

SHORT STRUCTURAL PAPERS

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Thiocyanato(2-dipropylaminoethanolato)copper(II)

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Abstract. $(C_8H_{18}NOCuNCS)_2$, monoclinic, $P2_1/c$; $a = 11.737$ (2), $b = 7.936$ (1), $c = 21.174$ (3) Å, $\beta = 140.16$ (1)°; $D_o = 1.40$, $D_x = 1.398$ g cm⁻³ for $Z = 2$. The structure consists of oxygen-bridged dimeric units. The dimers are linked in chains along b with additional thiocyanate bridges.

Introduction. Dark-green crystals of the title compound were prepared by the method reported by Nishida & Kida (1976), and were recrystallized from acetone. Preliminary Weissenberg photographs showed systematic absences $0k0$, k odd, and $h0l$, l odd, indicating space group $P2_1/c$. The unit-cell parameters and intensities were measured on a Syntex $P1$ automated diffractometer with monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The crystal used was ground to a sphere of radius 0.215 mm. The unit-cell parameters were determined by least-squares refinement from 15 reflexions within a range of $23 < 2\theta < 36^\circ$.

Intensity data were collected by the ω - 2θ scan technique with a variable scan rate of 4.0 to 24.0° min⁻¹. Three standard reflexions were monitored every 50 reflexions, and their intensities showed good stability. A total of 1403 independent reflexions were collected. 1158 reflexions with I greater than $2.33\sigma(I)$ were considered as 'observed' and were used for the structure analysis, where $\sigma(I)$ was calculated for each reflexion on the basis of counting statistics. Lorentz and polarization corrections were applied, but no absorption correction was made ($\mu r = 0.41$).

The structure was solved by a combination of heavy-atom and minimum-function methods. The position of the Cu atom was obtained from a three-dimensional Patterson synthesis and those of the S and O atoms were determined by a minimum-function method based on the Cu atom. Successive least-squares calculations and difference Fourier syntheses revealed all the non-H atoms. Refinement was carried out by the block-

Table 1. *Positional and thermal parameters ($\times 10^4$) with their estimated standard deviations in parentheses*

Anisotropic temperature factors have the form $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	620 (1)	1545 (1)	-58 (1)	230 (2)	111 (2)	57 (1)	84 (2)	153 (2)	37 (1)
S	-1471 (3)	6880 (2)	-1473 (1)	327 (5)	129 (3)	66 (1)	82 (6)	218 (4)	48 (3)
O	1544 (6)	-440 (5)	717 (3)	228 (9)	108 (7)	72 (3)	103 (13)	156 (9)	53 (7)
N(1)	-430 (8)	3584 (7)	-827 (4)	301 (14)	158 (11)	67 (4)	95 (19)	209 (13)	27 (10)
N(2)	2979 (8)	1491 (7)	447 (5)	209 (12)	192 (13)	76 (4)	-5 (18)	159 (13)	26 (11)
C(1)	-850 (8)	4963 (8)	-1096 (4)	232 (14)	129 (11)	50 (4)	17 (19)	164 (13)	4 (11)
C(2)	3182 (10)	-1025 (11)	1190 (6)	239 (15)	222 (15)	91 (6)	146 (28)	190 (17)	125 (17)
C(3)	4218 (10)	491 (11)	1380 (6)	236 (17)	247 (18)	83 (6)	100 (28)	141 (17)	133 (17)
C(4)	2689 (12)	548 (13)	-271 (7)	339 (21)	366 (24)	108 (7)	108 (37)	313 (21)	40 (20)
C(5)	1275 (16)	1172 (16)	-1278 (8)	469 (30)	427 (27)	103 (7)	147 (50)	338 (27)	33 (25)
C(6)	1051 (16)	50 (19)	-1979 (8)	572 (38)	538 (36)	148 (10)	6 (61)	511 (37)	-47 (34)
C(7)	3633 (13)	3345 (12)	685 (8)	317 (22)	297 (23)	129 (8)	-55 (32)	292 (25)	31 (20)
C(8)	5473 (15)	3522 (15)	1200 (9)	331 (25)	446 (35)	141 (10)	-87 (43)	281 (28)	33 (28)
C(9)	5820 (16)	5402 (14)	1299 (10)	532 (34)	298 (24)	207 (13)	-418 (48)	526 (39)	-192 (29)

diagonal least-squares method with anisotropic thermal parameters. The final R for observed reflexions was 0.050 and the largest shift of a parameter was less than one fifteenth of the standard deviation.* A difference Fourier synthesis at this point showed some peaks of less than $0.66 \text{ e } \text{Å}^{-3}$; however, the H atoms could not be reasonably allocated to these peaks. The final positional and thermal parameters with estimated standard deviations are given in Table 1.

The quantity minimized by the block-diagonal least-squares method was $w(|F_o| - k|F_c|)^2$, and the weighting scheme was $w = 1.0$ for $|F_o| \leq 12.69$ and $w = (12.69/|F_o|)^2$ for $|F_o| > 12.69$ (Hughes, 1941). Atomic scattering factors for Cu^{2+} , S, O, N and C_{var} were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. Nishida & Kida (1976) reported the magnetic and spectroscopic properties of a series of alkoxo-bridged Cu^{II} complexes with N,N -dialkylamino-alcohols, $\text{Cu}(\text{R}_2\text{NCH}_2\text{CH}_2\text{O})\text{X}$ (where $\text{R} = \text{CH}_3$, C_2H_5 , $n\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$; $\text{X} = \text{Cl}^-$, Br^- , NCS^-), and classified them into four groups, A , B , $C(a)$ and $C(b)$, based on the temperature dependence of their magnetic susceptibilities (80–295 K). The complexes of A , B and $C(a)$ had been studied by X-ray analyses (Merghehn & Haase, 1975; Merghehn, Haase & Allmann, 1975) and the correlation between molecular structure and magnetism was discussed (Hasse, 1973). However, no structural analyses have ever been reported for the $C(b)$ -group complexes. The magnetic moments of the $C(b)$ -group complexes are considerably subnormal at room temperature, but cannot be interpreted by the Bleaney–Bowers equation (Bleaney & Bowers, 1952) based on a binuclear struc-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31991 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

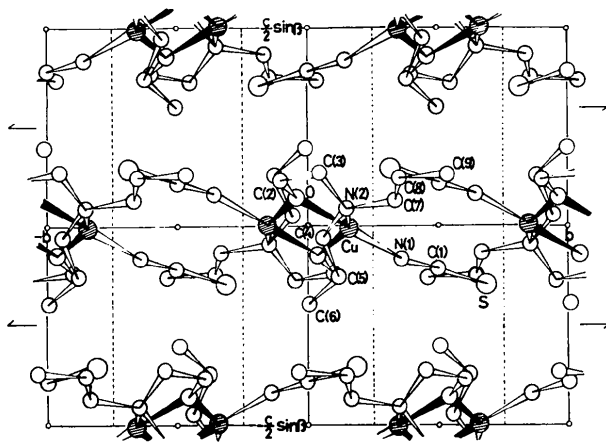


Fig. 1. A drawing of the structure viewed along a .

ture. Accordingly, we have carried out a single-crystal X-ray analysis of the title compound, one of the $C(b)$ -group complexes, in order to elucidate the correlation between the structure and the unique properties of the $C(b)$ -group complexes.

A drawing of the structure viewed along a is shown in Fig. 1. The bond distances and angles with their standard deviations are listed in Table 2.

The compound essentially consists of alkoxo-oxygen-bridged binuclear units. Each Cu atom is coordinated by amino and thiocyanate nitrogens and two alkoxo-oxygen atoms with normal Cu–O and Cu–N in-plane coordination distances. It should be noted that the amino nitrogen deviates by 0.87 Å from the $\text{Cu}-\text{O}-\text{Cu}$ plane, whereas the thiocyanate nitrogen deviates by only 0.13 Å . In addition to these coordinations, a thiocyanate S atom of a neighbouring binuclear unit approaches the Cu atom [Cu–S $2.846(6) \text{ Å}$] forming a distorted tetragonal pyramid; thereby binuclear units are weakly linked in chains parallel to b throughout the crystal. This weak bonding may accompany a weak intermolecular magnetic interaction through thiocyanate bridges. This probably accounts for the unusual magnetic behaviour of the $C(b)$ -group complexes.

The calculations were carried out at the Computer Center of Kyushu University, with the UNICS (1967) program system.

Table 2. Interatomic distances (Å) and angles ($^\circ$) with their estimated standard deviations in parentheses

$\text{Cu} \cdots \text{Cu}^{(\text{ii})}$	2.956 (2)	$\text{O}-\text{Cu}-\text{O}^{(\text{i})}$	79.0 (5)
$\text{Cu}-\text{N}(1)$	1.925 (7)	$\text{O}-\text{Cu}-\text{N}(1)$	175.2 (5)
$\text{Cu}-\text{N}(2)$	2.066 (12)	$\text{O}-\text{Cu}-\text{N}(2)$	83.5 (4)
$\text{Cu}-\text{O}$	1.902 (6)	$\text{O}^{(\text{i})}-\text{Cu}-\text{N}(1)$	97.9 (5)
$\text{Cu}-\text{O}^{(\text{i})}$	1.930 (10)	$\text{O}^{(\text{i})}-\text{Cu}-\text{N}(2)$	149.5 (3)
$\text{O} \cdots \text{O}^{(\text{i})}$	2.438 (19)	$\text{N}(1)-\text{Cu}-\text{N}(2)$	100.8 (5)
$\text{O}-\text{C}(2)$	1.398 (14)	$\text{Cu}-\text{O}-\text{Cu}^{(\text{i})}$	101.0 (5)
$\text{N}(1)-\text{C}(1)$	1.155 (8)	$\text{Cu}-\text{O}-\text{C}(2)$	116.9 (7)
$\text{N}(2)-\text{C}(3)$	1.495 (13)	$\text{Cu}^{(\text{i})}-\text{O}-\text{C}(2)$	133.6 (5)
$\text{N}(2)-\text{C}(4)$	1.481 (18)	$\text{Cu}-\text{N}(1)-\text{C}(1)$	165.3 (7)
$\text{N}(2)-\text{C}(7)$	1.533 (11)	$\text{Cu}-\text{N}(2)-\text{C}(3)$	104.6 (9)
$\text{S}-\text{C}(1)$	1.609 (6)	$\text{Cu}-\text{N}(2)-\text{C}(4)$	108.6 (7)
$\text{C}(2)-\text{C}(3)$	1.529 (15)	$\text{Cu}-\text{N}(2)-\text{C}(7)$	106.3 (8)
$\text{C}(4)-\text{C}(5)$	1.453 (17)	$\text{C}(3)-\text{N}(2)-\text{C}(4)$	108.2 (8)
$\text{C}(5)-\text{C}(6)$	1.569 (27)	$\text{C}(3)-\text{N}(2)-\text{C}(7)$	109.7 (7)
$\text{C}(7)-\text{C}(8)$	1.503 (24)	$\text{C}(4)-\text{N}(2)-\text{C}(7)$	118.6 (12)
$\text{C}(8)-\text{C}(9)$	1.518 (17)	$\text{S}-\text{C}(1)-\text{N}(1)$	178.6 (11)
		$\text{O}-\text{C}(2)-\text{C}(3)$	107.8 (7)
$\text{Cu} \cdots \text{S}^{(\text{ii})}$	2.846 (6)	$\text{N}(2)-\text{C}(3)-\text{C}(2)$	107.5 (7)
$\text{Cu} \cdots \text{Cu}^{(\text{ii})}$	5.727 (2)	$\text{N}(2)-\text{C}(4)-\text{C}(5)$	115.9 (11)
		$\text{N}(2)-\text{C}(7)-\text{C}(8)$	113.6 (10)
		$\text{C}(4)-\text{C}(5)-\text{C}(6)$	111.5 (12)
		$\text{C}(7)-\text{C}(8)-\text{C}(9)$	106.0 (12)
		$\text{S}^{(\text{ii})} \cdots \text{Cu}-\text{O}$	85.0 (3)
		$\text{S}^{(\text{ii})} \cdots \text{Cu}-\text{O}^{(\text{i})}$	98.0 (4)
		$\text{S}^{(\text{ii})} \cdots \text{Cu}-\text{N}(1)$	91.8 (4)
		$\text{S}^{(\text{ii})} \cdots \text{Cu}-\text{N}(2)$	105.1 (5)

Symmetry code

(i) $-x, -y, -z$ (ii) $-x, 1-y, -z$

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Cuivre–Etain–Soufre Cu_4SnS_4

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Abstract. Cu_4SnS_4 orthorhombic, space group $Pnma$, $a = 13.558$ (3), $b = 7.681$ (1), $c = 6.412$ (1) Å, $D_m = 4.86$, $D_c = 5.05$ g cm⁻³ for $Z = 4$. Single-crystal X-ray diffraction analysis; parameters were refined by least-squares methods to the final R value 0.071. All metallic atoms have tetrahedral coordination: Sn is regular, while the Cu atoms are far from the centres of the tetrahedra.

Introduction. Lors de l'étude du binaire Cu_2S – SnS_2 , la phase Cu_4SnS_4 a été mise en évidence par Khanafér, Rivet & Flahaut (1974). Elle est préparée par union directe des éléments. Le mélange des trois constituants est introduit dans une ampoule de silice; cette dernière est ensuite scellée sous un vide de 10⁻³ torr, puis chauffée progressivement jusqu'à la fusion du cuivre, c'est-à-dire 1083°C. On termine la préparation par une trempe. Ce composé se présente sous forme de beaux cristaux prismatiques noirs à reflets métalliques qui d'après les auteurs précédents subit un changement de phase à -41°C. L'étude cristallographique qui a été menée ici porte sur la variété stable à la température du laboratoire.

Les conditions systématiques d'existence des réflexions sont les suivantes: hkl sans conditions, $h0l$ sans conditions, $hk0$ $h = 2n$, $0kl$ $k + l = 2n$. Deux groupes spatiaux sont compatibles avec ces conditions: $Pnma$ et $Pn2_1a$. La répartition statistique des facteurs de structure normalisés en fonction de leur intensité et la position des pics de la fonction de Patterson montrent que

le groupe est centrosymétrique. Les intensités de 536 réflexions ont été enregistrées à l'aide d'un diffractomètre Nonius CAD 4 avec la radiation $\text{Mo K}\alpha$. Pour la mesure on utilise un balayage sur ω - 2θ . Les intensités ont été corrigées des facteurs de Lorentz et de polarisation.

Les facteurs de structure normalisés E ont été calculés en utilisant les valeurs du coefficient global de température et de facteur d'échelle déterminés par la méthode de Wilson. C'est à partir des réflexions:

hkl	E	
223	4,19	+
726	2,85	+
116	2,27	+
628	5,58	<i>A</i>
668	4,58	<i>B</i>
620	3,00	<i>C</i>

que les phases de 194 facteurs de structure normalisés de valeur absolue supérieure à 1,50 ont été calculées par le programme *LSAM* de Germain, Main & Woolfson (1970).

Deux solutions fournissent des séries de Fourier identiques sur lesquelles il est possible d'identifier les atomes lourds Cu et Sn (deux autres solutions fournissent des coordonnées pour ces atomes avec un décalage d'origine).

Les densités électroniques calculées, avec les phases déterminées par les atomes de métal, donnent les positions des atomes de soufre.