Copper Co-ordination to Thioether Ligands: Crystal and Molecular Structures of Bis(2,5-dithiahexane)copper(II) Bis(tetrafluoroborate) and Bis(3,6-dithiaoctane)copper(I) Tetrafluoroborates

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The crystal and molecular structures of two copper–thioether complexes, (1) bis(2,5-dithiahexane)copper(II) bis(tetrafluoroborate) and (2) bis(3,6-dithiaoctane)copper(I) tetrafluoroborate, have been determined by single-crystal *X*-ray diffraction techniques, from diffractometer data. The red crystals of (1) are monoclinic, a = 8.082(3), b = 10.282(3), c = 11.893(4) Å, β = 115.3°, space-group $P2_1/c$, with Z = 2. The colourless crystals of (2) are orthorhombic, a = 14.581(2), b = 13.421(2), and c = 10.781(2) Å, space-group $Pna2_1$, with Z = 4. Both structures were refined by full matrix least-squares methods, to R 0.057 [1 238 independent reflections; (1)] and 0.082 [1 177 independent reflections; (2)]. The co-ordination geometry in (1) is distorted octahedral with four equatorial Cu–S bonds [mean 2.317(2) Å], and two axial Cu–F bonds [2.579(5) Å]. In (2) it is distorted tetrahedral, mean Cu–S 2.303(5) Å. The $[BF_4]^-$ group is not co-ordinated to the copper(I) atom and is disordered. The close similarity between the Cu^{II}–S and Cu^{I}–S bond lengths may be of relevance to the co-ordination in some copper-containing redox proteins, where the thioether side-chain of the amino-acid methionine is a potential ligand.

MUCH current interest in copper complexes with sulphur ligands derives from their relevance to the so-called ' blue ' copper proteins. These show unusual spectroscopic properties,[1,2] which have led to much speculation about the nature of the copper co-ordination sphere, and its significance for biological function. It has been suggested that the characteristic intense band observed in the 600 nm region of the absorption spectrum, and the very low values of the copper hyperfine coupling constant, $A_{\parallel}$, obtained from the e.s.r. spectra of ' blue ' copper proteins, may arise from a highly distorted ligand stereochemistry about copper.[1,3,4] The involvement of at least one sulphur ligand in the copper co-ordination sphere, as has been strongly indicated by several recent spectroscopic studies,[5-7] probably also contributes to these phenomena, however, and may have considerable functional significance.

No crystal-structure analysis of any of the ' blue ' copper proteins has yet been reported. Even when such data do become available, the resolution afforded by *X*-ray crystallographic studies of proteins is rarely high enough to reveal very fine structural detail. Thus the structures of suitably chosen low molecular-weight copper complexes are likely to be useful in establishing the variations in bond lengths and types associated with different copper–ligand systems.

The ' blue ' copper proteins are all involved in either electron transfer or oxidation–reduction processes.[1] Thus small changes in bond lengths, bond types, or co-ordination geometry accompanying a change in the oxidation state of the copper atom may be vitally important for the functions of such proteins (as, *e.g.*, are changes in iron co-ordination for the function of haemoglobin). We have therefore undertaken a comparison of copper(I) and copper(II) complexes in which the same ligand system is employed. Because of the paucity of data on copper(II) complexes of sulphur ligands, and because of the probable co-ordination of at least one sulphur ligand to copper in the ' blue ' proteins, we chose thioether ligands. Their co-ordination properties should be similar to those of the side-chain of the amino-acid methionine, a potential ligand for metal atoms in proteins.

The complexes bis(2,5-dithiahexane)copper(II) and bis(2,5-dithiahexane)copper(I) tetrafluoroborates were both prepared in crystalline form as in ref. 8. Crystals of the copper(I) complex were all found to be twinned, however, and the very closely related complex bis(3,6-dithiaoctane)copper(I) tetrafluoroborate has therefore been taken as the copper(I) complex in this comparison.

EXPERIMENTAL

Bis(2,5-*dithiahexane*)*copper*(II) *Bis*(*tetrafluoroborate*), $[Cu(dth)_2][BF_4]_2$, (1).—The crystals of (1) were deep red. The space group and cell dimensions were deduced from oscillation and Weissenberg photographs. More accurate cell dimensions were determined from least-squares analysis of the positions of 12 general reflections on a four-circle *X*-ray diffractometer.

Crystal data. $C_8H_{20}B_2CuF_8S_4$, M = 481.4, Monoclinic, a = 8.082(3), b = 10.282(3), c = 11.893(4) Å, β = 115.3°, U = 885 Å^3, $F(000)$ = 487, D_m = 1.80(1) g cm^{-3} (by flotation), Z = 2, D_c = 1.807 g cm^{-3}. Mo-K_α radiation; μ(Mo-K_α) = 18.0 cm^{-1}. Space-group $P2_1/c$, from systematic absences.

Data collection and reduction. Intensity measurements were made with a computer-controlled Hilger and Watts four-circle *X*-ray diffractometer, by use of zirconium-filtered Mo-K_α radiation from a crystal with dimensions *ca.* 0.07 × 0.04 × 0.03 cm, mounted inside a thin-walled glass capillary tube, with the longest dimension of the crystal along the axis of the tube. The orientation of the crystal was defined by a least-squares treatment of the

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positions of 12 general reflections. Intensities were measured by means of a θ—2θ scan, consisting of 50 steps of 0.02°, through each reflection, with a count of 1 s at each step, and a background count of 10 s at the beginning and end of each scan. Three standard reflections, chosen from different regions of reciprocal space, were monitored every 50 general reflections. An overall drop of *ca.* 5% in intensities was noted during the course of the data collection, and since no movement of the crystal had occurred, this fall-off was attributed to radiation damage, and correction made for it. Reflections hkl, hkl, $h\bar{k}l$, and $h\bar{k}l$ were measured, up to θ 25°. Equivalent reflections were merged, to give a total of 1 238 reflections for which $I_{hkl} > 2\sigma(I_{hkl})$ (342 unobserved). The usual Lorentz and polarisation corrections were applied, but no correction was made for absorption.

Structure determination. With $Z = 2$ in space-group $P2_1/c$, the copper atoms must be situated on centres of symmetry. The positions of the remaining non-hydrogen atoms were deduced from two successive Fourier syntheses, phased first by the copper atoms, and then with sulphur atoms added. The structure was refined by use of a full-matrix least-squares program CUCLS (a local version of the program ORFLS,[9] adapted for the Burroughs B6700 computer by the University of Canterbury). The quantity minimised was $\Sigma w(\Delta F)^2$, where $\Delta F = K|F_o| - |F_c|$ and the weight $w = 4F_o^2/[\sigma(F_o)^2]^2$. Three cycles of least-squares refinement, with isotropic temperature factors for all atoms, reduced R to 0.138. Further least-squares refinement, in which anisotropic thermal motion was allowed for, reduced R to 0.064, and the weighted R factor, R', to 0.090 [where $R' = \Sigma w|\Delta F|^2/\Sigma w(K|F_o|)^2$]. Hydrogen atoms, located from a difference-Fourier synthesis, were given temperature factors *ca.* 1.2 times those of the carbon atoms to which they were attached, and included in subsequent structure-factor calculations (but not refined). One more least-squares cycle saw refinement converge, with final values of R 0.057 and R' 0.080 for the 1 238 observed reflections.

A final electron-density difference map contained two troughs of *ca.* -1.6 eÅ^{-3}, and several peaks of 0.8—1.0 eÅ^{-3}, all in the vicinity of the $[BF_4]^-$ group or the bridging carbon atoms, C(2) and C(3). These features apparently indicated either a small degree of disorder, or inadequate treatment of the thermal motion of those atoms. Although no satisfactory model could be devised to account for them, it was considered that they were of minor significance to the structure, and certainly would not have any effect on the copper co-ordination sphere.

Final atomic co-ordinates and thermal parameters are listed in Table 1, and calculated bond lengths and angles in Table 2. The numbering system for non-hydrogen atoms is shown in Figure 1, hydrogen atoms being numbered according to the carbon atoms to which they are attached.

Bis(3,6-*dithiaoctane*)*copper*(I) *Tetrafluoroborate*, $[Cu(dto)_2][BF_4]$, (2).—Colourless, needle-shaped crystals of (2) were prepared as described in ref. 8. Accurate cell dimensions were obtained from diffractometer measurements, as for (1). Diffraction symmetry and systematic absences indicated that the space-group was either *Pna*2 or *Pnma*. With $Z = 4$ the latter would require the molecules either to be centred on centres of symmetry, or to lie on or across mirror planes. Both possibilities were considered chemically

TABLE 1

Atomic co-ordinates and isotropic thermal parameters for (1), with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*	*B*/Å^2
Cu	0.000 0	0.000 0	0.000 0	
S(1)	0.088 3(2)	0.059 6(2)	0.205 6(1)	
S(2)	−0.277 0(2)	−0.067 7(2)	−0.005 3(2)	
C(1)	0.304(1)	−0.013 9(7)	0.299 2(6)	
C(2)	−0.064(1)	−0.046(1)	0.241 8(8)	
C(3)	−0.243(1)	−0.043(1)	0.154 1(8)	
C(4)	−0.286(1)	−0.241 9(7)	−0.023 3(8)	
F(1)	−0.236 1(8)	0.425 8(4)	−0.058 1(5)	
F(2)	−0.133 1(7)	0.226 3(5)	−0.083 4(6)	
F(3)	−0.429 3(8)	0.274 2(6)	−0.177 0(6)	
F(4)	−0.291 0(9)	0.248 3(6)	0.022 7(7)	
B	−0.274(1)	0.298 2(8)	−0.080 0(8)	
H(1a)	0.290	−0.110	0.286	7.6
H(1b)	0.330	0.000	0.378	7.6
H(1c)	0.380	−0.016	0.207	7.6
H(2a)	−0.040	−0.016	0.334	10.0
H(2b)	−0.020	−0.135	0.240	10.0
H(3a)	−0.330	−0.115	0.160	10.0
H(3b)	−0.275	0.042	0.155	10.0
H(4a)	−0.290	−0.260	−0.100	6.6
H(4b)	−0.390	−0.277	−0.027	6.6
H(4c)	−0.170	−0.281	0.036	6.6

TABLE 2

Bond lengths (Å) and angles (°) for (1) *

(*a*) Distances			
Cu–S(1)	2.315(2)	S(2)–C(4)	1.800(8)
Cu–S(2)	2.319(2)	C(2)–C(3)	1.370(10)
Cu–F(2)	2.579(5)	B–F(1)	1.346(9)
S(1)–C(1)	1.783(7)	B–F(2)	1.374(9)
S(1)–C(2)	1.830(10)	B–F(3)	1.312(9)
S(2)–C(3)	1.811(8)	B–F(4)	1.380(10)
(*b*) Angles			
S(1)–Cu–S(2)	87.86(6)	C(3)–C(2)–S(1)	113.8(8)
S(1)–Cu–F(2)	93.2(1)	C(2)–C(3)–S(2)	115.4(7)
S(2)–Cu–F(2)	91.3(1)	F(3)–B–F(1)	114.1(7)
C(1)–S(1)–Cu	108.7(2)	F(3)–B–F(2)	111.3(6)
C(1)–S(1)–C(2)	100.2(4)	F(3)–B–F(4)	106.6(8)
C(2)–S(1)–Cu	99.2(3)	F(1)–B–F(2)	114.1(6)
C(3)–S(2)–C(4)	104.1(5)	F(1)–B–F(4)	106.9(6)
C(4)–S(2)–Cu	106.8(3)	F(2)–B–F(4)	102.8(7)
C(3)–S(2)–Cu	102.8(3)		

* C–H bond lengths range from 0.82 to 1.07, mean 0.95 Å. Bond angles involving H atoms are as expected.

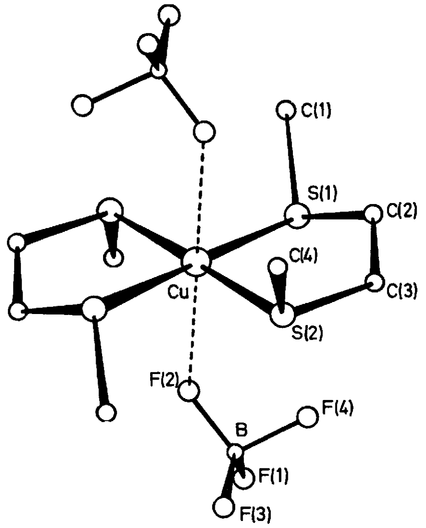

FIGURE 1 A view of the molecule of $[Cu(dth)_2][BF_4]_2$, (1), showing the numbering of the non-hydrogen atoms

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unlikely. The space-group was therefore assumed to be $Pna2_1$, and this was confirmed by the subsequent structure analysis.

Crystal data. $C_{12}H_{28}BCuF_4S_4$, $M = 450.3$, Orthorhombic, $a = 14.581(2)$, $b = 13.421(2)$, $c = 10,781(2)$ Å, $U = 2\,106$ Å^3, $F(000) = 937$, $D_m = 1.405(5)$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.42$ g cm^{-3}. Mo-K_α radiation; μ(Mo-K_α) = 14.6 cm^{-1}. Space group $Pna2_1$.

Data collection and reduction. The crystal chosen for data collection had dimensions *ca.* 0.05 × 0.03 × 0.03 cm. Intensity measurements were made, as before, on a Hilger and Watts four-circle diffractometer, using Mo-K_α radiation. Crystal-setting procedures and data-collection strategy were similar to those described for (1). A θ—2θ scan of 35 steps of 0.02°, with a count of 1.6 s at each step, was employed, with a background count of 7 s on each side of the scan. Reflections hkl and $\bar{h}kl$ were measured, and equivalent reflections later merged. Preliminary photographs had shown that the diffraction data fell off very markedly in intensity at higher values of θ, and the intensity data were therefore collected in two shells, one up to θ 20° and a second of θ 20—27°. In the inner shell a total of 868 reflections for which $I_{hkl} > 2\sigma(I_{hkl})$ were obtained, a further 156 reflections being considered unobserved. In the outer shell only 309 observed reflections were obtained, with 880 unobserved. No scaling of the data to correct for radiation damage was required. Lorentz and polarisation corrections were made as usual, but no correction for absorption was made.

Structure determination. The copper atom position was deduced from a three-dimensional Patterson synthesis, and the remaining non-hydrogen atoms from subsequent electron-density syntheses. The $[BF_4]^-$ group was poorly defined, and clearer positions for these atoms were sought by calculation of an electron-density difference synthesis, following a structure-factor calculation based on the atoms of the cation only. The map showed, however, that the peaks due to the five atoms were diffuse, and overlapped to a considerable extent, suggesting that the group was disordered.

Three cycles of full-matrix least-squares refinement of the structure, with isotropic temperature factors for all atoms, gave R 0.109. Two further cycles, in which the copper and sulphur atoms were given anisotropic temperature factors, reduced R to 0.102. The inclusion of anisotropic temperature factors for carbon atoms produced only marginal improvement and was not considered justified in view of the resulting increased number of parameters. Attempts to refine the atoms of the $[BF_4]^-$ group with anisotropic temperature factors were unsuccessful, probably because of the high degree of overlap of the electron density of the five atoms. In fact, all refinements of these atoms were rather unsatisfactory. The boron atom, in particular, was poorly defined, had a very high temperature factor, and tended to move in the y direction to a position which gave a very distorted tetrahedron.

Careful examination of a difference electron-density map showed that a better interpretation of the electron density could be made if the $[BF_4]^-$ group was regarded as being disordered among two positions. In these, the boron atom and three of the fluorine atoms were approximately shared by both orientations, while one fluorine atom was different in each case. The populations of the two approximately-tetrahedral $[BF_4]^-$ groups were estimated to be 0.8 and 0.2, and the movement of the boron atom in the y direction during least-squares refinement was seen to have been in the direction of the new, low-occupancy, fluorine atom. This disorder model could not, however, be refined successfully by least-squares methods, presumably because of the

TABLE 3

Atomic co-ordinates, isotropic thermal parameters, and group parameters for (2)

Atom	x/a	y/b	z/c	B/Å^2
Cu	0.209 4(1)	0.027 9(1)	0.259 5(9)	
S(1)	0.348 7(3)	0.031 4(3)	0.355(1)	
S(2)	0.133 2(3)	0.117 4(3)	0.411(1)	
S(3)	0.152 7(3)	−0.124 4(3)	0.198(1)	
S(4)	0.188 2(3)	0.101 1(3)	0.067(1)	
C(1)	0.427(2)	−0.083(2)	0.541(3)	11.9(7)
C(2)	0.349(1)	−0.087(1)	0.446(2)	7.3(5)
C(3)	0.321(1)	0.130(1)	0.464(2)	5.7(4)
C(4)	0.224(1)	0.119(1)	0.522(2)	6.9(4)
C(5)	0.133(1)	0.243(1)	0.347(2)	6.9(4)
C(6)	0.087(1)	0.318(1)	0.425(2)	8.8(5)
C(7)	−0.013(1)	−0.212(2)	0.248(3)	13.6(7)
C(8)	0.039(1)	0.122(1)	0.266(3)	8.7(5)
C(9)	0.137(1)	−0.094(1)	0.037(2)	6.8(4)
C(10)	0.113(1)	0.006(1)	0.006(2)	6.0(4)
C(11)	0.300(1)	0.083(1)	−0.006(2)	8.0(5)
C(12)	0.300(2)	0.108(2)	−0.147(3)	12.4(7)
H(1a)	0.466	−0.074	0.476	14.3
H(1b)	0.403	−0.023	0.596	14.3
H(1c)	0.429	−0.146	0.568	14.3
H(2a)	0.358	−0.140	0.390	8.8
H(2b)	0.289	−0.075	0.485	8.8
H(3a)	0.328	0.197	0.420	6.8
H(3b)	0.370	0.133	0.532	6.8
H(4a)	0.224	0.060	0.585	8.3
H(4b)	0.209	0.175	0.580	8.3
H(5a)	0.105	0.243	0.256	8.3
H(5b)	0.197	0.265	0.319	8.3
H(6a)	0.020	0.300	0.440	10.6
H(6b)	0.095	0.312	0.512	10.6
H(6c)	0.110	0.385	0.376	10.6
H(7a)	0.003	−0.264	0.243	16.3
H(7b)	−0.002	−0.225	0.158	16.3
H(7c)	−0.052	−0.194	0.305	16.3
H(8a)	−0.002	−0.064	0.234	10.4
H(8b)	0.037	−0.110	0.357	10.4
H(9a)	0.091	−0.142	−0.005	8.2
H(9b)	0.188	−0.118	−0.018	8.2
H(10a)	0.046	−0.015	0.032	7.2
H(10b)	0.112	0.010	−0.061	7.2
H(11a)	0.321	0.008	−0.002	9.6
H(11b)	0.351	0.115	0.031	9.6
H(12a)	0.258	0.157	−0.139	14.9
H(12b)	0.247	0.071	−0.171	14.9
H(12c)	0.342	0.050	−0.180	14.9

Atomic parameters derived for group atoms

Atom	x/a	y/b	z/c	B
B(I)	0.377	0.350	0.176	16.8
F(Ia)	0.370	0.349	0.052	13.4
F(Ib)	0.455	0.395	0.209	15.8
F(Ic)	0.376	0.257	0.219	12.7
F(Id)	0.306	0.401	0.223	13.0
B(II)	0.397	0.346	0.174	17.3
F(IIa)	0.458	0.306	0.095	13.9
F(IIb)	0.428	0.336	0.290	16.3
F(IIc)	0.316	0.300	0.163	13.2
F(IId)	0.386	0.443	0.148	13.5

Group parameters *

Group	Occupancy	X_o	Y_o
I	0.75	0.377	0.350
II	0.25	0.397	0.346

Group	Z_o	ϕ	θ	ρ
I	0.176	−152.0	178.9	−86.0
II	0.174	152.2	−175.8	−140.3

* X_o, Y_o, Z_o are fractional co-ordinates of rigid-group centres; angles ϕ, θ, ρ are defined in ref. 10.

high correlation between neighbouring part-atoms. The two $[BF_4]^-$ groups were therefore regarded as rigid groups with B–F bonds of 1.34 Å and normal tetrahedral angles, and refined by rigid-body least-squares methods, following the procedure described by Doedens.[10] The final occupancies of the two groups were 0.75 and 0.25, and values for the reliability factors R and R' following this refinement were 0.089 and 0.074. Parameters for the cation did not change by $>0.5\sigma$ as a result of this new model for the $[BF_4]^-$ group.

TABLE 4

Bond lengths (Å) and angles (°) for (2) *

(*a*) Distances			
Cu–S(1)	2.280(4)	S(3)–C(9)	1.80(2)
Cu–S(2)	2.310(5)	S(4)–C(10)	1.81(2)
Cu–S(3)	2.303(5)	S(4)–C(11)	1.82(2)
Cu–S(4)	2.318(5)	C(1)–C(2)	1.52(3)
S(1)–C(3)	1.81(2)	C(3)–C(4)	1.55(2)
S(1)–C(2)	1.87(2)	C(5)–C(6)	1.47(2)
S(2)–C(4)	1.78(2)	C(7)–C(8)	1.45(2)
S(2)–C(5)	1.81(2)	C(9)–C(10)	1.44(2)
S(3)–C(8)	1.81(2)	C(11)–C(12)	1.56(3)
(*b*) Angles			
S(1)–Cu–S(2)	95.6(2)	Cu–S(3)–C(9)	97.1(6)
S(1)–Cu–S(3)	117.9(2)	C(8)–S(3)–C(9)	105.7(9)
S(1)–Cu–S(4)	121.1(2)	Cu–S(4)–C(10)	93.3(5)
S(2)–Cu–S(3)	119.5(2)	Cu–S(4)–C(11)	102.1(6)
S(2)–Cu–S(4)	110.4(2)	C(10)–S(4)–C(11)	106.9(8)
S(3)–Cu–S(4)	94.0(2)	C(1)–C(2)–S(1)	109.0(1.4)
Cu–S(1)–C(2)	103.0(6)	S(1)–C(3)–C(4)	113.5(1.1)
Cu–S(1)–C(3)	96.1(5)	C(3)–C(4)–S(2)	114.0(1.2)
C(2)–S(1)–C(3)	106.5(7)	S(2)–C(5)–C(6)	115.4(1.4)
Cu–S(2)–C(5)	102.6(6)	C(7)–C(8)–S(3)	114.4(1.6)
Cu–S(2)–C(4)	97.0(6)	S(3)–C(9)–C(10)	118.1(1.3)
C(4)–S(2)–C(5)	104.2(8)	C(9)–C(10)–S(4)	115.2(1.2)
Cu–S(3)–C(8)	101.1(6)	S(4)–C(11)–C(12)	113.4(1.5)

* C–H bond lengths range from 0.75 to 1.12, mean 0.97 Å, and bond angles involving H atoms are as expected.

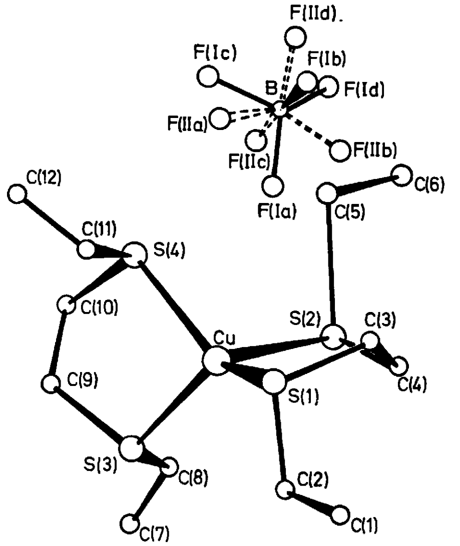

FIGURE 2 A view of the molecule of $[Cu(dto)_2][BF_4]$, (2), showing the numbering of the non-hydrogen atoms. The $[BF_4]^-$ group of lower occupancy is shown with broken lines

A difference electron-density map then gave reasonable positions for all hydrogen atoms, and the inclusion of these in the structure-factor calculations, together with two more cycles of refinement of the non-hydrogen atoms, saw the refinement converge with R 0.082 and R' 0.064. A final electron-density difference map contained two peaks of height 0.7 eÅ^{-3} and one trough of -1.1 eÅ^{-3}, all in the neighbourhood of the $[BF_4]^-$ groups, but no other features >0.5 or <-0.6 eÅ^{-3}.

Final atomic co-ordinates and temperature factors and the group parameters are listed in Table 3, and calculated bond lengths and angles for non-hydrogen atoms other than those of the $[BF_4]^-$ group in Table 4. The numbering system for non-hydrogen atoms is shown in Figure 2; the numbering of the hydrogen atoms is based on that of the carbon atoms to which they are attached. Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21960 (12 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Structure of Bis(2,5-*dithiahexane*)*copper*(II) *Tetrafluoroborate*, (1).—Within the crystal, the copper atoms are situated on centres of symmetry, so that the two halves of each molecule are centrosymmetrically related, and therefore identical. Co-ordination about each copper atom is distorted octahedral, with four short Cu–S bonds arranged in a plane, and two longer axial bonds to fluorine atoms of the two $[BF_4]^-$ groups.

The mean Cu–S bond length [2.317(2) Å] is only very slightly shorter than the sum of the covalent-bond radii *viz.* 2.34 Å [taking the in-plane radius of copper(II) as 1.30 Å,[11] and that of sulphur as 1.04 Å (ref. 12)], and therefore represents an essentially single bond. The Cu–S bond lengths also fall within the range (2.26—2.34 Å) found in copper(II) complexes of other sulphur ligands such as thiourea,[13,14] dithiocarbamates,[15,16] and thiosemicarbazides.[17] Few copper(II)-thioether complexes have previously been characterised. A Cu–S bond of 2.341 Å is found in the structure of dichloro-[*N*-{2-(methylthio)phenyl}-1-(2-pyridyl)methyleneimine]-copper(II).[18] A much closer comparison is afforded by the copper(II) complex of a macrocyclic polythioether ligand, 1,4,8,11-tetrathiacyclotetradecane (14-ane-S4),[19] in which the copper co-ordination sphere is remarkably similar to that observed here, with four Cu–S bonds of 2.30 Å, and two axial bonds of 2.65 Å to the oxygen atoms of $[ClO_4]^-$ groups.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, **1976**, Index issue.

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In the structure of (1) the two Cu–F bonds [2.579(5) Å] are close to the value expected (2.54 Å) if the fluorine atoms are regarded as semi-co-ordinated to a tetragonally-distorted copper(II) ion with an out-of-plane radius of 1.9 Å.[11] A similar distance (2.56 Å) is found in *e.g.* bis(ethylenediamine)copper(II) tetrafluoroborate.[20]

Other aspects of the copper co-ordination sphere are quite regular. The S–Cu–S bond angle [87.9(1)°] is slightly less than the idealised value of 90°, presumably because of the chelate effect. The S–Cu–F angles (91.3 and 93.2°) indicate only very slight displacement of the fluorine atoms from a precise axial position. The copper and four sulphur atoms are exactly coplanar, as required by crystallographic symmetry.

Bond lengths within the dithiahexane ligand are as expected, with the exception of the bond between the two bridging carbon atoms, C(2)–C(3), whose length (1.37 Å) is markedly shorter than that expected for a carbon–carbon single bond (1.54 Å). It is also shorter than the corresponding bonds in several dithiaoctane complexes, *viz.* 1.55(2) and 1.44(2) Å in (2) and 1.512(4) Å in tetracarbonyl(3,6-dithiaoctane)chromium(0).[21] The apparent shortening of this bond may, however, arise from thermal vibration.[22] Both atoms have large amplitudes of vibration [0.48 for C(2), 0.38 Å for C(3)] in a direction perpendicular to the plane of the dithiahexane ligand. Alternatively, it may arise from a slight degree of disorder in the S–C–C–S bridge, a possibility suggested both by the high vibrational amplitudes of C(2) and C(3) and by several small peaks in the neighbourhood of the two carbon atoms in the final electron-density difference map. That the S–C–C–S bridge may be fairly flexible is suggested by its conformation. A plane calculated through the copper and four sulphur atoms showed that both carbon atoms lie on the same side of this plane, at distances C(2) 0.71 and C(3) 0.12 Å from it. Such a conformation has been observed before for similar bridges,[23] but the usual one is the gauche configuration, in which one carbon atom lies above the plane and one below (see *e.g.* refs. 20 and 21). In the present case the unusual conformation may arise from intermolecular steric interactions. The fluorine atom F(1) from the $[BF_4]^-$ group of a neighbouring molecule lies 3.61 and 3.46 Å from the bridging carbon atoms, on the opposite side of the CuS_4 plane, and the conformation may be adopted in order to prevent closer contacts.

Other bond lengths and angles in the ligand are as expected. The C–S bonds range between 1.78(1) and 1.83(1) Å, and the bond angles at the sulphur atoms between 99.2(3) and 108.7(2)°. The S–C–C angles of the S–C–C–S bridge are 113.8(8) and 115.4(7)°. Although both are greater than the ideal tetrahedral angle, similar values have been observed in other dithioether chelate rings.[21,24] The $[BF_4]^-$ ion is approximately tetrahedral, with the B–F bonds ranging from 1.31(1) to 1.38(1) Å (mean 1.35 Å) and F–B–F angles from 102.8(7) to 114.1(6)° (mean 109.3°). Such variations are quite commonly found for $[BF_4]^-$ groups (see *e.g.* ref. 20).

Contacts between molecules are normal, none being shorter than the usual van der Waals contacts.

Structure of Bis(3,6-dithiaoctane)copper(I) *Tetrafluoroborate*, (2).—The crystal structure consists of discrete monomeric ions, the closest contact between the copper atom and any of the fluorine atoms being >4 Å.

The copper(I) ion is tetrahedrally surrounded by the four sulphur atoms from two dithiaoctane ligands, the Cu–S distances ranging from 2.280(4) to 2.318(5), mean 2.303 Å. This is similar to the Cu^I–S distances found (2.30—2.34 Å) in other tetrahedral complexes.[24-27] Taking the tetrahedral covalent-bond radius of copper(I) as 1.35 Å (ref. 12), the predicted Cu^I–S single-bond length is 2.39 Å. The bonds in (2) are on average 0.09 Å shorter than this, and while the suitability of the Pauling radius for detailed comparisons may be questioned we believe that the shortening may indicate a possible π-component in the Cu^I–S bonds. In support of this, we note that the same thioether ligand has been shown to be involved in metal–ligand π-bonding in a chromium(0) complex, tetracarbonyl(3,6-dithiaoctane)-chromium(0),[21] and that there is evidence for a π-component in the Cu^I–S bonds of several aliphatic disulphide complexes of copper(I).[27] In the latter complexes the Cu^I–S bond lengths are very similar to those in (2).

The angles about the copper atom vary from 94.0(2) to 121.0(2)°, the distortions from ideal tetrahedral angles arising mainly from the constraints of the two chelate rings; the two S–Cu–S angles in the chelate rings are 94.0(2) and 95.6(2)°. The dihedral angle between the planes through the copper and sulphur atoms of the two dithiaoctane ligands is 84.7°.

Other bond distances and angles within the dithiaoctane ligands are much as expected. Carbon–sulphur bond distances (mean 1.81 Å) are similar to those in (1) and in similar molecules, and mean C–C bonds are 1.50(2) Å. The internal Cu–S–C angles in the chelate rings range from 93.3(5) to 97.1(6), mean 95.9°. All are notably lower than the corresponding angles in the chelate rings of (1) (mean 101.0°), probably as a result of the expansion of the angle at the copper atom in the tetrahedral copper(I) complex. Other angles at the sulphur atoms range from 101.1(6) to 106.9(8)°. A comparison of the bond angles about the sulphur atoms in the present structures with those in two other metal–dithioether complexes [21,24] shows quite a wide variation

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(93.3 to 113.0°, mean 102°) indicating considerable flexibility. As in the structure of (1), the S–C–C angles [mean 115(1)°] in the chelate ring are larger than ideal tetrahedral values. The bridging atoms of both chelate rings have the normal gauche configuration, though in neither case is this symmetrical. In one ligand C(3) lies 0.47 Å above the plane through Cu, S(1), S(2), and C(4) 0.26 Å below it; in the other C(9) is 0.15 Å above the plane through Cu, S(3), S(4), and C(10) 0.47 Å below it.

The only intermolecular contacts of <3.5 Å involve fluorine atoms of $[BF_4]^-$ groups. Apart from one of 2.94 Å between a low-occupancy fluorine atom and one of the bridging carbon atoms [C(9)] of a dithiaoctane ligand, none are <3.2 Å. While they may have a slight influence on the conformation of the ligands, they are unlikely to affect the copper co-ordination in any way.

Comparison of the Copper(II) *and Copper*(I) *Structures.*—The Cu–S bonds in the two complexes are approximately equal, means 2.317(2) in the copper(II) and 2.303(5) Å in the copper(I) complex. Thus although the radius of copper(I) is expected to be greater than that of copper(II), and hence Cu^{I}–S longer than Cu^{II}–S bonds, a greater π-component in the former bond apparently compensates for this. A similar effect is seen in some thiourea complexes of copper(I) and copper(II) where, *e.g.* mean Cu–S bonds of 2.314 Å are found for both dichlorobis(tetramethylthiourea)copper(II) [13] and decakis(thiourea)tetracopper(I) hexafluorosilicate monohydrate.[25] The observation, that Cu–S bonds do not change significantly in length when a copper atom, co-ordinated to thioether ligands, changes oxidation state, suggests that such a metal–ligand system may be well suited for rapid electron-transfer processes. Such processes should be facilitated if structural changes are slight.

The co-ordination geometries in the two complexes are quite different, as expected, being the normal stereochemistries for copper(II) complexes (tetragonal) and copper(I) (tetrahedral). It is likely that neither will closely approximate that existing in copper proteins, since spectroscopic studies on the latter suggest an asymmetric co-ordination geometry,[1] possibly distorted tetrahedral, intermediate between the normal requirements of copper(II) and copper(I). The effect of such a geometry on metal–ligand bond lengths is difficult to estimate. The Cu–S bonds in dichlorobis(tetramethylthiourea)copper(II),[13] where the geometry is intermediate between square planar and tetrahedral are, however, comparable to those in other, more regular copper(II) complexes, the Cu–S(thioether) bond in the distorted square-pyramidal complex dichloro{*N*-[2-(methylthio)phenyl]-1-(2-pyridyl)methyleneimine}copper(II) [18] is only slightly longer than those in square-planar (1), and distorted copper(II) complexes of nitrogen ligands [28] also show bond lengths similar to those in square-planar complexes.

Several observations suggest that the system chosen here may be relevant to copper co-ordination in proteins. The thioether ligands closely resemble the side-chain of the amino-acid methionine, and the formation of stable complexes of both copper(I) and copper(II) is comparable to the situation in copper proteins, where the same set of ligands presumably interacts with both copper(I) and copper(II). We have also noted the remarkable structural similarity between (1) and the copper(II) complex of the macrocyclic ligand 14-ane-S4 (see above). Spectroscopic studies of the latter complex show very intense visible absorption bonds which have been likened to those of the blue copper proteins. Reflectance spectra of crystals of (1) show absorption bands of similar energy,[8] although no values of extinction coefficients are available.

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