Table 3. *Short intra- and intermolecular distances* (Å)

Cl···C(1)	3·38 (1)	C(3)···C(18)	3·39 (2)
Cl···C(10)	3·41 (1)	C(4)···C(20)	3·30 (2)
Cl···C(19)	3·40 (1)	C(4)···C(21)	3·33 (2)
Cl···C(10′)	3·37 (2)	C(5)···C(20)	3·38 (2)
Cl···C(10″)	3·68 (2)	C(9)···C(20)	3·32 (2)
Cl···C(19′)	3·38 (2)	C(11)···C(27)	3·28 (2)
Cl···C(19″)	3·71 (2)	C(11)···C(22)	3·29 (2)
C(2)···C(13)	3·28 (2)	C(11)···C(23)	3·39 (2)
C(2)···C(14)	3·38 (2)	C(12)···C(27)	3·38 (2)
C(2)···C(18)	3·33 (2)	C(12)···C(22)	3·31 (2)
C(3)···C(13)	3·30 (2)		
Intermolecular distances			
C(13)···C(10′)	3·53 (2)	C(1″)···C(1″)	2·21 (8)
C(15)···C(1‴)	3·68 (4)	C(1‴)···C(10″)	3·80 (4)
C(1′)···C(1″)	3·55 (5)	C(10′)···C(10′)	3·81 (2)
C(1″)···C(1‴)	3·34 (6)		

observed for the bond to the ethyl-substituted C atom of the indenyl ring. A slight bending is also observed between the five- and six-membered portions of the indenyl rings [8 (2), 8 (3) and 6 (3)° respectively for rings I, II and III]. This bending results from steric crowding in the coordination sphere of the Th atom. Indeed, there appear to be several non-bonded intramolecular contacts (Table 3) shorter than normal van der Waals values (Pauling, 1960). The ethyl substituents on two of the indenyl ligands (II and III) are almost in plane with the indenyl rings, as shown by torsion angles reported in Table 2, but on the third indenyl ligand (I) the ethyl groups appear with two possible orientations. These correspond to a statistical disorder of the terminal ethyl carbon position [C(1″) or C(1‴)] and correspond to a 102° rotation about the C—C ethyl–indenyl bond. This disorder results from stacking hindrance between the two positions of C(1″) which are symmetrically related by inversion through a center of symmetry [2(*d*) or 2(*c*)]. These two positions are only 2·21 (8) Å apart (Table 3).

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Structure of a Cu^{I} Complex with a Saturated N_2S_2 Macrocycle

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Abstract. (1,5-Dithia-9,13-diazacyclohexadecane-*S*,*S*′,*N*,*N*′)copper(I) tetrafluoroborate, $[Cu(C_{12}H_{26}N_2S_2)][BF_4]$, M_r = 412·82, monoclinic, $P2_1/c$, a = 13·077 (5), b = 8·997 (3), c = 16·502 (3) Å, β = 112·78 (3)°, V = 1790·1 Å^3, Z = 4, D_x = 1·532 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 1·413 mm^{-1}, $F(000)$ = 856, T = 298 K, R = 0·063 for 2120 reflections with $I \geq 2\sigma(I)$. The Cu^{I} is coordinated by the two amino nitrogens and by the two thioether sulfurs of 1,5-dithia-9,13-diazacyclohexadecane in a slightly distorted tetrahedral geometry. The Cu—S bonds (2·25–2·26 Å) are distinctly longer than the Cu—N bonds (2·05–2·06 Å) and the angles N—Cu—S for the N and S atoms *trans* to each other are somewhat larger (117–121°) than the tetrahedral angle.

Introduction. The structure determination of plastocyanin in its oxidized (Guss & Freeman, 1983) and reduced (Guss, Harrowell, Murata, Norris & Freeman, 1986) form and the observation that both Cu^{2+} and Cu^{+} (at high pH) are tetrahedrally coordinated by two imidazole nitrogens, a methionine thioether and a cysteine thiolate has generated great interest in Cu–N_2S_2 systems. The spectral, EPR, electrochemical and structural properties of Cu^{2+}

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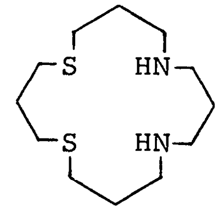
and Cu^+ complexes with open-chain and cyclic N_2S_2 ligands have been studied extensively (Karlin & Zubieta, 1983, 1986).

During our investigations of the Cu^{2+} and Cu^+ complexes with N_2S_2 macrocycles of different ring size (Balakrishnan, Kaden, Siegfried & Zuberbühler, 1984) we found that the 16-membered ligand (1) is able to stabilize the Cu^+ form so that the rate of autoxidation becomes negligible (Balakrishnan & Zuberbühler, 1984). Since this ligand contains no π-acceptor group which would electronically stabilize the Cu^+ state, it was interesting to determine the structure of the Cu^+ complex in order to understand its lack of reactivity.



Experimental. The Cu^+ complex was prepared by reacting an acetonitrile/methanol solution of 1,5-dithia-9,13-diazacyclohexadecane (1) [obtained from 50 mg of the dihydrochloride (Siegfried & Kaden, 1984) by ion exchange chromatography] with 47 mg $[Cu(CH_3CN)_4]BF_4$ under nitrogen. The solution was rotatory evaporated and the white solid crystallized from a minimum quantity of CH_3CN to which about 5 ml EtOH were added. Anal. calc. for $C_{12}H_{26}BCuF_4N_2S_2$ (412·82): C 34·92, H 6·35, N 6·79, S 15·53; found: C 35·12, H 6·15, N 6·92, S 15·52%.

X-ray data collection: An Enraf–Nonius CAD-4 diffractometer controlled by a Digital MicroVAX computer was used for measurements. The Mo *Kα* radiation was monochromated by graphite. Cell parameters were taken on a crystal of size 0·1 × 0·2 × 0·2 mm from least-squares refinement of the setting angles of 25 strong reflections in the 2θ range 10–30°. 4159 reflections ($2 \leq \theta \leq 27°$) were measured in the range $-16 \leq h \leq 16$, $0 \leq k \leq 11$, $0 \leq l \leq 21$ by the $\omega/2\theta$ scan technique. No significant variation in the intensities of four standards ($\bar{2}\bar{3}3$; $0\bar{3}1$, $\bar{4}\bar{4}2$; $0\bar{2}\bar{2}$) monitored every 3600 s was observed. 2120 reflections were considered observed $[I > 2\sigma(I)]$. The raw data set was corrected for polarization effects, but no corrections for absorption were made. Positional parameters of the metal ion were determined from a three-dimensional Patterson map (*SHELXS*86; Sheldrick, 1986). The remaining atoms were localized by subsequent difference Fourier maps. Anisotropic thermal parameters for all non-H atoms and isotropic H atoms in calculated positions were refined in a full-matrix refinement on F with 205 parameters. $R = 0·063$; $wR = 0·069$; $w = 0·89/[\sigma^2(F) + 4·36 \times 10^{-3}F^2]$. The maximum ratio of least-squares shift/e.s.d. was 0·02, and the largest positive peak on the ΔF map was 0·74, the largest negative peak $-0·59$ e Å^{-3}. Scattering factors for C, H, B, N, O, and S are given in *SHELX*76 (Sheldrick, 1976), and those for Cu are from Cromer & Mann (1968). Atomic parameters are given in Table 1,* selected bond lengths and angles in Table 2, and the numbering scheme is shown in Fig. 1.

Discussion. The Cu^+ ion is surrounded in a slightly distorted tetrahedral arrangement by two amino nitrogens and two thioether sulfurs. The bond lengths Cu—N (2·05–2·06 Å) are in the normal range, whereas the Cu—S bonds are relatively short (2·25–2·26 Å) compared to examples in the Cambridge Structural Database, which range from 2·23 to 2·46 Å. Whereas the angles S(1)—Cu—N(1) and S(2)—Cu—N(2) are distinctly larger (117–121°) than tetrahedral, the others are somewhat smaller. The dihedral angle between the two planes S(1)—Cu—N(1) and S(2)—Cu—N(2) is 89·6 (2)° so that a pseudo C_2 axis is present. The tetrahedron is compressed along this C_2 axis. The macrocycle is in the *ttt* configuration, in which all of the six-membered chelate rings adopt the twist conformation, as was found in the structure of the Cu^{2+} complex with an analogous N_2S_2 macrocycle 3,3,7,7,11,11,15,15-octamethyl-1,9-dithia-5,13-diazacyclohexadecane (McCrindle, Ferguson, McAlees, Parvez, Ruhl, Stephenson & Wieckowski, 1986). The BF_4^- ion has normal bond distances and angles.

A survey of the Cambridge Structural Database on Cu^I–N_2S_2 structures revealed that up to now all mononuclear Cu^I complexes have at least one nitrogen π acceptor either in the form of a heterocycle, such as pyridine (Brubaker, Brown, Yoo, Kinsey, Kutchan & Mottel, 1979; Karlin, Dahlstrom, Stanford & Zubieta, 1979; Karlin, Dahlstrom, Hyde & Zubieta, 1980) or phenanthroline (Hall, Kepert, Raston & White, 1977), or of a Schiff base (Martin, Organ, Wainwright, Weerasuria, Willis & Wild, 1987). The fact that no complex with only σ-donor nitrogens was structurally characterized has been attributed to the stabilization effect of π ligands on Cu^+ (Martin *et al.*, 1987). Our example, however, shows that a π acceptor is not necessary, but that the tetrahedral arrangement is of paramount importance. The 16-membered macrocycle is flexible enough to adapt itself to the geometrical requirements of the Cu^+ ion and thus is able to stabilize the metal ion in

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52711 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and* U_{eq} (Å^2) *values*

$U_{eq} = 1/3\sum_i U_{ii}(\times 10^{-2})$.

	x	y	z	U_{eq}
Cu	0·2414 (1)	0·1180 (1)	0·0051 (1)	3·9
S(1)	0·4120 (1)	0·2197 (2)	0·0495 (1)	4·3
S(2)	0·2630 (2)	−0·1243 (2)	0·0422 (1)	4·5
N(1)	0·1482 (5)	0·1155 (7)	−0·1283 (4)	4·6
N(2)	0·1495 (5)	0·2538 (7)	0·0506 (4)	4·5
C(1)	0·4815 (6)	0·1126 (8)	0·1511 (4)	4·3
C(2)	0·4929 (6)	−0·0459 (8)	0·1285 (5)	4·3
C(3)	0·4004 (6)	−0·1509 (9)	0·1272 (5)	5·3
C(4)	0·2797 (6)	−0·1928 (9)	−0·0552 (5)	5·2
C(5)	0·1795 (7)	−0·1585 (10)	−0·1378 (6)	6·0
C(6)	0·1738 (7)	−0·0064 (10)	−0·1765 (5)	5·8
C(7)	0·0283 (6)	0·1270 (10)	−0·1463 (5)	5·5
C(8)	0·0002 (6)	0·2590 (10)	−0·1026 (5)	5·8
C(9)	0·0292 (6)	0·2432 (10)	−0·0043 (5)	5·9
C(10)	0·1901 (7)	0·4104 (8)	0·0626 (6)	5·4
C(11)	0·3106 (7)	0·4208 (8)	0·1276 (5)	5·4
C(12)	0·3989 (7)	0·4019 (8)	0·0905 (6)	5·6
B	0·2610 (9)	0·4361 (11)	−0·2091 (7)	5·8
F(1)	0·2265 (7)	0·4520 (8)	−0·1427 (4)	14·2
F(2)	0·1816 (8)	0·3514 (11)	−0·2686 (5)	15·2
F(3)	0·2653 (8)	0·5653 (9)	−0·2449 (6)	19·4
F(4)	0·3545 (7)	0·3609 (10)	−0·1901 (6)	15·9

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

Cu—S(1)	2·255 (2)	Cu—S(2)	2·253 (2)
Cu—N(1)	2·063 (6)	Cu—N(2)	2·050 (6)
S(1)—C(1)	1·839 (7)	S(2)—C(3)	1·816 (7)
S(1)—C(12)	1·806 (8)	S(2)—C(4)	1·811 (8)

S(1)—Cu—S(2)	107·5 (1)	Cu—S(1)—C(1)	99·3 (3)
S(1)—Cu—N(1)	116·9 (2)	Cu—S(1)—C(12)	105·4 (3)
S(1)—Cu—N(2)	106·6 (2)	C(1)—S(1)—C(12)	102·7 (4)
S(2)—Cu—N(1)	103·9 (2)	Cu—S(2)—C(3)	108·7 (3)
S(2)—Cu—N(2)	120·5 (2)	Cu—S(2)—C(4)	97·7 (3)
N(1)—Cu—N(2)	102·1 (2)	C(3)—S(2)—C(4)	102·6 (4)

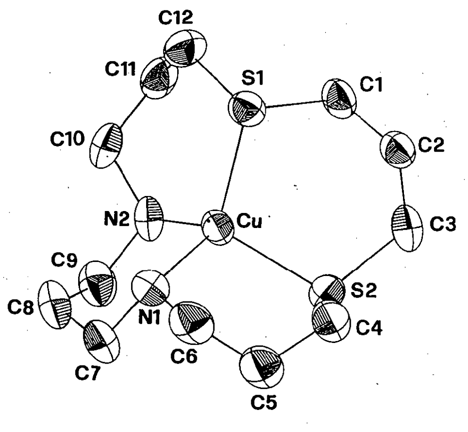

Fig. 1. *ORTEP* plot of the Cu^I-N_2S_2 macrocyclic unit with atomic numbering scheme.

this oxidation state. Finally it is worth pointing out that the *cis*-N_2S_2 arrangement as in (1) is superior in stabilizing Cu^+ to the *trans*-N_2S_2 arrangement as indicated by the redox potential (Balakrishnan, Kaden, Siegfried & Zuberbühler, 1984) and the autoxidation rate (Balakrishnan & Zuberbühler, 1984). This is probably also the reason that the Cu^+ complexes of *trans*-N_2S_2 16-membered N_2S_2 macrocycles could not be isolated (McCrindle, Ferguson, McAlees, Parvez, Ruhl, Stephenson & Wieckowski, 1986; Martin, Organ, Wainwright, Weerasuria, Willis & Wild, 1987).

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