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Structure of Bis(*N,N*-diisopropyldithiocarbamato)copper(II)

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Abstract. $C_{14}H_{28}CuN_2S_4$, $[Cu(C_7H_{14}NS_2)_2]$, $M_r = 416{\cdot}2$, triclinic, $P\bar{1}$, $a = 11{\cdot}573\,(4)$, $b = 11{\cdot}706\,(4)$, $c = 7{\cdot}626\,(5)$ Å, $\alpha = 96{\cdot}25\,(4)$, $\beta = 96{\cdot}30\,(4)$, $\gamma = 88{\cdot}72\,(3)°$, $U = 1020{\cdot}7$ Å^3, $D_x = 1{\cdot}354$ Mg m^{-3}, μ(Mo $K\alpha$) = $1{\cdot}46$ mm^{-1}, $Z = 2$. The structure was refined to $R = 0{\cdot}057$ for 2445 independent reflexions by the block-diagonal least-squares method. A unit cell contains two crystallographically independent centrosymmetric monomers. Each Cu atom is coordinated in a plane by four S atoms. The observed Cu—S distances, 2·279 (2)–2·291 (2) Å, are shorter than those found in related dialkyldithiocarbamate complexes of Cu.

Introduction. As part of a series of investigations on coordination compounds with metal—sulfur bonds, the crystal structure of the title complex was determined. A powder of the complex was prepared by mixing aqueous solutions of cupric chloride and sodium *N,N*-diisopropyldithiocarbamate; deep-red prismatic crystals were grown from an acetone solution.

Intensity data were collected on a Rigaku automated four-circle diffractometer with a specimen of approximate dimensions 0·45 × 0·15 × 0·1 mm. The reflexions within the range $2\theta < 55°$ were measured by the ω–2θ scan technique using graphite-monochromated Mo $K\alpha$ radiation. 2446 independent reflexions with $|F_o|$ values greater than three times their standard deviations were collected. The intensities were corrected for Lorentz and polarization factors but not for absorption. At the final stage of the refinement the reflexion with the largest $|F_o|$ value (index 101) was found to suffer from extinction, and was omitted from the data set.

All the non-hydrogen atoms were located by a routine application of the heavy-atom technique. Difference Fourier syntheses gave the positions of all the H atoms. The structure was refined by the block-diagonal least-squares method, with anisotropic temperature factors for non-hydrogen atoms and isotropic for H, to an R of 0·057 for 2445 reflexions. The weighting scheme used was: $w = 0{\cdot}5$ if $|F_o| < 10$, $w = 1$ if $10 \leq |F_o| < 34$ and $w = (34/F_o)^2$ if $|F_o| \geq 34$. The atomic form factors and the correction terms for anomalous scattering were taken from *International Tables for X-ray Crystallography* (1974). All the calculations were performed on a FACOM 230-75 computer of this Institute using the *UNICS*-3 program system (Sakurai & Kobayashi, 1979). The final atomic coordinates are shown in Table 1.*

Discussion. Crystals of the title compound contain monomeric molecules of the complex $[Cu(S_2CN\textit{i}Pr_2)_2]$. The two dithiocarbamate ligands coordinate to Cu through S atoms. The two molecules, *A* and *B*, are crystallographically independent. Each Cu atom occupies a center of inversion, and, accordingly, the Cu and four S atoms are coplanar. The mean molecular planes of *A* and *B* are nearly perpendicular to each other, the dihedral angle being 89 (1)°. The crystal structure projected along the *c* axis is presented in Fig. 1, and interatomic distances and angles are listed in Table 2.

A planar configuration of the monomeric complex is also seen in a methyl analog, $[Cu(S_2CNMe_2)_2]$ (Einstein & Field, 1974). However, the features of the intermolecular interactions in these two complexes are entirely different. In the latter complex each Cu atom is also weakly bonded to two S atoms of adjacent molecules at 3·159 Å, giving rise to the polymeric nature of the complex. No intermolecular Cu—S contacts occur in the present crystal. A closely related ethyl analog is dimeric $[Cu(S_2CNEt_2)_2]_2$, in which the metal atom is surrounded by five S atoms with a tetrahedral pyramidal geometry and the two carbamate ligands make an angle of about 164° (Bonamico, Dessy, Mugnoli, Vaciago & Zambonelli, 1965). The Cu—S bond lengths observed within the chelate rings evidently reflect the number of Cu—S interactions: the mean Cu—S distance, 2·285 Å in the present case, is significantly shorter than those in the methyl and ethyl analogs (2·311 and 2·314 Å respectively).

The dimensions within each ligand are normal. The central Cu atom lies approximately in the plane of the ligand, the deviations being 0·10 (3) and 0·28 (2) Å for

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35201 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates with estimated standard deviations in parentheses*

Positional parameters for non-hydrogen atoms are multiplied by 10^4; those for hydrogen atoms by 10^3. *B* values for non-hydrogen atoms are equivalent isotropic temperature factors.

	x	*y*	*z*	*B* (Å^2)
Cu(*A*)	0 (0)	0 (0)	0 (0)	3·5
Cu(*B*)	5000 (0)	5000 (0)	5000 (0)	3·8
S(1*A*)	−1499 (2)	671 (1)	1550 (3)	4·4
S(2*A*)	−9 (2)	1932 (1)	−218 (3)	4·9
S(1*B*)	3383 (2)	3962 (2)	3863 (3)	4·4
S(2*B*)	4851 (2)	3769 (2)	7081 (3)	4·5
N(*A*)	−1651 (4)	2983 (4)	1640 (7)	3·3
N(*B*)	3170 (4)	2227 (4)	5852 (7)	3·3
C(1*A*)	−1152 (5)	2006 (5)	1070 (8)	3·1
C(2*A*)	−2600 (6)	3078 (6)	2821 (10)	4·1
C(3*A*)	−1272 (7)	4085 (5)	1079 (10)	4·2
C(4*A*)	−2195 (8)	2744 (7)	4667 (11)	5·8
C(5*A*)	−3698 (7)	2511 (8)	1946 (14)	6·6
C(6*A*)	−768 (10)	4878 (7)	2637 (13)	6·9
C(7*A*)	−2248 (9)	4619 (8)	−51 (14)	7·1
C(1*B*)	3716 (5)	3179 (5)	5634 (8)	3·4
C(2*B*)	2216 (6)	1771 (6)	4478 (9)	4·0
C(3*B*)	3449 (6)	1545 (5)	7365 (9)	4·0
C(4*B*)	2546 (8)	594 (8)	3624 (12)	6·6
C(5*B*)	1062 (7)	1787 (7)	5235 (12)	5·8
C(6*B*)	4641 (7)	994 (7)	7403 (11)	5·4
C(7*B*)	3231 (7)	2198 (6)	9127 (9)	4·5
H(2*A*)	−280 (6)	389 (6)	311 (9)	5 (2)
H(3*A*)	−69 (6)	389 (6)	45 (9)	6 (1)
H(4*A*1)	−261 (7)	293 (6)	558 (10)	6 (2)
H(4*A*2)	−195 (7)	194 (7)	431 (11)	7 (2)
H(4*A*3)	−139 (7)	298 (7)	499 (11)	7 (2)
H(5*A*1)	−379 (8)	264 (7)	62 (12)	8 (2)
H(5*A*2)	−432 (8)	271 (7)	244 (11)	8 (2)
H(5*A*3)	−364 (6)	176 (6)	168 (10)	6 (2)
H(6*A*1)	−7 (6)	445 (6)	331 (9)	5 (2)
H(6*A*2)	−41 (6)	549 (6)	236 (9)	5 (2)
H(6*A*3)	−127 (8)	496 (8)	375 (12)	9 (2)
H(7*A*1)	−193 (7)	527 (7)	−54 (11)	7 (2)
H(7*A*2)	−300 (7)	471 (7)	54 (11)	7 (2)
H(7*A*3)	−278 (7)	396 (7)	−102 (10)	7 (2)
H(2*B*)	212 (5)	229 (5)	355 (8)	4 (2)
H(3*B*)	286 (6)	102 (6)	713 (9)	5 (2)
H(4*B*1)	186 (6)	52 (6)	263 (9)	5 (2)
H(4*B*2)	227 (8)	19 (8)	456 (12)	9 (2)
H(4*B*3)	328 (6)	62 (5)	329 (9)	4 (3)
H(5*B*1)	93 (6)	244 (6)	590 (9)	5 (2)
H(5*B*2)	39 (7)	155 (6)	426 (10)	6 (2)
H(5*B*3)	110 (8)	137 (7)	612 (11)	8 (3)
H(6*B*1)	485 (7)	55 (7)	820 (10)	6 (2)
H(6*B*2)	492 (7)	78 (7)	624 (11)	7 (2)
H(6*B*3)	537 (7)	158 (6)	786 (10)	6 (2)
H(7*B*1)	385 (6)	277 (6)	972 (9)	5 (2)
H(7*B*2)	255 (6)	247 (6)	900 (9)	5 (2)
H(7*B*3)	312 (6)	171 (6)	999 (10)	6 (2)

Table 2. *Bond distances* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

	Molecule *A*	Molecule *B*
Cu–S(1)	2·283 (2)	2·291 (2)
Cu–S(2)	2·286 (2)	2·279 (2)
S(1)–C(1)	1·710 (6)	1·718 (7)
S(2)–C(1)	1·727 (7)	1·725 (6)
C(1)–N	1·321 (7)	1·328 (8)
N–C(2)	1·490 (9)	1·501 (8)
N–C(3)	1·492 (8)	1·477 (9)
C(2)–C(4)	1·523 (11)	1·518 (11)
C(2)–C(5)	1·502 (11)	1·512 (12)
C(3)–C(6)	1·498 (11)	1·508 (11)
C(3)–C(7)	1·511 (12)	1·516 (10)
S(1)–Cu–S(2)	76·66 (8)	77·30 (8)
Cu–S(1)–C(1)	86·4 (2)	85·0 (2)
Cu–S(2)–C(1)	85·9 (2)	85·2 (2)
S(1)–C(1)–S(2)	111·1 (3)	112·0 (4)
S(1)–C(1)–N	125·6 (5)	123·9 (5)
S(2)–C(1)–N	123·3 (5)	124·1 (5)
C(1)–N–C(2)	124·5 (5)	119·5 (5)
C(1)–N–C(3)	119·6 (6)	124·5 (5)
C(2)–N–C(3)	115·8 (5)	116·0 (5)
N–C(2)–C(4)	112·4 (6)	110·5 (6)
N–C(2)–C(5)	112·4 (6)	111·4 (6)
C(4)–C(2)–C(5)	115·0 (7)	113·1 (7)
N–C(3)–C(6)	111·5 (6)	113·1 (6)
N–C(3)–C(7)	110·6 (6)	113·0 (5)
C(6)–C(3)–C(7)	113·7 (6)	112·8 (6)

A and *B* respectively. The difference in these deviations results in a slight variation of the overall conformation of molecules *A* and *B*: the dihedral angles between the CuS_4 and S_2CNC_2 planes are 2·8 (10) and 8·6 (10)° for *A* and *B* respectively. This difference in the molecular geometry might result from the difference of the molecular environments, especially with respect to the intermolecular Cu···H interactions. Atom Cu(*A*) makes close contact with H(4*B*1) atoms of adjacent molecules at 2·80 (7) Å. As the Cu–H(4*B*1) vector is nearly perpendicular to the CuS_4(*A*) plane, an octahedral configuration around the Cu atom is completed. On the other hand, the nearest neighbors of Cu(*B*) are two H(2*A*) and two H(5*A*2) in adjacent molecules, each at about 3·25 (8) Å, so that the intermolecular interaction at the metal site should be weaker as compared with that in molecule *A*. This situation can probably be correlated with the fact that the Cu–S(1) and Cu–S(2) bond lengths are nearly equal for molecule *A* while they differ at the 5σ significance level for *B*. The features of the S···H interaction seem to be roughly equal for *A* and *B* (Table 3).

Table 3. *Intermolecular* Cu···H *and* S···H *distances* (Å) *and selected angles* (°) *with estimated standard deviations in parentheses*

Note: An asterisk denotes the atom related by a center of symmetry. The C–H bond lengths obtained range from 0·85 (8) to 1·15 (7) Å, the mean value being 0·97 (7) Å.

Cu(*A*)···H(4*B*1)	2·80 (7)
Cu(*B*)···H(2*A*, +*a*)	3·24 (7)
H(5*A*2, +*a*)	3·27 (8)
S(1*A*)···H(3*B**, +*c*)	2·89 (7)
H(5*B*3*, +*c*)	3·12 (9)
S(2*A*)···H(7*B*2, *c*)	3·17 (7)
S(1*B*)···H(5*A*2, +*a*)	3·24 (9)
H(7*A*1*, +*b*)	3·09 (8)
S(2*B*)···H(7*A*3, +*a* + *c*)	2·96 (8)

S(1*A*)–Cu(*A*)–H(4*B*1)	84 (4)
S(2*A*)–Cu(*A*)–H(4*B*1)	99 (4)
S(1*B*) Cu(*B*)–H(2*A*, +*a*)	72 (4)
S(2*B*)–Cu(*B*)–H(2*A*, +*a*)	79 (4)
S(1*B*) Cu(*B*)–H(5*A*2, +*a*)	69 (5)
S(2*B*)–Cu(*B*)–H(5*A*2, +*a*)	85 (5)

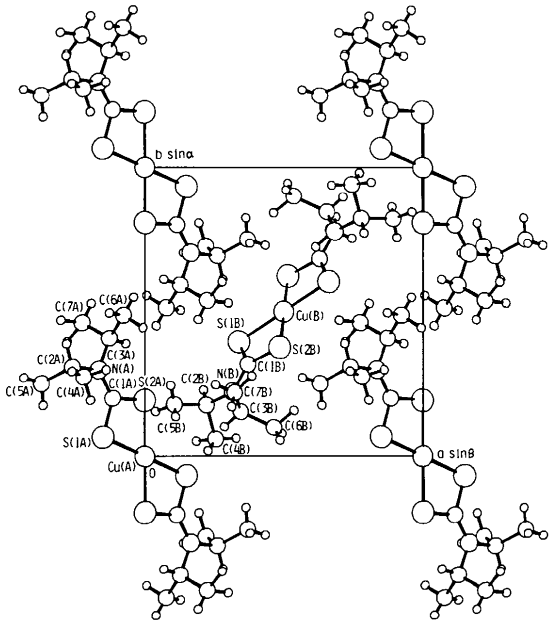

Fig. 1. The crystal structure projected along the *c* axis.

An octahedral configuration as seen around atom Cu(*A*) has also been noticed in [$Cu(S_2CNMe_2)_2$] and [$Cu(S_2CNEt_2)_2]_2$. In the case of the methyl analog the fifth and sixth octahedral positions are occupied by weakly bonded S atoms in the polymeric chain mentioned above. In the ethyl analog the sixth position is occupied by one of the methylene H atoms at 2·86 Å. Thus, the Cu atom in dithiocarbamate complexes may essentially favor an octahedral site, although this is not realized for molecule *B* of the present crystal.

The difference in the modes of molecular aggregation in diethyl- and diisopropyldithiocarbamates might, at first sight, be considered to result entirely from the difference in bulkiness of the alkyl groups. However, it should be noted that the closely related zinc isopropyldithiocarbamate (Miyamae, Ito & Iwasaki, 1979) is isostructural with zinc diethyldithiocarbamate (Bonamico, Mazzone, Vaciago & Zambonelli, 1965), both being dimeric in the crystalline state. Zinc dimethyldithiocarbamate is monomeric, as in the case of the Cu complex (Klug, 1966), although the crystal and molecular structures are not similar. Thus the change of molecular-aggregation modes of the copper dithiocarbamate series on varying the alkyl group is not paralleled by that of the corresponding Zn series. Obviously the dimeric nature of [$Zn(S_2CNi\text{Pr}_2)_2]_2$ cannot be explained by the bulkiness of the isopropyl group. Thus, the molecular association in the solid must be determined by alkyl effects combined with some processes involving the electronic structure of the metal atom.

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Structure of Tris(*N,N*-dimethyldithiocarbamato)cobalt(III)

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Abstract. $C_9H_{18}CoN_3S_6$, [$Co(C_3H_6NS_2)_3$], M_r = 419·6, monoclinic, $P2_1/n$, a = 13·992 (7), b = 9·770 (3), c = 13·555 (6) Å, β = 101·50 (4)°, U = 1815·8 Å^3, D_x = 1·535 Mg m^{-3}, μ(Mo $K\alpha$) = 1·60 mm^{-1}, Z = 4. The structure was refined to R = 0·050 for 2532 independent reflexions by the block-diagonal least-squares method. The molecule has approximate 32 symmetry. The Co atom is surrounded by six S atoms at distances of 2·254 (2)–2·273 (2) Å.

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