Crystal Structures of Thiocyanate Polyamine Copper(II) Complexes. Part VI.† Di-(3-aminopropyl)aminebis(isothiocyanato)copper(II)

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The crystal structure of the title compound has been determined by three-dimensional *X*-ray data. Crystals are monoclinic, space group $P2_1/a$, with $Z = 4$ in a unit cell of dimensions: a = 7·58(2), b = 14·12(2), c = 13·58(2) Å, β = 113·2(3)°. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to R 0·033 for 1689 refined reflections measured by diffractometer. The co-ordination polyhedron is a tetragonal pyramid with the basal plane occupied by the amine [Cu–N(prim) 2·02, Cu–N(sec) 2·06] and thiocyanate nitrogen (Cu–N 2·04) atoms; the apical position is filled by the nitrogen atom of the second thiocyanate group (Cu–N 2·14 Å). The mutually *trans* Cu–N(sec) and Cu–N(NCS) bonds evidence an antisymbiotic *trans*-effect with hard metal and ligands. The bonding of the thiocyanate group in other polyamine copper complexes is discussed in terms of Pearson's concept of hard and soft acids and bases (HSAB).

THE crystal structure of Cu(dpt)(NCS)$_2$ [dpt = di-(3-aminopropyl)amine] was undertaken to confirm the bonding mode of the thiocyanate ion deduced by i.r. spectra[1] (a procedure which is known to be often deceptive), to compare the results with those previously reported[2] for Cu(den)(NCS)$_2$ [den = di-(2-aminoethyl)amine] and to investigate how the differences in ligand flexibility and conformation affect the geometrical features of the co-ordination polyhedron.

EXPERIMENTAL

The compound prepared according to ref. 1 forms blue prismatic crystals by evaporation of a concentrated methyl alcohol solution, containing a few drops of water.

Crystal Data.—$C_8H_{17}N_5CuS_2$, M 310·95, Monoclinic, a = 7·58(2), b = 14·12(2), c = 13·58(2) Å, β = 113·2(3)°, U = 1337·5 Å^3, D_m (flotation) = 1·53, Z = 2, D_c = 1·543 g cm^{-3}, $F(000)$ = 644. Space group $P2_1/a$ from systematic absences. Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K_α) = 19·54 cm^{-1}. Unit-cell parameters and their estimated standard deviations were determined by a least-squares fit to 15 values of θ, χ, φ, accurately measured by use of a very narrow counter aperture.

Intensity Measurements.—A crystal of dimensions 0·023 × 0·020 × 0·043 mm was mounted on the Siemens automatic single-crystal AED diffractometer, with the c axis nearly coincident with the polar φ axis of the goniostat. The procedure was similar to that previously described.[3] The θ—2θ scan technique with a five-value measuring procedure was used. A total of 2080 independent intensities up to $2\theta \leqslant 50°$ were recorded. The intensities of three standard reflections were measured after every 200 reflections and their net counts did not vary noticeably during the data collection (*ca.* 5 days). Intensities were assigned standard deviations according to the formula $\sigma^2(I) = P + B + (pI)^2$, where P is the total integrated peak count, B is the total background count, and $I = P - B$; p was 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 2080 reflections, 391 having $I/\sigma(I) < 3$ were considered unobserved and were not used in the analysis.

Solution and Refinement of the Structure.—The positions of the copper, two sulphur, and one light atoms were determined from a three-dimensional Patterson synthesis; a successive three-dimensional Fourier map gave the positions of all non-hydrogen atoms.

The R factor, obtained by use of the overall temperature and scale factors derived from a Wilson plot, was 0·21 for 1689 observed reflections. Both positional and isotropic thermal parameters were then refined by the block-diagonal least-squares method using the program written by R. 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] Four cycles of refinement reduced R factor to 0·085.

At this stage, the hydrogen atoms were introduced at

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† Part V, ref. 8.

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[3] 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.

calculated positions (assuming C–H 1·05 and N–H 1·00 Å) and given an isotropic B value of 4·5 Å^2, but their parameters were held fixed in the next cycles.

Two more cycles, by use of the ORFLS program adapted to the IBM 360/67 of CNUCE, Pisa,[5] and anisotropic thermal parameters reduced R to 0·033 and R' to 0·053 [$R' = \Sigma w(\Delta F)^2/\Sigma w F_o^2$] for 1689 observed reflections. The value of the goodness of fit, S, was, 0·76 {$S = [\Sigma w(\Delta F)^2/(m - n)]^{\frac{1}{2}}$, where m is the number of Δ values and n the number of variables}. The final R for all 2080 measured reflections is 0·044.

TABLE 1

Atomic co-ordinates and anisotropic * temperature factors (× 10^4), with standard deviations in parentheses

	X/a	Y/b	Z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	1783(0)	242(0)	1226(1)	40(0)	35(0)	121(1)	1(0)	21(0)	4(0)
S(1)	−705(1)	1548(1)	−4669(1)	68(1)	67(1)	153(2)	0(1)	7(1)	17(0)
S(2)	4756(1)	1936(11)	551(2)	80(1)	79(1)	427(3)	−32(1)	117(1)	−36(1)
N(1)	593(2)	772(3)	−1166(4)	71(2)	53(2)	178(7)	9(2)	20(3)	16(3)
N(2)	3057(3)	1098(3)	1110(4)	70(2)	65(2)	263(7)	−17(2)	66(3)	14(3)
N(3)	1204(2)	1075(3)	2755(4)	63(2)	51(2)	208(6)	1(2)	47(3)	−25(3)
N(4)	2805(2)	−435(2)	3670(4)	48(2)	59(2)	124(5)	1(2)	15(2)	15(2)
N(5)	1745(2)	−894(2)	−419(4)	61(2)	43(2)	153(6)	6(2)	29(3)	−4(3)
C(1)	62(2)	1095(3)	−2624(4)	48(2)	38(2)	159(7)	−7(2)	27(3)	−7(3)
C(2)	3766(3)	1441(3)	905(4)	59(2)	39(2)	162(7)	−4(2)	32(3)	2(3)
C(3)	1962(4)	1517(4)	4531(6)	85(3)	69(3)	249(9)	−14(3)	54(4)	−62(4)
C(4)	2560(4)	767(4)	5920(6)	105(4)	111(4)	152(8)	−10(3)	41(4)	−45(5)
C(5)	3339(4)	209(4)	5331(6)	76(3)	86(3)	141(9)	−4(3)	−8(4)	−11(4)
C(6)	3672(3)	−993(3)	3394(6)	48(2)	66(3)	219(9)	16(2)	9(4)	33(4)
C(7)	3261(3)	−1750(3)	1857(7)	82(3)	51(2)	293(12)	30(2)	69(5)	36(4)
C(8)	2769(4)	−1369(3)	−138(7)	81(3)	53(2)	234(10)	21(2)	72(5)	6(4)

* In the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Atomic scattering factors were interpolated from values given in ref. 6. Final atomic parameters, with estimated standard deviation, are given in Table 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20950 (11 pp., 1 microfiche).*

DISCUSSION

The Co-ordination Polyhedron and the Bonding Mode of Thiocyanate.—The co-ordination polyhedron (Figure 1) is square pyramidal with the amine nitrogen atoms co-ordinated on the basis and the thiocyanate nitrogen atoms on the remaining positions. The main features are similar to those found in the den complex but there are interesting differences. The *trans* Cu–N(sec) and Cu–N(NCS) bond lengths are significantly longer (*ca.* 0·06 Å). The apical bond length is much shorter, with the resulting tetragonal distortion, measured by the ratio $R_S/R_L \simeq 0.96$ (R_S and R_L are the basal and apical bond lengths respectively) being the lowest value so far observed for 4 + 1 co-ordination in copper(II) complexes.[7] The distances of the basal nitrogen atoms from the least-squares plane are 0·09 Å higher [±0·14 in Cu(dpt)(NCS)$_2$ and ±0·05 Å in Cu(den)(NCS)$_2$, see Table 2]. The lengthening of the Cu–N(sec) distance occurs in both Cu(dpt)(NCS)$_2$ and [Cu(dpt)NCS]ClO$_4$ compounds[8] possibly as a result of strains in the six-membered chelate rings which share a Cu–N(sec) bond; this effect has not been observed in the analogous and other den complexes where five-membered rings are formed. Lengthening due to the *trans*-effect also appears in the Cu–N(NCS) bond; a *trans*-effect was reported by Chatt and Heaton for the case when two soft ligands are attached to a soft metal atom (antisymbiotic effect);[9] the situation reported here is unusual since both metal and ligands are hard.

The lengthening of these bonds as well as the larger departure from planarity results in a lower in-plane field strength for the CuN$_4$ chromophore in the dpt

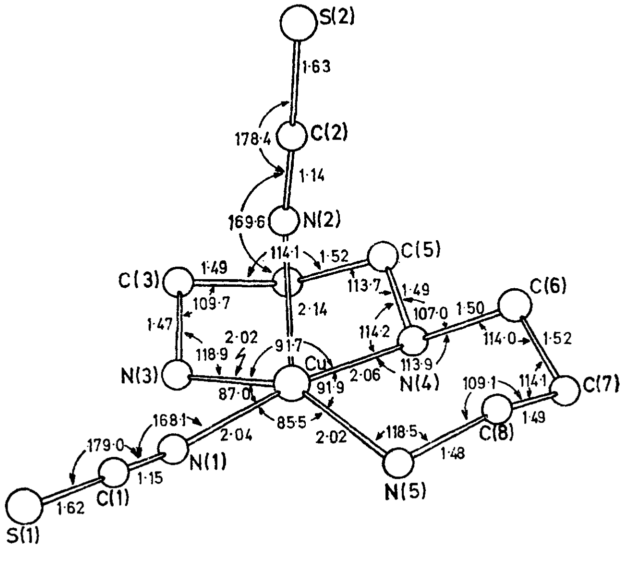

FIGURE 1 Bond distances and angles in Cu(dpt)(NCS)$_2$. Calculated standard deviations are 0·01 Å for all bond distances, 0·4° for bond angles involving copper and sulphur atoms, and 0·5° for other bond angles. Non-quoted angles are: N(2)–Cu–N(1) 97·2, N(2)–Cu–N(3) 101·6, N(2)–Cu–N(4) 91·7, N(2)–Cu–N(5) 104·2, N(1)–Cu–N(4) 171·0, and N(3)–Cu–N(5) 153·8°

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

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[9] J. Chatt and B. T. Heaton, *J. Chem. Soc.* (*A*), 1968, 2745.

as compared to the den complex. The absorption maximum in the electronic reflectance spectra is at 15·1 kK for Cu(dpt)$(NCS)_2$ and at 15·7 kK for Cu(den)$(NCS)_2$ and this is in agreement with the theory that the position of this band gives a useful indication of the degree of tetragonal distortion.[10]

We consider the magnitudes of the Cu–N basal bond lengths, and therefore the in-plane field strength, to be strongly related to the different bonding mode of thiocyanate in polyamine copper(II) complexes, since it has been deduced by an analysis of results of the crystal-structure determinations of compounds of this type. We have not included the situations where –NCS– bridging occurs, since there are then only four donor nitrogen atoms, including N(NCS), and the sulphur atom therefore co-ordinates in order to satisfy the additional bonding requirements of copper(II);[8] >NCS and NCS< bridging are excluded because they are the consequence of peculiar reticular requirements.[11,12]

TABLE 2

Bond lengths (Å) in co-ordination polyhedra from crystal-structure determinations of polyamine thiocyanate copper(II) complexes; estimated standard deviations are given in parentheses

Compound *	Geometry †	Basal Cu–N	Apical Cu–S or Cu–N
$Cu(NH_3)_4(SCN)_2$ [a]	4 + 2	1·98	3·00
$Cu(en)_2(SCN)_2$ [b]	4 + 2	1·99(1), 2·01(1)	3·27(1)
$Cu(tn)_2(SCN)_2$ [c]	4 + 2	2·029(5), 2·005(5)	3·154(2)
Cu(trien)SCN(SCN) [d]	4 + 1	2·013(7), 2·030(5), 2·015(6), 2·008(7)	2·607(2)
Cu(tren)NCS(SCN) [e]	5	2·055(4), 2·144(4), 2·055(4)	2·033(4), 1·959(5)
Cu(bispictn)$(NCS)_2$ [f] α- and β-forms	5	α: 2·029(11), 2·038(11), 2·119(12); β: 2·045(11), 2·061(10), 2·162(14)	α: 1·987(11), 1·989(10); β: 1·984(11), 1·991(11)
$Cu(tn)_2NCS(ClO_4)$ [g]	5	2·10(1), 2·09(1), 2·11(1)	2·00(1), 2·03(1)
$Cu(enMe)_2(NCS)_2$ [h]	4 + 1	2·067(11), 2·049(12), 2·029(11), 2·070(13)	2·238(14)
$Cu(enMe_2)_2(NCS)_2$ [i]	4 + 2	2·062(6), 2·064(6)	2·517(7)
Cu(den)$(NCS)_2$ [j]	4 + 1	2·03(1), 2·03(1), 2·00(1), 1·97(1)	2·26(1)
Cu(dpt)$(NCS)_2$ [k]	4 + 1	2·02(1), 2·02(1), 2·06(1), 2·04(1)	2·14(1)

* Ligand abbreviations: en = $H_2N\cdot[CH_2]_2\cdot NH_2$, tn = $H_2N\cdot[CH_2]_3\cdot NH_2$, trien = $(H_2N\cdot[CH_2]_2\cdot NHCH_2)_2$, tren = $(H_2N\cdot[CH_2]_2)_3N$, bispictn = 2-pyridyl-$CH_2\cdot NH\cdot[CH_2]_3\cdot NHCH_2$-2-pyridyl, enMe = $H_2N\cdot[CH_2]_2\cdot NHMe$, $enMe_2$ = $MeNH\cdot[CH_2]_2\cdot NHMe$. † 4 + 2, 4 + 1, and 5 indicate distorted octahedral, tetragonal pyramidal, and trigonal bipyramidal geometry.

[a] Ref. 13. [b] Ref. 14. [c] Ref. 15. [d] Ref. 16. [e] Ref. 17. [f] Ref. 18. [g] Ref. 3. [h] Ref. 19. [i] Ref. 20. [j] Ref. 2. [k] Present work.

From the results reported[2,3,13-20] in Table 2 it can be seen that the general trend is as follows: when all the nitrogen atoms in the CuN_4 chromophore are only σ donors and Cu–N bond lengths fall in the range of short covalent bonds, mean 2·00 Å, thiocyanate is sulphur bonded, or more correctly, the sulphur atom faces the copper ion; if the bond strength in the CuN_4 chromophore is lower, mean Cu–N 2·05 Å, or one or more of the nitrogen atoms belong to a π acceptor group, *N*-bonding is favoured.

We consider that the HSAB theory of Pearson[21] can explain this fact, if nitrogen and sulphur are considered as hard and soft centres, respectively, and copper(II) occupies a borderline position in the classification of Lewis acids, so that small changes may be sufficient to impart a soft or hard character to it. Then, if σ donation is rather strong, the fractional charge δ+ on the metal is reduced, it becomes soft and favours sulphur-bonded thiocyanate; the situation is *vice versa* when σ donation is weak, or when one or more of the nitrogen atoms in the CuN_4 chromophore belong to a π acceptor group (which takes part of the metal atom excess charge through back-donation): the fractional δ+ charge is then relatively high and thiocyanate co-ordinates through nitrogen.

It cannot, of course, be excluded that other factors may also influence the thiocyanate bonding mode; in *N*-methylethylenediamine complexes, for instance, the steric hindrance of the methyl group might be responsible for the linear Cu–N–C–S grouping instead of Cu–SCN bent at 90°; in $Cu(en)_2(SCN)_2$ and $Cu(tn)_2(SCN)_2$ hydrogen bonding between thiocyanate nitrogen and amine NH_2 groups of nearest neighbour molecules might be the determining factor in stabilizing crystal structure, so favouring *S*-bonding.

The Ligands.—All bond lengths and angles are close to the expected values, the greatest differences between the corresponding values in the two chelated rings and thiocyanate groups being only 0·01 Å and 0·6°, which emphasizes the accuracy of the analysis.

Atomic distances from the planes (*b*) and (*c*) in Table 3 show that the two fused chelated rings adopt the chair

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conformation, like that observed in the complexes of 1,3-diaminopropane.

TABLE 3

Equations of molecular planes, referred to *a*, *b*, and *c* axes, with deviations (Å) of atoms from the planes given in square brackets

Plane (*a*): N(1), N(3), N(4), N(5)

$$11{\cdot}0835x + 8{\cdot}0411y - 3{\cdot}0945z = 1{\cdot}4884$$

[N(1) 0·15, N(3) −0·14, N(4) 0·14, N(5) −0·14, Cu 0·30, S(1) 0·42, S(2) 5·17, N(2) 2·44, C(1) 0·27, C(2) 3·56, C(3) 0·50, C(4) 0·13, C(5) 0·73, C(6) 0·73, C(7) 0·14, C(8) 0·52]

Plane (*b*): Cu, N(3), N(4)

$$9{\cdot}8746x + 9{\cdot}5746y - 1{\cdot}4770z = 1{\cdot}8112$$

[C(3) 0·91, C(4) 0·58, C(5) 0·90]

Plane (*c*): Cu, N(4), N(5)

$$12{\cdot}4929x + 5{\cdot}1009y - 3{\cdot}8111z = 1{\cdot}8837$$

[C(6) 0·90, C(7) 0·59, C(8) 0·93]

The dihedral angle between the plane through N(3), Cu, N(4) and the mean plane through N(3), C(3), N(4), C(5) is 38·1, and between this last plane and that through C(3)—(5) is 61·6°; corresponding values for the other ring are 38·4 and 62·0°. The closeness of these values is unusual, the two rings generally being differently distorted, because of intra- and inter-molecular contacts.[22-24]

The remarkable difference between N(2)–Cu–N(prim) and N(2)–Cu–N(sec) angle (10°) is likely to be due to conformational requirements and not to steric hindrance between apical and basal positions; in fact, the closest contacts around N(2) do not involve the NH_2 group, but N(4) (3·01), C(5) (3·32), C(6) (3·35), and two hydrogen atoms bonded to the last two atoms (2·78 and 2·79 Å).

The projection of the crystal structure along the *c* axis (Figure 2) is quite similar to that for the analogous den complex. Molecules around the centre 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 4·50 Å: corresponding distance in the den complex is 4·30 Å, the difference being due to the smaller distance of the copper ion from the mean basal plane of the pyramid in the latter case. The contacts indicated between sulphur and nitrogen atoms could be considered as weak hydrogen bonds.

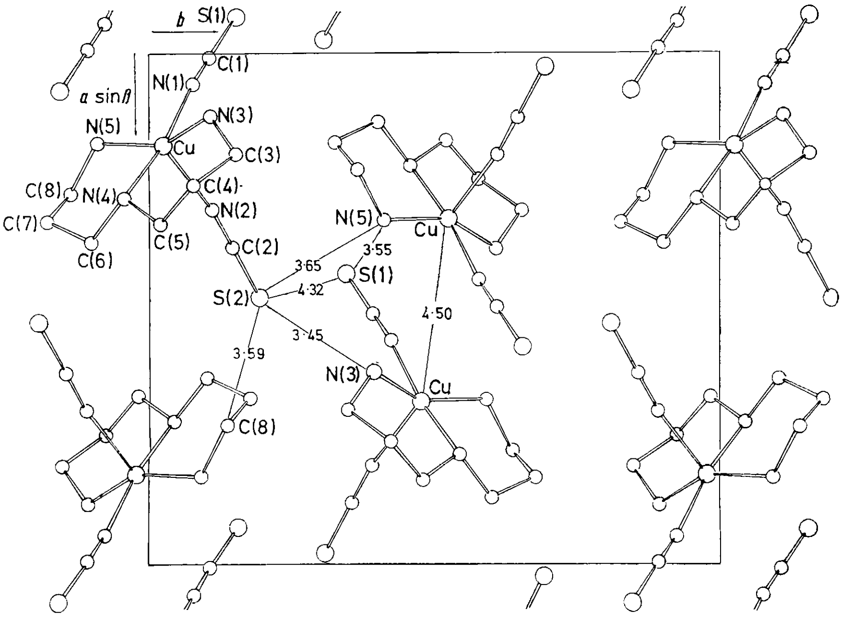

FIGURE 2 Projection of the crystal structure along the *c* axis; shortest molecular contacts are shown

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