Crystal Structures of Thiocyanate Polyamine Copper(II) Complexes. Part 7.† (3,6-Diazaoctane-1,8-diamine)isothiocyanatocopper(II) Perchlorate: A Disordered Structure

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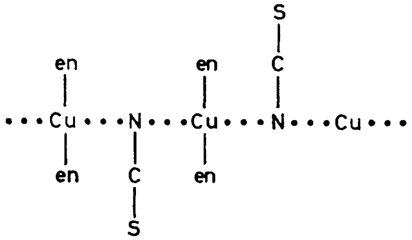
The crystal structure of the title complex has been determined by three-dimensional *X*-ray data. Crystals are orthorhombic, space group $Pca2_1$ with $Z = 8$ in a unit cell of dimensions $a = 23.90(4)$, $b = 8.56(2)$, and $c = 14.71(3)$ Å. The structure has been solved by Patterson and Fourier methods and refined by least-squares techniques to R 0.106 for 1 489 refined reflections measured photographically. In contrast to the corresponding bis(thiocyanate) derivative, the thiocyanate group in the present complex is bonded *via* the nitrogen atom; the co-ordination polyhedron of the copper(II) ion is intermediate between square pyramidal and trigonal bipyramidal. A qualitative interpretation of the structural disorder is given.

In the crystal structures of $[Cu(en)_2(SCN)_2]$ [1] (en = ethylenediamine) and $[Cu(pd)_2(SCN)_2]$ [2] (pd = propane-1,3-diamine) the copper atoms have an elongated octahedral co-ordination with the amine nitrogen atoms in the basal plane and the sulphur atoms of the thiocyanate groups in the apical positions at distances of 3.27 and 3.15 Å respectively; a network of N(NCS) • • • N(amine) contacts (*ca.* 3.0 Å) is present in both structures. Replacement of a thiocyanate ligand by perchlorate in the two complexes leads to different structural arrangements where N • • • N are replaced by O • • • N contacts: $[Cu(en)_2(NCS)][ClO_4]$ [3] gives a highly packed structure (D 1.72 g cm^{-3}) formed by chains [Cu–N as in (I) 2.73 Å] and by $[ClO_4]^-$ ions, while $[Cu(pd)_2(NCS)][ClO_4]$ [4] gives a loose (D 1.50 g cm^{-3}), highly symmetrical, structure where the trigonal-bipyramidal $[Cu(pd)_2(NCS)]^+$ cations are arranged around the $[ClO_4]^-$ ions, which lie along the three-fold axes.



(I)

In the crystal structure of $[Cu(3,6NH\text{-}od)(SCN)][SCN]$ [5] (3,6NH-od = 3,6-diazaoctane-1,8-diamine) the five-co-ordinate $[Cu(3,6NH\text{-}od)(SCN)]^+$ cation and $[SCN]^-$ anions are connected by a network of N–H • • • N and N–H • • • S hydrogen bonds; the co-ordination polyhedron around copper is square pyramidal with the four nitrogen atoms of the ligand in the basal plane and the sulphur atom of a thiocyanate group in the apical position (Cu–S 2.607 Å). To investigate further the effect of replacement of one thiocyanate group by perchlorate we have undertaken the crystal-structure analysis of $[Cu(3,6NH\text{-}od)(NCS)][ClO_4]$.

EXPERIMENTAL

The complex was prepared by Barbucci *et al.*[6] who kindly provided us with a sample. Crystals suitable for *X*-ray analysis were obtained by evaporation of a concentrated methanol solution with a few drops of water added. All the crystals examined gave diffraction patterns showing diffuse streaks, parallel to the c^* direction, along the lattice rows for which h is odd, indicating the presence of one-dimensional disorder; the streaks have maxima in positions corresponding to integer l values.

Crystal Data.—$C_7H_{18}ClCuN_5O_4S$, $M = 367.3$, Orthorhombic, $a = 23.90(4)$, $b = 8.56(2)$, $c = 14.71(3)$ Å, $U = 3\,009$ Å^3, D_m (picnometric) = 1.60 g cm^{-3} $Z = 8$, $D_c = 1.62$ g cm^{-3}, Cu-K_α radiation, μ(Cu-K_α) = 50.7 cm^{-1}. From systematic absences of both sharp and diffuse reflections ($0kl$ for $l = 2n + 1$ and $h0l$ for $h = 2n + 1$) the possible space groups are $Pca2_1$ (no. 29) and $Pcam$ (no. 57). Intensities for $h0$—$6l$ and $0kl$, $2kl$, $4kl$ were collected on an integrating Weissenberg camera, and determined photometrically with the aid of a microdensitometer; diffuse reflections were measured on the peak position. A total of 1 276 reflections was measured; after correction for Lorentz and polarization factors, they were placed on the same relative scale by the least-squares procedure of Rae [7] and reduced to a set of 1 060 independent reflections. The weakest reflections (429) were visually estimated with the aid of a calibrated scale. Unobserved reflections (1 034) were given an F_o value equal to F_o(min.)/2. The atomic scattering factors were taken from Cromer and Waber [8]; that of copper was corrected for the real part of the anomalous dispersion.

Structure Determination and Refinement.—The structure was solved by neglecting the disorder effects; diffuse reflections were therefore considered as sharp, but the measured F_o values were arbitrarily multiplied by 1.5, which seemed a reasonable factor to allow for the streak contribution to their intensities. Because of peak overlapping, the analysis of the three-dimensional Patterson map was not straightforward. Some of the highest peaks were eventually found consistent with the co-ordinates of three atoms in space group $Pca2_1$; they were introduced as two copper and one chlorine atoms in the structure-factor calculation (R 0.42). The following three-dimensional Fourier synthesis showed the two sulphur and a few light atoms, whose contribution lowered R to 0.31. All the remaining non-hydrogen atoms were located with some difficulty in three successive three-dimensional difference-Fourier syntheses, and their positions definitely confirmed the choice of $Pca2_1$ as the space group.

The scale factors of sharp (945) and diffuse reflections (544) together with atomic positional and isotropic thermal parameters were refined by block-diagonal least-squares

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† Part 6 is ref. 9.

methods. The function minimized was $\Sigma w \Delta F^2$, where w was taken as $1/(22.7 + F_o + 0.005F_o^2)$. Refinement was terminated after six cycles. The final R value for 1 489 observed reflections was 0.106. The final atomic parameters with estimated standard deviations are given in Table 1. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22347 (14 pp.).*

TABLE 1

Atomic co-ordinates ($\times 10^4$) with standard deviations in parentheses

	x/a	y/b	z/c
Cu(1)	−158(2)	392(5)	0(0)
Cu(2)	2 316(1)	5 343(4)	1 779(3)
Cl(1)	2 116(3)	−11(8)	−18(5)
Cl(2)	4 570(2)	5 019(7)	1 640(4)
S(1)	970(3)	−985(9)	2 628(5)
S(2)	3 490(3)	6 113(10)	−954(5)
O(11)	2 271(16)	37(37)	970(26)
O(12)	2 575(12)	−255(27)	−547(18)
O(13)	1 842(14)	1 430(40)	−180(24)
O(14)	1 675(9)	−1 116(27)	−173(16)
O(21)	4 937(10)	4 848(27)	2 456(16)
O(22)	4 858(7)	5 073(20)	800(11)
O(23)	4 164(8)	3 769(24)	1 666(14)
O(24)	4 301(8)	6 515(24)	1 763(15)
N(1)	290(12)	59(29)	1 225(19)
N(2)	2 752(10)	5 441(29)	468(18)
N(11)	−898(9)	1 085(26)	440(15)
N(12)	−524(9)	−1 807(27)	−105(16)
N(13)	465(10)	−634(29)	−659(16)
N(14)	17(9)	2 456(25)	−709(14)
N(21)	1 537(8)	5 994(26)	1 306(14)
N(22)	1 988(9)	3 224(27)	1 881(16)
N(23)	2 985(8)	4 537(25)	2 504(15)
N(24)	2 510(13)	7 401(30)	2 416(21)
C(1)	559(9)	−451(27)	1 798(17)
C(2)	3 040(11)	5 701(33)	−141(19)
C(11)	−1 223(15)	−289(38)	688(25)
C(12)	−1 139(12)	−1 446(36)	−54(22)
C(13)	−311(9)	−2 482(26)	−975(16)
C(14)	314(13)	−2 433(36)	−915(23)
C(15)	581(15)	265(38)	−1 592(23)
C(16)	585(17)	1 802(48)	−1 313(28)
C(21)	1 233(13)	4 459(36)	1 117(21)
C(22)	1 350(13)	3 344(37)	1 819(24)
C(23)	2 222(16)	2 657(48)	2 797(28)
C(24)	2 873(14)	2 984(43)	2 740(24)
C(25)	3 088(13)	5 620(38)	3 153(21)
C(26)	3 060(12)	7 244(39)	2 737(22)

DISCUSSION

This structure consisting of $[ClO_4]^-$ anions and $[Cu(3,6NH\text{-od})(NCS)]^+$ cations is a further example of the influence of the unco-ordinated anion on the bonding mode of the thiocyanate group; in fact, the bonding of this group changes from the S-type in [Cu(3,6NH-od)(SCN)][NCS] to the N-type in the present $[Cu(3,6NH\text{-od})(NCS)][ClO_4]$. This result and those reported in the introduction suggest that the bonding mode of the thiocyanate ion in $CuL(SCN)_2$ and $CuL(CNS)(ClO_4)$ is influenced by packing conditions rather than by electronic effects. In fact the presence of Cu • • • S interactions in the bis(thiocyanate) derivatives should not be explained as a soft–soft interaction, as previously suggested.[9] This is because recent structural investigations of several cadmium complexes containing chelating amines ($[Cd(en)_2(NCS)_2]$,[10] $[Cd(en)_2Cl(NCS)]$,[10] $[Cd(en)(NCS)]_2[C_2O_4]$,[11] $[Cd\{N(CH_2CH_2NH_2)_2H\}(NCS)_2]$,[12] $[Cd\{N[CH_2CH_2CH_2NH_2]_2H\}(NCS)_2]$ [13]) have shown that thiocyanate is always N-bonded although Cd^{2+} ion follows Cu^{2+} in order of softness.[14] Moreover, Cu–S interactions, which take place at the apical position of an elongated octahedron or of a square pyramid, are always weak whereas Cu • • • N ones are generally close to normal covalent bonds and by far more frequent.

TABLE 2

Bond distances (Å) and angles (°), with calculated standard deviations in parentheses

(*a*) Distances

Cu(1)–N(1)	2.12(3)	Cu(2)–N(2)	2.19(3)
Cu(1)–N(11)	1.98(2)	Cu(2)–N(21)	2.07(2)
Cu(1)–N(12)	2.08(2)	Cu(2)–N(22)	1.98(2)
Cu(1)–N(13)	1.98(3)	Cu(2)–N(23)	2.04(2)
Cu(1)–N(14)	2.10(2)	Cu(2)–N(24)	2.05(3)
S(1)–C(1)	1.63(3)	S(2)–C(2)	1.65(3)
N(1)–C(1)	1.15(4)	N(2)–C(2)	1.15(4)
N(11)–C(11)	1.46(4)	N(21)–C(21)	1.53(4)
N(12)–C(12)	1.50(4)	N(22)–C(22)	1.53(4)
N(12)–C(13)	1.49(3)	N(22)–C(23)	1.54(5)
N(13)–C(14)	1.63(4)	N(23)–C(24)	1.40(4)
N(13)–C(15)	1.60(4)	N(23)–C(25)	1.35(4)
N(14)–C(16)	1.71(5)	N(24)–C(26)	1.40(5)
C(11)–C(12)	1.49(5)	C(21)–C(22)	1.43(5)
C(13)–C(14)	1.50(4)	C(23)–C(24)	1.58(5)
C(15)–C(16)	1.38(5)	C(25)–C(26)	1.52(5)
Cl(1)–O(11)	1.50(4)	Cl(2)–O(21)	1.49(3)
Cl(1)–O(12)	1.36(3)	Cl(2)–O(22)	1.42(2)
Cl(1)–O(13)	1.42(4)	Cl(2)–O(23)	1.45(2)
Cl(1)–O(14)	1.43(5)	Cl(2)–O(24)	1.44(2)

(*b*) Angles

N(1)–Cu(1)–N(11)	102(1)	N(2)–Cu(2)–N(21)	97(1)
N(1)–Cu(1)–N(12)	99(1)	N(2)–Cu(2)–N(22)	107(1)
N(1)–Cu(1)–N(13)	89(1)	N(2)–Cu(2)–N(23)	96(1)
N(1)–Cu(1)–N(14)	116(1)	N(2)–Cu(2)–N(24)	105(1)
N(11)–Cu(1)–N(12)	85(1)	N(21)–Cu(2)–N(22)	85(1)
N(11)–Cu(1)–N(13)	165(1)	N(21)–Cu(2)–N(23)	167(1)
N(11)–Cu(1)–N(14)	95(1)	N(21)–Cu(2)–N(24)	97(1)
N(12)–Cu(1)–N(13)	83(1)	N(22)–Cu(2)–N(23)	88(1)
N(12)–Cu(1)–N(14)	144(1)	N(22)–Cu(2)–N(24)	147(1)
N(13)–Cu(1)–N(14)	89(1)	N(23)–Cu(2)–N(24)	83(1)
Cu(1)–N(1)–C(1)	164(2)	Cu(2)–N(2)–C(2)	167(2)
Cu(1)–N(11)–C(11)	108(2)	Cu(2)–N(21)–C(21)	105(2)
Cu(1)–N(12)–C(12)	103(2)	Cu(2)–N(22)–C(22)	109(2)
Cu(1)–N(12)–C(13)	106(2)	Cu(2)–N(22)–C(23)	102(2)
C(12)–N(12)–C(13)	117(2)	C(22)–N(22)–C(23)	116(3)
Cu(1)–N(13)–C(14)	111(2)	Cu(2)–N(23)–C(24)	108(2)
Cu(1)–N(13)–C(15)	110(2)	Cu(2)–N(23)–C(25)	106(2)
C(14)–N(13)–C(15)	107(2)	C(24)–N(23)–C(25)	121(3)
Cu(1)–N(14)–C(16)	98(2)	Cu(2)–N(24)–C(26)	106(2)
S(1)–C(1)–N(1)	174(2)	S(2)–C(2)–N(2)	176(2)
N(11)–C(11)–C(12)	106(3)	N(21)–C(21)–C(22)	110(3)
N(12)–C(12)–C(11)	108(3)	N(22)–C(22)–C(21)	106(3)
N(12)–C(13)–C(14)	106(2)	N(22)–C(23)–C(24)	105(3)
N(13)–C(14)–C(13)	105(2)	N(23)–C(24)–C(23)	112(3)
N(13)–C(15)–C(16)	102(3)	N(23)–C(25)–C(26)	110(3)
N(14)–C(16)–C(15)	117(3)	N(24)–C(26)–C(25)	105(3)
O(11)–Cl(1)–O(12)	111(2)	O(21)–Cl(2)–O(22)	115(1)
O(11)–Cl(1)–O(13)	105(2)	O(21)–Cl(2)–O(23)	107(1)
O(11)–Cl(1)–O(14)	111(2)	O(21)–Cl(2)–O(24)	104(1)
O(12)–Cl(1)–O(13)	114(2)	O(22)–Cl(2)–O(23)	112(1)
O(12)–Cl(1)–O(14)	114(2)	O(22)–Cl(2)–O(24)	107(1)
O(13)–Cl(1)–O(14)	102(2)	O(23)–Cl(2)–O(24)	111(1)

A view of the two cations in the asymmetric unit and the atom labelling are shown in Figure 1, and values of

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

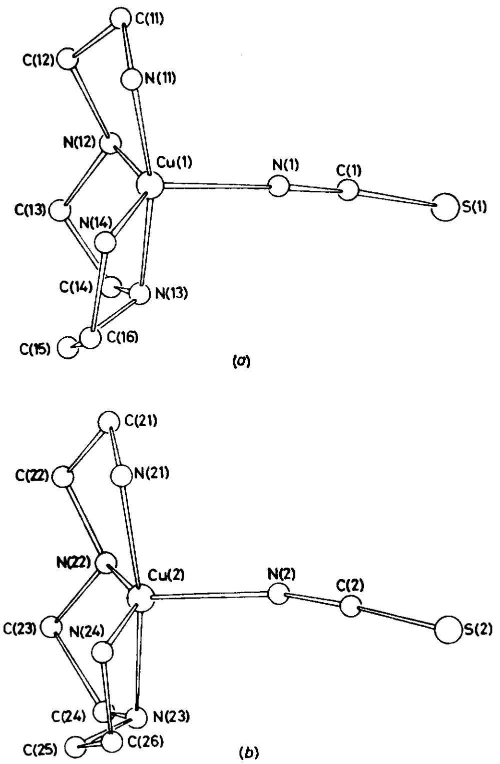

FIGURE 1 A view of the $[Cu(3,6\text{-}NH\text{-}od)(NCS)]^+$ cations

the bond distances and angles are reported in Table 2. Because of the reticular disorder, which affects an entire family of reflections (those with h odd), the accuracy of the molecular parameters is rather poor; this affects the values of the bond distances and angles, particularly those involving light atoms.

The geometries of the two co-ordination polyhedra are very close, the main difference being the orientation of the thiocyanate groups, as reflected in the values of the angles involving Cu(1)-N(1) and Cu(2)-N(2) bonds. The polyhedra are intermediate between square pyramidal and trigonal bipyramidal, as also shown by the equations of selected least-squares planes (Table 3).

TABLE 3

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

Plane (a): N(1), N(12), N(14)

$$-18.921x + 3.369y + 6.877z = 0.308$$

[Cu(1) 0.12]

Plane (b): N(2), N(22), N(24)

$$-19.998x + 3.268y - 5.780z = -4.001$$

[Cu(2) 0.09]

Plane (c): N(11), N(12), N(13), N(14)

$$11.261x + 0.482y + 12.949z = -0.592$$

[N(11) 0.21, N(12) −0.23, N(13) 0.22, N(14) −0.20, Cu(1) 0.43]

Plane (d): N(21), N(22), N(23), N(24)

$$-11.122x - 0.341y + 13.007z = -0.061$$

[N(21) −0.16, N(22) 0.18, N(23) −0.18, N(24) 0.16, Cu(2) −0.39]

All the ethylenediamine rings in the ligands of the two asymmetric units have a *gauche* conformation. The

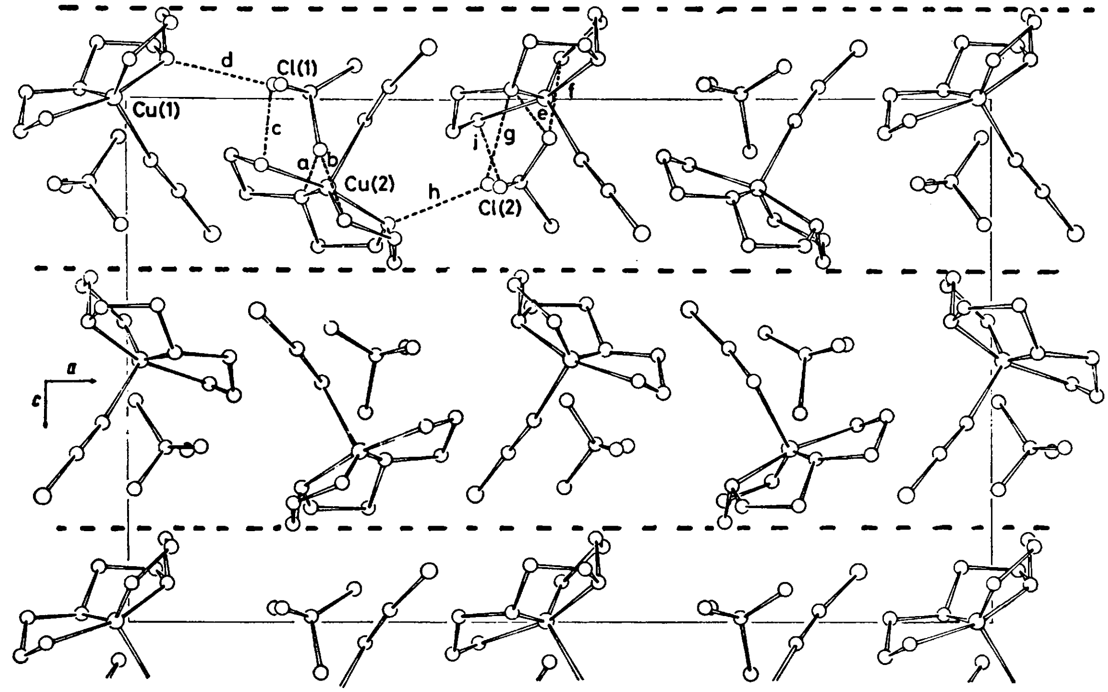

FIGURE 2 Projection of the hypothetical ordered structure along the b axis, showing the boundaries of the A_1 and A_2 layers. Intermolecular contacts (Å) within each layer are as follows: (a) $O(11^{I}) \cdots N(22^{I})$ 3.12, (b) $O(11^{I}) \cdots N(24^{II})$ 3.15, (c) $O(14^{I}) \cdots N(21^{II})$ 3.31, (d) $O(14^{I}) \cdots N(13^{I})$ 3.00, (e) $O(22^{I}) \cdots N(12^{III})$ 3.23, (f) $O(22^{I}) \cdots N(14^{IV})$ 3.09, (g) $O(23^{I}) \cdots N(12^{III})$ 3.19, (h) $O(23^{I}) \cdots N(23^{I})$ 3.15, and (i) $O(24^{I}) \cdots N(11^{IV})$ 2.87, where I = x, y, z, II = $x, y - 1, z$, III = $\frac{1}{2} + x, -y, z$, and IV = $\frac{1}{2} + x, 1 - y, z$

distances (Å) of carbon atoms from their pertinent N-Cu-N planes are: C(11) 0.36; C(12) −0.40; C(13) −0.76; C(14) −0.05; C(15) −0.59; C(16) 0.10; C(21) −0.31; C(22) 0.37; C(23) 0.72; C(24) 0.09; C(25) 0.37; and C(26) −0.39; the configurations are *k'kk* and *kk'k'* for the rings attached to Cu(1) and Cu(2) respectively.

The presence in the Weissenberg photographs of streaks along c^* for all reflections with h odd is consistent with a crystal structure formed by layers which are periodic along the a and b directions and are stacked disorderly along c. These layers, called A_1 and A_2, are $c/2$ thick and are shown in Figure 2; inside each layer the anions and cations are held together by O · · · N intermolecular contacts in the range 2.86—3.30 Å.

In the hypothetical ordered structure (Figure ,2) layers A_1 and A_2 would stack indefinitely one on top of the other giving rise to an unusually short S(1) · · · S(2) contact (3.49 Å) and to weak S · · · N contacts (3.50—3.63 Å); replacement of A_1 or A_2 by its mirror image across (010) (*i.e.* translation of one of the two layers by $a/2$) leads to S · · · N distances which fall in the same range, to S(1) · · · S(2) distances of *ca.* 4.8 Å, but to two short S · · · C contacts (2.77, 2.87 Å).

The presence of short contacts in both models is most probably the cause of their instability and, consequently, of the disordered structure. If we call B_1 and B_2 the mirror images of A_1 and A_2 respectively, the disordered structure could originate from the following stackings: $A_1A_2A_1A_2 \cdots A_1A_2A_1B_2 \cdots B_1B_2B_1B_2 \cdots B_1A_2B_1A_2 \cdots A_1A_2A_1A_2$.

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