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N,N-Dimethylthioformamidecopper(I) Cyanide

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$C_4H_7N_2SCu$, orthorhombic, *Pbca*, $a = 14{\cdot}558$ (2), $b = 21{\cdot}998$ (3), $c = 8{\cdot}698$ (1) Å, $V = 2785{\cdot}5$ Å^3, $M_r = 178{\cdot}67$, $Z = 16$, $D_x = 1{\cdot}677$ g cm^{-3}. The structure is built up of layers parallel to (100), each containing a network of two sorts of Cu coordination tetrahedra connected by some of the C–N triple bonds. The Cu^{I} coordination comprises C and N atoms of the cyanide moieties and two S atoms of the thioformamide residues, which occupy the gaps between the tetrahedra.

Introduction

The title compound (Fig. 1) was synthesized by Professor K. Fickentscher (Pharmazeutisches Institut der Universität Bonn). A crystal, 0·2 × 0·2 × 0·2 mm, was selected for the diffraction experiments. Intensity measurements were carried out in the θ–2θ mode on an automatic Syntex $P2_1$ four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) monochromatized by a graphite crystal. 2792 reflexions were recorded, resulting in a set of 2429 unique reflexions, of which 675 were regarded as unobserved ($I < 3\sigma$). No absorption correction was applied ($\mu = 32{\cdot}43$ cm^{-1}). The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) which fixed the positions of the Cu and S atoms. The completion of the structure solution was achieved by Fourier methods. Refinement was by full-matrix least-squares calculations with adjustable weights and anisotropic temperature factors. The copper was assumed to be Cu^{+}. The positions of the H atoms bonded to C(2) and C(2′) were calculated. They were allocated the isotropic temperature factors of their carrier atoms, but were refined for positional parameters. Secondary extinction was taken into account {Zachariasen, 1963: $F_c = kF_o[1 + \beta(2\theta)gI_c]$} by including g in the list of variables. The final value, however, was smaller than 10^{-7}. The final R was 0·108 (0·077 omitting unobserveds) with $R_w = 0{\cdot}061$ (0·060 omitting unobserveds) ($w = 20{\cdot}0$ for $|F_o| \geq 80{\cdot}0$, and $0{\cdot}00004|F_o|^2$ for $|F_o| < 80{\cdot}0$).*

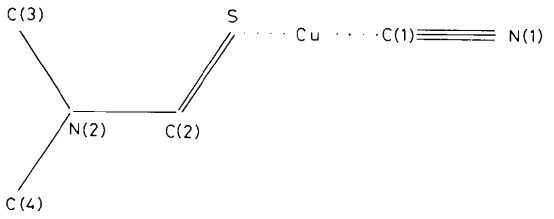

Fig. 1. The numbering scheme of atoms.

Discussion

In the presence of an acid chloride, the reaction of CuCN with *N,N*-dimethylformamide (DMF) results in an unexpected oxidative cyclic dimerization of two DMF molecules, bonding simultaneously with four CN groups (Fickentscher, Günther & Eckhardt, 1975). The mechanism of this reaction is not yet understood. CuCN is not only a donor of CN groups, but also forms a complex with DMF leading to a sterically favoured, activated Cu^{I} complex. Because of its instability this CuCN–DMF (1:1) complex could not be investigated further. However, if O is replaced by S in DMF, the reaction of *N,N*-dimethylthioformamide with CuCN yields a stable (1:1) complex which can be crystallized. An X-ray structure analysis of this compound was undertaken in order to obtain information to help in the understanding of the dimerization of two DMF molecules in the presence of CuCN.

Tables 1 and 2 give the fractional coordinates and bond distances and angles. An *ORTEP* drawing (Johnson, 1965) of the asymmetric unit is depicted in Fig. 2. Table 3 contains results for least-squares planes, showing the atoms of each formula unit (planes *A* and *B*) in almost planar configurations. This applies, as expected, exactly for the thioformamide moieties (planes *C* and *D*). The main planes *A* and *B*, as well as *C* and *D*, are roughly parallel with tilt angles of 7·2 and 5·6° respectively. The Cu and S atoms (plane *E*) are essentially planar and form a somewhat distorted rectangle with edges formed by Cu–S bonds of

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32570 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

2·300 (3) and 2·321 (3) Å within the molecules and 2·705 (3) and 2·973 (3) Å between them. Since plane *E* is almost perpendicular to planes *A* and *B* ($\angle AE$ 86°, $\angle BE$ 89°) the mean distance between *A* and *B* is defined by the latter Cu–S distances. Further close Cu distances are given by Cu–C(1) 1·885 (8), Cu′–C(1′)^{i} 1·872 (9), Cu–N(1)^{i} 1·952 (8) and Cu′–N(1′)^{i} 1·938 (9) Å.

Table 1. *Positional parameters*

The parameters and standard deviations (in parentheses) are $\times 10^4$ (for hydrogen atoms $\times 10^3$).

	x	*y*	*z*
Cu	2552 (1)	4477 (1)	4650 (1)
Cu′	1539 (1)	3033 (1)	3842 (1)
S	3363 (2)	3641 (1)	3748 (3)
S′	898 (1)	3920 (1)	4746 (3)
C(1)	2699 (7)	4793 (4)	6650 (10)
C(1′)	1551 (7)	2729 (4)	1833 (11)
C(2)	3275 (7)	3727 (5)	1842 (12)
C(2′)	920 (8)	3820 (5)	6668 (11)
C(3)	4037 (7)	2772 (5)	1227 (15)
C(3′)	241 (9)	4818 (5)	7333 (16)
C(4)	3395 (8)	3459 (5)	−884 (11)
C(4′)	722 (9)	4094 (6)	9346 (12)
N(1)	2690 (6)	5015 (4)	7849 (9)
N(1′)	1602 (6)	2489 (4)	634 (9)
N(2)	3579 (6)	3320 (4)	786 (10)
N(2′)	637 (5)	4200 (4)	7707 (10)
H(C2)	303 (8)	408 (5)	147 (13)
H(C2′)	110 (8)	348 (5)	704 (13)

Table 2. *Interatomic distances* (Å) *and angles* (°)

Standard deviations are given in parentheses for the last significant digits.

Cu–S	2·321 (3)	Cu′–S′	2·300 (3)
Cu–S′	2·705 (3)	Cu′–S	2·973 (3)
Cu–N(1)^{i}	1·956 (9)	Cu′–N(1′)^{i}	1·938 (9)
Cu–C(1)	1·885 (8)	Cu′–C(1′)	1·872 (9)
C(1)–N(1)	1·154 (11)	C(1′)–N(1′)	1·171 (11)
C(2)–S	1·673 (11)	C(2′)–S′	1·687 (11)
C(2)–N(2)	1·357 (14)	C(2′)–N(2′)	1·298 (14)
N(2)–C(3)	1·428 (13)	N(2′)–C(3′)	1·512 (14)
N(2)–C(4)	1·510 (13)	N(2′)–C(4′)	1·449 (14)
C(2)–H(C2)	0·920 (12)	C(2′)–H(C2′)	0·85 (12)
S–Cu–S′	96·0 (1)	S′–Cu′–S	89·5 (1)
S–Cu–C(1)	123·1 (3)	S′–Cu′–C(1′)	128·8 (3)
S–Cu–N(1)^{i}	105·8 (3)	S′–Cu′–N(1′)^{i}	104·3 (3)
C(1)–Cu–N(1)^{i}	123·2 (4)	C(1′)–Cu′–N(1′)^{i}	122·6 (4)
Cu–C(1)–N(1)	172·0 (9)	Cu′–C(1′)–N(1′)	173·4 (8)
C(1)–N(1)–Cu^{i}	165·9 (8)	C(1′)–N(1′)–Cu^{ii}	168·5 (8)
Cu–S–Cu′	83·9 (1)	Cu′–S′–Cu	90·7 (1)
C(2)–S–Cu	101·9 (4)	C(2′)–S′–Cu′	103·0 (4)
C(2)–S–Cu′	90·7 (4)	C(2′)–S′–Cu	94·2 (4)
S–C(2)–N(2)	124·7 (9)	S′–C(2′)–N(2′)	127·4 (9)
C(2)–N(2)–C(3)	121·8 (9)	C(2′)–N(2′)–C(3′)	123·1 (10)
C(2)–N(2)–C(4)	117·3 (9)	C(2′)–N(2′)–C(4′)	123·8 (9)
C(3)–N(2)–C(4)	120·9 (9)	C(3′)–N(2′)–C(4′)	113·0 (9)

Fig. 2. A stereoscopic view of the asymmetric unit.

Thus each Cu is in fourfold coordination with C(1), N(1), S and S′, forming distorted tetrahedra with a common edge [S–S′, 3·742 (4) Å] within the asymmetric unit. The other edge lengths vary between 3·35 and 3·93 Å. The bond angles around the Cu atoms are from 89·5 to 128·8° with a mean of 111·6°. From the tetrahedral coordination of Cu, one can expect a weak covalent bond towards N; this is supported by the C–N triple-bond lengths (mean 1·163 Å), which indicate for N(1) a partial electron transfer from the triple bond towards Cu and hence a connexion between the Cu atoms of adjacent asymmetric units *via* the cyanide moieties. This is confirmed by the fact that the Cu^{i}···N≡C–Cu atoms lie almost in a straight line. A comparable coordination of N to a neighbouring Cu has been found in $KCu(CN)_2$ (Cromer, 1957). A similar distorted tetrahedral coordination of Cu^{I} exists, for example, in Cu_2S with bond lengths between 2·21 and 2·89 Å (Evans, 1971), in Cu_9S_5 ($CuS.4Cu_2S$) 2·26–2·74 Å (Donnay, Donnay & Kullerud, 1957) and Cu_5FeS_4 ($2Cu_2S.CuS.FeS$) 2·253–2·979 Å (Koto & Morimoto, 1975). On variation of the multiplicities of Cu and Cu′, the charge character could be confirmed to be single and positive. Obviously the Cu atoms of the title compound show a similar bonding behaviour to that in the above-mentioned compounds, although two of the nearest neighbours are substituted by C and N.

Table 3. *Atom-to-plane distances* (Å)

Plane *A*				
Cu	S	C(1)	C(2)	
−0·305	−0·113	0·058	0·026	
C(3)	C(4)	N(1)	N(2)	
−0·005	0·100	0·184	0·056	
Plane *B*				
Cu′	S′	C(1′)	C(2′)	
0·193	0·102	−0·022	0·007	
C(3′)	C(4′)	N(1′)	N(2′)	
−0·023	−0·061	−0·144	−0·053	
Plane *C*				
S	C(2)	C(3)	C(4)	N(2)
−0·021	0·025	0·06	−0·022	0·019
Plane *D*				
S′	C(2′)	C(3′)	C(4′)	N(2′)
0·016	−0·013	0·003	0·021	−0·027
Plane *E*				
Cu	Cu′	S	S′	
−0·003	−0·003	0·003	0·003	

Hence one may conclude that the formula units are connected by Cu—S bonds within the asymmetric units and by weak Cu—N bonds between adjacent asymmetric units. Thus the two Cu coordination tetrahedra are connected to adjacent tetrahedra by some of the C—N triple bonds. The result is a network comprising two sorts of tetrahedra forming a layer parallel to (100). The gaps within the network are filled by the *N,N*-dimethylthioformamide residues (Fig. 3). The layers are puckered with an overall thickness of $a/2$ (Fig. 4). Closest distances between atoms of adjacent layers are N(2)—S$'^{ii}$, 3·651 (9) Å. Hence the cohesion between the layers is due solely to van der Waals forces.

Fig. 3. A stereoscopic view of a layer of molecules in projection parallel to [100].

Fig. 4. A stereoscopic view of the molecular arrangement viewed along **c**.

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Refinement of the PbFCl Types BaFI, BaFBr and CaFCl

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BaFI, BaFBr and CaFCl are of the PbFCl structure type with tetragonal space group $P4/nmm$: a = 4·654 (3), c = 7·962 (12) Å for BaFI; a = 4·508 (4), c = 7·441 (15) Å for BaFBr and a = 3·894 (3), c = 6·818 (20) Å for CaFCl. Least-squares refinement based on 348, 325 and 114 independent reflexions led to R values of 7·7% (R_w = 5·0%), 8·0% (R_w = 5·4%) and 8·1% (R_w = 6·7%) for BaFI, BaFBr and CaFCl respectively. The observed variations of interatomic distances and angles are discussed.

Introduction

The structures of BaFI, BaFBr and CaFCl refined in this work are of the tetragonal PbFCl ($E0_1$) structure type, a ternary derivative of the Cu_2Sb or Fe_2As type ($C38$). The structure and cell parameters of CaFCl and BaFI were first determined from powder diffraction data (Frevel, Rinn & Anderson, 1946). These values have recently been remeasured, by the same technique, including those for BaFBr (Beck, 1976). However, it was thought useful to obtain more accurate information on the bond distances and angles of the title compounds from the refinement of single-crystal data. Further, it is of interest to compare these results with those from the refined structures of SrFCl and BaFCl (Sauvage, 1974), who also confirmed the preliminary results of