Molecular Structures of an Aliphatic Disulphide and of its Cyclic Dimeric Copper(I) Complex

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Summary A binuclear Cu^{I} aliphatic disulphide complex with a central six-membered $\overline{\mathrm{CuSSCuSS}}$ ring shows modified SS bond lengths and CSSC dihedral angles, as compared to those in the free ligand.

THE complexation of aliphatic disulphide linkages by transition-metal ions has been suggested or reported in several systems,[1] and has been determined crystallographically in two.[1,2] Possible roles for such complexes in metalloprotein function have been discussed.[3] A dimeric Pd^{II} diphenyldisulphide complex has been isolated which, on the basis of i.r. and chemical evidence, has been assigned a structure[4] containing a $\overline{\mathrm{PdSSPdSS}}$ ring.

Herein are reported the molecular structures of (I) *cyclo*-di-μ-{bis-[2-(*NN*-dimethylamino)ethyl] disulphide}dicopper(I) tetrafluoroborate, $Cu_2(Me_2NCH_2CH_2SSCH_2CH_2NMe_2)_2(BF_4)_2$, which has a central six-membered $\overline{\mathrm{CuSSCuSS}}$ ring, and (II) bis-[2-(*NN*-dimethylamino)ethyl]disulphide dihydrochloride, $(Me_2NHCH_2CH_2SSCH_2CH_2NHMe_2)Cl_2$, in which the disulphide group is uncomplexed. A comparison of these two structures indicates that the disulphide bond is lengthened, and perhaps labilized, by Cu^{I} co-ordination. The complex (I) is unstable in the atmosphere and in the *X*-ray beam.

Crystal data: (I) $C_{16}H_{40}S_4N_4B_2F_8Cu_2$, $M = 358{\cdot}7$, orthorhombic, $a = 28{\cdot}763(8)$, $b = 11{\cdot}451(2)$, $c = 9{\cdot}293(4)$ Å, space group $Pn2_1a$, $Z = 4$, $D_m = 1{\cdot}55$, $D_c = 1{\cdot}557$, $R = 0{\cdot}063$ for 1178 reflections with $I > 3\sigma(I)$. (II) $C_8H_{22}N_2S_2Cl_2$, $M = 281{\cdot}3$, monoclinic, $a = 11{\cdot}646(2)$, $b = 11{\cdot}065(2)$, $c = 12{\cdot}370(3)$ Å, $\beta = 112{\cdot}40(2)°$, space group $P2_1/c$, $Z = 4$, $D_m = 1{\cdot}26$, $D_c = 1{\cdot}268$, $R = 0{\cdot}043$ for 1972 reflections with $I > 3\sigma(I)$.

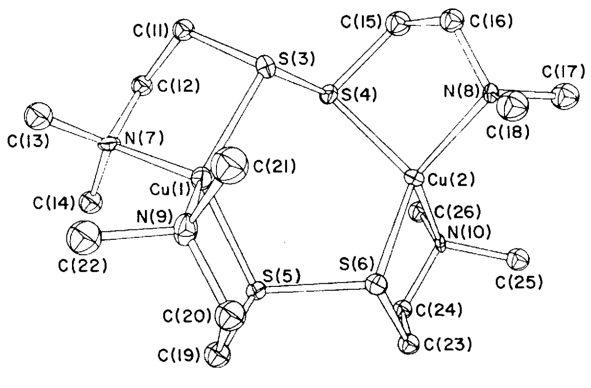

FIGURE. The molecular structure of the $[Cu_2(C_8H_{20}N_2S_2)_2]^{2+}$ ion. Hydrogen atoms and BF_4^- groups are not shown. Ellipsoids of 15% probability[9] are used.

A four-circle computer-controlled diffractometer with graphite-monochromatized Mo-K_α radiation ($\bar{\lambda} = 0{\cdot}71069$) was used to collect diffraction data at 20°. Both structures were solved by Patterson methods.

The molecular structure of the complexed cation is shown in the Figure. Each sulphur atom in each disulphide linkage is co-ordinated to a Cu^I ion, forming a six-membered ring in the boat configuration. Four five-membered rings, noticeably strained, are formed, and badly distorted tetrahedral co-ordination of the cations is observed. Average angles at Cu^I range from 90·2(3)° at the intra-ring N–Cu–S angle to 123·9(8)° for N–Cu–N.

The aliphatic disulphide bonds are 2·084(9) and 2·068(8) Å in length. The mean and its standard deviation are 2·075(6) Å. This is significantly longer than the value of 2·037(1) Å found in (II), the uncomplexed ligand. The latter value is near to the average S–S bond length found in unstrained aliphatic disulphides,[5,6] usually 2·03 to 2·05 Å with dihedral angles near 90°.

The dihedral angles for the C–S–S–C linkage [106·7° for C(19)–S(5)–S(6)–C(23) and 105·9° for C(11)–S(3)–S(4)–C(15)] are larger than those reported previously for aliphatic disulphide complexes (86°[1] and 98°[2]). The greater deviations from 90° observed here are expected to lengthen the S–S bond by a small amount (*ca.* 0·01 Å).[5] The dihedral angle in the unco-ordinated ligand is 82·4(4)°.

Cu^I–S bonds (2·288, 2·302, 2·283, and 2·326 Å) average 2·300(8) Å in length, less than the average of 2·37 Å [from 2·34(1) and 2·40(1) Å] found in chloro(diethyl disulphide)-copper(I).[2] In the Ni^{II} complex,[1] the Ni^{II}–S bond of 2·472(5) Å was 0·04 Å greater than the sum of the corresponding Pauling[7] covalent radii, 2·43 Å. For the Cu^I complex, the corresponding sum of the tetrahedral covalent radius of Cu^I, 1·35 Å, and the singly bonded radius of S, 1·04 Å, is 2·39 Å. Although this value is not suitable for detailed comparisons, it is 0·09 Å longer than the average Cu^I–S distance observed in this compound, and indicates a particularly strong interaction. The Cu^I–S distances in a Cu^I thiourea complex with a Cu_3S_3 ring[8] average 2·315 Å, nearly the same as that reported here.

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