Synthetic, Structural, and Spectroscopic Studies of the Ligating Properties of Organic Disulphides: *X*-Ray Structure of Copper(I) Iodide–Diethyl Disulphide (2/1)

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The synthesis of a series of derivatives of copper(I) halides with organic disulphides is reported. Although most of these complexes are unstable with respect to loss of ligand, the compound $2CuI{\cdot}Et_2S_2$ was sufficiently stable to be subjected to a single-crystal *X*-ray structure determination. Crystals are monoclinic, space group $P2_1/n$, with cell dimensions (at −100 ± 5 °C) $a = 8.163(4)$, $b = 15.651(3)$, $c = 8.746(4)$ Å, $\beta = 100.73(2)°$, and $Z = 4$. The structure was solved with data collected at −100(5) °C using direct methods followed by difference-Fourier techniques, and refined to R 0.038 (R' 0.047) for 1 157 observed reflections. The structure consists of double chains of copper atoms bridged by two iodines, with alternative pairs of copper atoms also bridged by diethyl disulphide molecules. The geometry of the disulphide is compared with that of related complexes, and Raman spectral studies of the ν(S–S) stretching frequency of the series of complexes are reported.

THE recognition of the disulphide group as a potential ligand for metal ions in biological systems has stimulated a number of recent studies. In particular there have been structural studies on several crystalline complexes of simple [1-3] and polyfunctional disulphides.[4-10] A paper by Sigel *et al.*[11] examined the stability of the disulphide complexes of a range of metal ions, and showed that disulphides are poorer donors than thioethers towards ' soft ' metal ions. A second thrust has been in the area of the possible roles of metal ions in mediating the nucleophilic cleavage of the S–S bond in disulphides, both from an experimental [12] and from a theoretical [13] point of view. Additionally, Stiefel *et al.*[14] considered the possibility of partial bond formation between two co-ordinated RS^- ligands at a molybdenum(VI) centre, in which an unusually short non-bonded S · · · S contact occurs. This phenomenon appears to be a fairly frequent feature in the structures of bis(thiolato)-complexes and its observation in thiolato-bridged ditungsten structures in our laboratory [15,16] prompted us to begin a structural study of complexes containing such interactions.

The limiting case, in a positive sense, is clearly the coordination of simple disulphide molecules and in this paper we present the synthesis, *X*-ray structural study, and a vibrational spectroscopic study of the compound $2CuI{\cdot}Et_2S_2$. The choice of Cu^I as the acceptor ion was predicated by its known ability to form complexes with disulphides,[1] and by its biological importance. The comparison of the structural and spectroscopic properties of this complex with those of similar compounds provides a useful extension of background knowledge in this area.

EXPERIMENTAL

Preparations.—All the compounds used in this study were prepared by dissolving the anhydrous copper(I) halide (*ca.* 1 g) in an excess of the disulphide, at room temperature, under an atmosphere of dry dinitrogen. Upon slow evaporation of the solvent (ligand) the complexes were formed as pale yellow crystalline solids. In most cases the solid complexes were unstable, and lost the disulphide upon standing. They were also sensitive towards moist air. The earlier report by Brändén [1] on the crystal structure of $CuCl{\cdot}Et_2S_2$ contains a comment on the difficulty encountered in obtaining good analytical data on this complex. Similar problems were encountered in this work. Thus, although our original intention was to characterize the complete series $nCuX{\cdot}R_2S_2$ (for X = Cl, Br, or I; R = Me or Et), this proved to be impracticable since samples sent for commercial analysis invariably proved to have a non-stoicheiometric ratio of $CuX : R_2S_2$. Nevertheless, their spectroscopic properties and crystallinity when freshly prepared suggested that initially a pure compound was formed. The successful crystal structure analysis of $CuCl{\cdot}Et_2S_2$ by Brändén,[1] and of $2CuI{\cdot}Et_2S_2$ reported here, would support this conclusion. Thus the Raman spectral data reported later were obtained on complexes approximating to the formulae shown.

Spectral Studies.—Raman spectra were obtained at room temperature on a Jarrell Ash model 25-100 double-monochromator spectrometer, using an ITT FW130 photomultiplier tube and a Princeton Applied Research photon counter. Excitation was provided by a Coherent Radiation CR-3 argon-ion laser, using either the line at 488.0 or 514.5 nm. Spectra were obtained on samples sealed under N_2 in a capillary, and also, in the case of the most stable compound, $2CuI{\cdot}Et_2S_2$, on a sample contained in a ' spinning-disc ' sample holder, rotated at *ca.* 2 000 revolutions min^{-1}. Laser power was maintained as low as possible to minimize photodecomposition. Slit widths were kept in the range 5—8 cm^{-1} in all instances. The spectrometer was calibrated with CCl_4 and the line positions are considered accurate to ±2 cm^{-1}.

X*-Ray Structure of* $2CuI{\cdot}Et_2S_2$.—*Collection and reduction of the* X*-ray data.* A crystal of *ca.* 0.15 × 0.12 × 0.10 mm in size was affixed with epoxy-resin to the end of a glass fibre and a thin coating of the resin was immediately applied to the entire crystal in order to protect it from hydrolysis and/or loss of Et_2S_2 during data collection. Preliminary photographic studies revealed a monoclinic cell. The crystal used for data collection was then mounted in an arbitrary orientation on an Enraf–Nonius CAD-4 automatic diffractometer equipped with a Universal low-temperature device. After optically centring the crystal, the Enraf–Nonius program SEARCH was used to obtain 25 accurately centred reflections in the range $5.7 < \theta < 19.2°$ at room temperature, and these data were used with the program INDEX to calculate initial cell constants and an orientation matrix. The program TRANS was then used to transform the triclinic cell parameters produced by INDEX into those of a monoclinic cell. The space group was identified as $P2_1/n$ from the systematic absences ($0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$) in a small data set ($2 < \theta < 10°$) covering an entire sphere of reflections. The E statistics later confirmed the centrosymmetric space group. The crystal was subsequently cooled to $-100(5)$ °C, and after repeating the centring procedures for the 25 reflections, the low-temperature monoclinic cell constants and orientation matrix were obtained by a least-squares fit of the instrumental settings for these reflections.

TABLE 1

Fractional co-ordinates for the non-hydrogen atoms of $2CuI\cdot Et_2S_2$, with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c
Cu(1)	0.385 9(2)	0.000 8(1)	0.586 7(2)
Cu(2)	0.477 4(2)	0.057 2(1)	0.889 1(2)
I(1)	0.375 6(1)	−0.103 90(6)	0.835 8(1)
I(2)	0.672 0(1)	0.084 52(6)	0.669 9(1)
S(1)	0.151 6(4)	0.079 4(2)	0.617 8(4)
S(2)	0.279 2(4)	0.159 8(2)	0.785 8(4)
C(1)	0.072(2)	0.151(1)	0.454(2)
C(2)	0.078(2)	0.104 4(9)	0.994(2)
C(3)	0.125(2)	0.183 8(9)	0.908(2)
C(4)	0.218(2)	0.193(1)	0.391(2)

Crystal data. $C_4H_{10}Cu_2I_2S_2$, $M = 503.0$, monoclinic, space group $P2_1/n$, $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 107.8$ cm^{-1}, $F(000) = 920$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å. Room-temperature (+23 °C) cell constants: $a = 8.25(2)$, $b = 15.81(4)$, $c = 8.80(1)$ Å, $\beta = 100.5(2)°$, $U = 1\,128$ Å^3, $D_c = 2.96$ g cm^{-3}. Final (−100 °C) cell constants: $a = 8.163(4)$, $b = 15.651(3)$, $c = 8.746(4)$ Å, $\beta = 100.73(2)°$, $U = 1\,097.9$ Å^3, $D_c = 3.04$ g cm^{-3}.

Data were collected at -100 ± 5 °C in the ω—2θ scan mode with a scan width of $\Delta\omega = 1.5\,(0.30 + 0.35 \tan\theta)$. Of the 2 019 independent reflections measured in the range $2 < \theta < 25°$, 1 157 had intensities greater than $3\sigma(I)$ where $\sigma(I) = (P + 4B)^{\frac{1}{2}}$, P is the sum of the counts accumulated in the central 64 steps of the scan, and B is the sum of the counts in the 16 steps at either end of the scan. Two standard reflections ($0\bar{5}1$ and $\overline{39}0$) were measured every 1 000 s of exposure, and their intensities were constant to within 2% of their original values throughout the data collection. Standard Lorentz and polarization corrections were applied to the data, and the program CADABS [17] was used to correct for absorption. The minimum and maximum values of the absorption correction were 2.597 and 3.476 respectively.

Solution and refinement of the structure. The structure was solved with the low-temperature data by direct methods (MULTAN 78 [18a]) from which the two Cu and two I atoms were located. Standard difference-Fourier procedures readily yielded the positions of the two S and four C atoms, but hydrogen atoms were not located and were omitted from the model. The full-matrix least-squares refinement proceeded smoothly and all ten atoms were successfully refined anisotropically. Secondary extinction was included in the final stages of the refinement [$g = 1.35(1) \times 10^{-8}$]. The maximum shift-to-error in the final cycle was 0.047, with the average value 0.0058. The final R factors were $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.038$, and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.047$, for 1 157 observed reflections. The weighting scheme was $w = [\sigma^2(F) + 0.002\,F^2]^{-1}$, where $\sigma(F)$ was derived from counting statistics. The standard deviation of an observation of unit weight was 0.99. No peaks of chemical significance could be located in the final difference map, which showed maximum fluctuations of ± 0.3 e Å^{-3}. The final atomic positional parameters are given in Table 1. The observed and calculated structure-factor amplitudes and the atomic thermal parameters are given in Supplementary Publication No. SUP 23279 (12 pp.).*

TABLE 2

Bond distances (Å) with estimated standard deviations in parentheses for $2CuI\cdot Et_2S_2$ *

Cu(1)–S(1)	2.333(4)	Cu(2)–S(2)	2.338(4)
Cu(1)–I(1)	2.739(2)	Cu(2)–I(1)	2.668(2)
Cu(1)–I(2)	2.659(2)	Cu(2)–I(2)	2.742(2)
Cu(1)–I(2′)	2.578(2)	Cu(2)–I(1″)	2.586(2)
Cu(1)–Cu(1′)	2.612(3)	Cu(2)–Cu(2″)	2.615(2)
Cu(1)–Cu(2)	2.756(3)		
S(1)–C(1)	1.84(2)	S(2)–C(3)	1.84(2)
S(1)–S(2)	2.063(5)		
C(1)–C(4)	1.55(3)	C(2)–C(3)	1.54(3)

* Shortest interchain contact is I(2) ··· C(2″) 3.95(2) Å, where C(2″) is related to C(2) by a unit translation along ***a***.

TABLE 3

Bond angles (°) in $2CuI\cdot Et_2S_2$

S(1)–Cu(1)–I(1)	94.4(1)
S(1)–Cu(1)–I(2)	113.9(1)
S(1)–Cu(1)–Cu(2)	78.5(1)
S(1)–Cu(1)–Cu(1′)	139.6(1)
S(1)–Cu(1)–I(2′)	110.7(1)
I(1)–Cu(1)–I(2)	103.46(6)
I(1)–Cu(1)–Cu(2)	58.10(6)
I(1)–Cu(1)–Cu(1′)	125.95(8)
I(2)–Cu(1)–Cu(2)	60.82(5)
I(2)–Cu(1)–I(2′)	120.18(7)
I(2)–Cu(1)–Cu(1′)	58.56(6)
Cu(2)–Cu(1)–I(2′)	166.96(8)
Cu(2)–Cu(1)–Cu(1′)	117.72(8)
I(2′)–Cu(1)–Cu(1′)	61.63(6)
I(1)–Cu(1)–I(2′)	110.78(8)
C(1)–S(1)–S(2)	103.8(5)
C(1)–S(1)–Cu(1)	114.1(6)
Cu(1)–S(1)–S(2)	95.1(2)
Cu(1)–I(1)–Cu(2)	61.27(6)
Cu(1)–I(1)–Cu(2″)	119.56(7)
Cu(2)–I(1)–Cu(2″)	59.66(6)
S(1)–C(1)–C(4)	110.9(9)
S(2)–Cu(2)–I(2)	94.1(1)
S(2)–Cu(2)–I(1)	114.26(7)
S(2)–Cu(2)–Cu(1)	78.7(1)
S(2)–Cu(2)–Cu(2″)	138.5(1)
S(2)–Cu(2)–I(1″)	109.5(1)
I(1)–Cu(2)–I(2)	103.13(7)
I(1)–Cu(2)–Cu(1)	60.63(5)
I(1)–Cu(2)–Cu(2″)	58.61(7)
I(2)–Cu(2)–Cu(1)	57.84(6)
I(2)–Cu(2)–I(1″)	112.19(7)
I(2)–Cu(2)–Cu(2″)	127.25(8)
Cu(1)–Cu(2)–I(1″)	168.29(8)
Cu(1)–Cu(2)–Cu(2″)	117.91(9)
I(1″)–Cu(2)–Cu(2″)	61.73(6)
I(1)–Cu(2)–I(1″)	120.34(8)
C(3)–S(2)–S(1)	103.2(5)
C(3)–S(2)–Cu(2)	114.6(5)
Cu(2)–S(2)–S(1)	94.5(2)
Cu(2)–I(2)–Cu(1)	61.34(6)
Cu(2)–I(2)–Cu(1′)	119.45(6)
Cu(1)–I(2)–Cu(1′)	59.82(6)
S(2)–C(3)–C(2)	112.3(9)

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Tables 2 and 3 list the bond lengths and bond angles respectively for $2CuI{\cdot}Et_2S_2$. The *X*-RAY 76 [18b] programs were used for all calculations, unless otherwise stated.

RESULTS AND DISCUSSION

The Structure of $2CuI{\cdot}Et_2S_2$.—The complex formed in the reaction of CuI with Et_2S_2 differs considerably from that between CuCl and Et_2S_2 which was reported by Brändén.[1] First, the stoicheiometry of the chloro-analogue, $CuCl{\cdot}Et_2S_2$, shows a 1 : 1 relationship between copper and ligand molecule whereas CuI forms a complex of formula $2CuI{\cdot}Et_2S_2$. This was unexpected, and leads to significant structural differences. The chloro-complex contains chains of –Cl–Cu–Cl–Cu–Cl– atoms, with alternative pairs of Cu atoms bridged by two Et_2S_2 molecules. Thus every copper atom is approximately tetrahedrally co-ordinated by two Cl and two S atoms. Paired copper atoms are separated by 3.22 Å, whereas those linked only by a μ-chloro-bridge are 3.68 Å apart. The Figure shows a portion of the double-chain structure of $2CuI{\cdot}Et_2S_2$ in relation to the unit-cell axes. It can be seen that each iodine is three-co-ordinated by Cu atoms, and that copper atoms have an approximately tetrahedral co-ordination sphere containing three I and one S atoms. However, the copper atoms are much closer to one another in the iodo-complex structure. Those pairs bridged by disulphide are separated by 2.756(3) Å, whereas contacts between adjacent symmetry-related copper atoms bridged only by iodide are 2.612(3) Å. The Cu–I–Cu angles subtended at the bridging iodides involving adjacent copper atoms are very acute, 59.7—61.3°, a phenomenon which is expected in bridged metal–metal bonded structures. The ' double chain ' structure is similar to that reported by Harding and co-workers [19] for CuI·MeNC, and contrasts with the closed tetrameric copper iodide clusters described by Churchill and co-workers.[20-22]

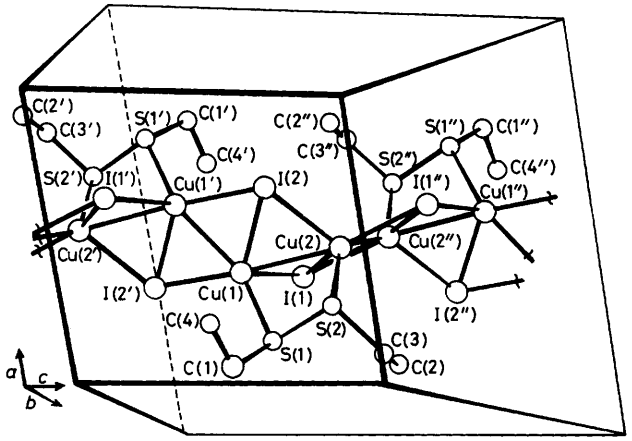
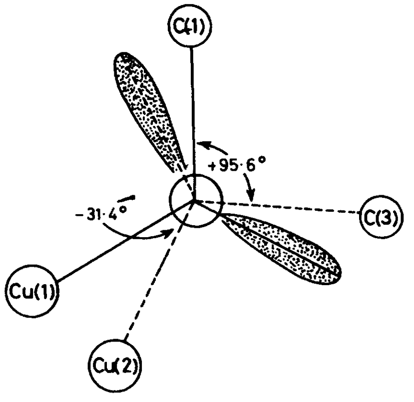


FIGURE A view of part of the double-chain structure of $2CuI{\cdot}Et_2S_2$ in relation to the unit-cell axes; the ' primed ' atoms are related to the ' unprimed ' atoms by an inversion operation, and the ' double primed ' atoms are related to the ' primed ' atoms by a unit translation along *c*. The atoms are represented by arbitrary sized spheroids

The tendency for copper(I) to cluster has been discussed by Mehrotra and Hoffmann,[23] who concluded that in the absence of metal *s* and *p* functions the expected closed-shell repulsions between d^{10} centres would occur. However, mixing of *s* and *p* functions with the *d* functions will lead to metal–metal interactions which are slightly attractive. The structure of $2CuI{\cdot}Et_2S_2$ is interesting in that its shortest copper–copper distance is apparently not induced by the geometrical constraints of the bridging ligands. The shortest contact is between di-iodo-bridged Cu atoms, rather than between pairs of coppers bridged by a disulphide molecule and two iodide ions. In the absence of ligands, copper(I) iodide displays no tendency towards clustering,[24] even though average Cu–I bond lengths are comparable with those reported here. Thus a possible conclusion is that the attractions are at least partially electronic in origin, and are influenced by the nature of the other ligands present. The geometry of the Et_2S_2 ligand in the complex is shown in the Figure and the bond angles are detailed in Table 3. In view of the known preference for disulphides to adopt a conformation with C–S–S–C angles close to 90°,[25,26] the observed C(1)–S(1)–S(2)–C(3) torsion angle of 95.6(10)° in $2CuI{\cdot}Et_2S_2$ can be considered as normal. However, the model used to account for such stability involves minimizing the repulsion between two lone pairs of electrons contained in *p* orbitals on the adjacent sulphur atoms.[22] According to this scheme, one might have expected the Cu–S–S–Cu torsional angle also to be around 90°, instead of the observed −31.4(2)°. The sum of the angles subtended at sulphur, *ca.* 313°, and the observed torsional angles, could be accounted for on the basis of the sulphur atoms having an approximately tetrahedral distribution of valence electron pairs in the complexed disulphide molecule. The geometry of a co-ordinated disulphide does not reflect the electronic constraints of the unco-ordinated molecule. Torsion angles, for example, no longer follow the 90° rule.



The lengthening of the S–S bond upon co-ordination is no more than 0.05 Å, whereas in $[Re_2Br_2(CO)_6(S_2Me_2)]$ the S–S bond lengthens from 2.022(3) to 2.111(13) Å upon co-ordination.[3] The change in the C–S–S–C torsional angle in the rhenium complex was 37.3° upon complexation,[3] whereas the change on complexation of Et_2S_2 to CuI is only 11.6° (assuming that EtSSEt has a structure and conformation analogous to that established for MeSSMe by electron diffraction [27]).

A comparison of the geometry of Et_2S_2 in the complex $CuCl{\cdot}Et_2S_2$ [1] with that of $2CuI{\cdot}Et_2S_2$ is given in Table 4.

TABLE 4

Comparison of the geometry of Et_2S_2 in $CuCl{\cdot}Et_2S_2$ [1] and $2CuI{\cdot}Et_2S_2$

Parameter	$CuCl{\cdot}Et_2S_2$	$2CuI{\cdot}Et_2S_2$
d(S–Cu) [a]	2.37(1)	2.335(4)
d(S–S)/Å	2.04(2)	2.063(5)
d(S–C)/Å [a]	1.83(6)	1.84(2)
S–S–C/° [a]	101(2)	103.5(5)
Cu–S–C/° [a]	117(2)	114.4(5)
Cu–S–S/° [a]	99.7(6)	94.8(2)
C–S–S–C/° [b]	97.7	95.6(10)

[a] Average value. [b] Torsion angle.

The two structures show remarkably constant properties for the co-ordinated Et_2S_2, in spite of the fact that the complexes are otherwise very different. The one notable difference lies in the Cu–S–S angles, that for the iodo-complex being 5° lower than for the chloro-complex. This is a corollary of the shorter Cu–Cu bond contained in the iodo-complex.

Raman Spectral Studies of $nCuX{\cdot}R_2S_2$ *Complexes*.—The ν(S–S) stretching vibration has been used as a probe for studying the disulphide group.[28] The dependence of the bond strength upon the C–S–S–C torsional angle has been discussed by several authors.[28,29] Little information is available, however, on the Raman spectra of co-ordinated disulphide molecules. We therefore initiated a study of a series of copper(I) complexes related to $CuCl{\cdot}Et_2S_2$ and $2CuI{\cdot}Et_2S_2$ to establish the feasibility of using changes in ν(S–S) as a probe for complexation. The data are presented in Table 5. The changes in ν(S–S) upon co-ordination vary from 14 to 29 cm^{-1}. For the only two complexes of known structure, $CuCl{\cdot}Et_2S_2$ and $2CuI{\cdot}Et_2S_2$, the change is minimal, as might be expected from the similar geometry of the complexed Et_2S_2 to the unco-ordinated molecule. Much larger changes in ν(S–S) were reported by Seff and co-workers for complexes of amino alkyl disulphides [7] and pyridyl alkyl disulphides,[6] but in these cases the C–S–S–C torsional angles deviated rather more from the stable 85° conformation.

TABLE 5

Raman spectra (Δν in cm^{-1}) for Me_2S_2 and Et_2S_2, and some complexes * with copper(I) halides

Compound	ν(S–S)	Compound	ν(S–S)
Et_2S_2 (liquid)	508	Me_2S_2 (liquid)	504
$CuCl{\cdot}Et_2S_2$	494	$CuCl{\cdot}Me_2S_2$	482
$CuBr{\cdot}Et_2S_2$	479	$CuBr{\cdot}Me_2S_2$	477
$2CuI{\cdot}Et_2S_2$	486	$nCuI{\cdot}Me_2S_2$	475

* See Experimental section for a discussion of syntheses and characterization.

Thus the conclusion from the present study and Seff's work would be that Raman shifts are potentially useful as a diagnostic tool for co-ordination of disulphides. However, the possibility of changes in ν(S–S) arising exclusively from the freezing of a less stable conformer in the crystal structure, without co-ordination *via* the sulphur, cannot be ignored particularly when other substituents are present which are capable of co-ordination to the metal. This was observed by Seff and co-workers [30] for (dipyrimidin-2-yl disulphide)copper(I), in which the C–S–S–C torsional angle was 180° but the sulphur atoms were not ligating. The S–S bond length was 2.113(1) Å. The expected change in ν(S–S) in such a case might well exceed that which would arise from complexation of the two sulphur atoms.

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