and angles is shown in Figure 1. The geometry

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. Items less than 10 pp. are sent as full size copies.

[2] W. R. Busing, K. O. Martin, and H. A. Levy, A Fortran Crystallographic Least-squares Program, Oak Ridge National Laboratory, Tennessee, 1962.

[3] 'International Tables for *X*-Ray Crystallography,' vol. III, 1962, Kynoch Press, Birmingham.

is closer to trigonal-bipyramidal than to square-pyramidal, as a result of the deviation of the N–Cu–N angles from the values given by Gillespie for idealized geometries:[4] an almost regular trigonal bipyramid would in fact result from a bending of *ca.* 10° of the Cu–N(2) and Cu–N(4) bonds in a direction which would decrease the N(2)–Cu–N(4) angle; square-pyramidal geometry with N(1) on the apex would result from a bending of *ca.* 10° of all four basal Cu–N(amine) bonds. Trigonal bipyramidal geometry is also supported by the values of Cu–N(amine) bond lengths: those bonds considered as apical, Cu–N(3) and Cu–N(5), are in fact significantly shorter (*ca.* 0·1 Å) than the basal ones [Cu–N(4) and Cu–N(2)] as usually found in copper(II) complexes exhibiting this geometry.[5] The length of the Cu–N(NCS) basal bond is *ca.* 0·1 Å longer than that found in copper compounds where it occupies either the apical position in a trigonal bipyramid or the basal position in other geometries.[6]

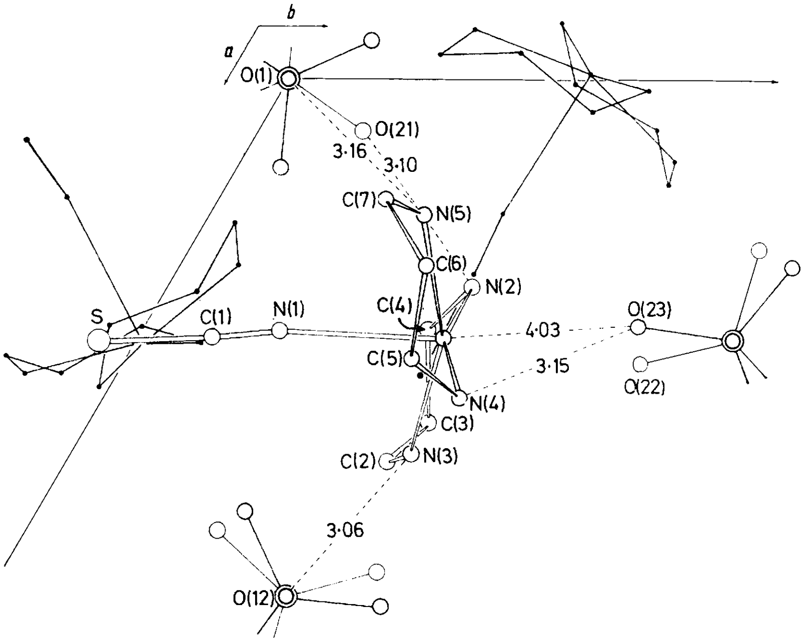

FIGURE 2 Projection of the crystal structure along the *c* axis. For simplicity only the packing around the asymmetric unit is shown

The bonding of thiocyanate through nitrogen in this structure is a further example of the fact that this occurs whenever the copper ion is in a trigonal bipyramidal environment.[7]

From the analysis of electronic spectra it was reasonably assumed that the same cation geometry, and, most likely, the same bonding mode of thiocyanate, is retained in solution;[8] in the case of the analogous Cu(tn)$_2$(SCN)$_2$, the trigonal bipyramidal geometry of [Cu(tn)$_2$(NCS)]$^+$ cation seems still to be maintained in solution, but it changes to elongated octahedral (4 + 2) in the solid state. This suggests the influence of ClO$_4^-$ on the bonding mode of thiocyanate: owing to its low co-ordination ability, this anion does not induce any change in the co-ordination polyhedron, nor therefore in the bonding mode, while passing from the liquid to the solid state.

Because of a lack of high-order reflections and a considerable degree of thermal motion for all oxygen and some carbon atoms, the accuracy of the structure with respect to the C–N, C–C, and Cl–O bonds is such that no significance can be attached to the fairly wide range of bond distances observed; nevertheless, the values for bond angles in the intrachelate rings fall in the range generally found for six-membered rings, with high values for the Cu–N–C angles and with a general trend of all internal angles to have values higher than tetrahedral. Also, the chair conformation is similar to that found in other compounds:[9] the dihedral angle between the N(2)–Cu–N(3) plane and that defined by the C(4)–N(2) and C(2)–N(3) bonds is 43°; the dihedral angle between this last plane and that defined by C(2)–C(3)–C(4) is 59°. Corresponding values in the other ring are 42 and 69°.

Figure 2 shows the projection of the structure along the *c* axis. [Cu(tn)$_2$(NCS)]$^+$ cations are arranged around six- and three-fold axes, along which are stacked ClO$_4^-$ anions; these are very loosely packed since each of them has a height equal to half the *c* axis (7·26 Å), which is much longer than the actual length of the ion in this direction (5·0 Å); in connection with this fact are the

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[4] R. J. Gillespie, *J. Chem. Soc.*, 1963, 4679.

[5] R. F. Ziolo, M. Allen, D. D. Titus, H. B. Gray, and Z. Dori, *Inorg. Chem.*, 1972, **11**, 3044, and references therein.

[6] M. Cannas, G. Carta, and G. Marongiu, following papers.

[7] P. C. Jain and E. C. Lingafelter, *J. Amer. Chem. Soc.*, 1967, **89**, 6131; J. L. Huang, J. M. Li, and J. X. Lu, *Acta Chim. Sinica*, 1966, **32**, 168; N. A. Bailey, E. D. McKenzie, and J. R. Mullins, *Chem. Comm.*, 1970, 1103.

[8] R. Barbucci, P. Paoletti, and G. Ponticelli, *J. Chem. Soc.* (*A*), 1971, 1637.

[9] R. J. Geue and M. R. Snow, *J. Chem. Soc.* (*A*), 1971, 2981.

high thermal motion of the oxygen atoms and the small density increment with respect to $Cu(tn)(SCN)_2$ (0·06 g cm^{-3}). This increment is, on the other hand, equal to 0·17, 0·14, and 0·17 g cm^{-3} for $CuL(SCN)_2$ with respect to $CuL(SCN)ClO_4$ [L = bis(ethylenediamine),[10] di-(2-aminoethyl)amine,[6] and di-(2-aminopropyl)amine [11]]. The shortest intermolecular contacts are between nitrogen and oxygen atoms and are shown in Figure 2.

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[10] (*a*) B. W. Brown and E. C. Lingafelter, *Acta Cryst.*, 1964, **17**, 254; (*b*) M. Cannas, G. Carta, and G. Marongiu, *J.C.S. Dalton*, 1973, 251.

[11] M. Cannas, G. Carta, and G. Marongiu, unpublished observations.