

Sulphur-bonded-only Thiocyanate Bridges: The Synthesis and X-Ray Crystal Structure of a Di- μ -thiocyanato-(*S*)-di-copper(I) Complex of a 20-membered Macrocyclic

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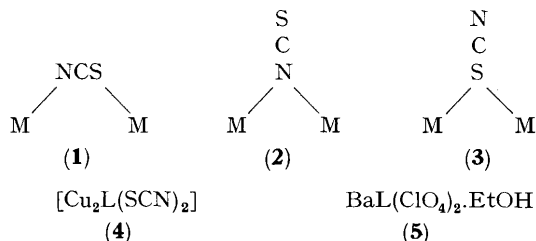
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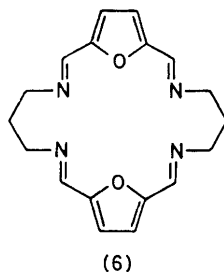
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Summary In the di-copper(I) complex $[\text{Cu}_2\text{L}(\text{SCN})_2]$ of a 20-membered macrocyclic Schiff base ligand (L), the two tetrahedrally co-ordinated Cu^{I} ions are intramolecularly linked *via* the sulphur atoms only of the thiocyanate groups.

THE ambidentate nature of the thiocyanate ion when acting as a ligand to metal ions is well known.¹ Thus, it may co-ordinate in a terminal mode either *via* the nitrogen or *via* the sulphur atom. It may also act as a bridging ligand between metal atoms. With a single exception,^{2,3} all known cases of bridging thiocyanate involve bonding of the nitrogen to one metal atom and sulphur to the other [structure (1)]. The exception occurs in the dinuclear ion $[\text{Re}_2(\text{NCS})_{10}]^{3-}$ in which the two metal ions are linked *via* the nitrogen atom only of two of the thiocyanate groups [structure (2)].² We here report the first observation of thiocyanate bridging *via* the sulphur atom only [structure (3)]. Although bridging mode (3) has occasionally been suggested⁴ previously on the basis of i.r. spectra, now recognized as an often unreliable criterion, it has never been proven.



The complex $[\text{Cu}_2\text{L}(\text{SCN})_2]$ (4) was prepared by means of a three-stage synthesis involving (i) the use of Ba^{2+} as a template for the cyclic [2 + 2] condensation of two molecules of 2,5-diformylfuran with two molecules of 1,3-diaminopropane to give the mononuclear complex $\text{BaL}(\text{ClO}_4)_2 \cdot \text{EtOH}$ (5) of the 20-membered 'N₄O₂' macrocycle L [structure (6)], (ii) transmetalation of (5) with Cu^{2+} to



yield the dinuclear complex $\text{Cu}_2\text{L}(\text{OH})_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (7), and (iii) treatment of (7) with NaNCS to afford (4) in 43% overall yield. The halide complexes $[\text{Cu}_2\text{LX}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) may be prepared similarly. The agent responsible for the $\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}}$ reduction in step (iii) is thought to be co-ordinated OH^- rather than NCS^- since the yield of (7) \rightarrow (4) is *ca.* 75% when the stoichiometric quantity of NaNCS is used. The rate of reaction (iii) is also appreciably suppressed in the presence of 2 equiv. of HClO_4 .

The red or brown $[\text{Cu}_2\text{LX}_2]$ complexes are diamagnetic and unreactive to dioxygen. They are poorly soluble in common solvents but solid state electronic spectra show a fairly intense, broad, absorption in the region 25,000–19,000 cm^{-1} , probably attributable to $\text{Cu}^{\text{I}} \rightarrow$ imine charge transfer transitions. Apart from features associated with co-ordinated NCS^- , all four Cu^{I} complexes have virtually identical i.r. spectra, suggesting a common structure. In (4) the ν_{asym} (mainly CN) stretching vibration occurs as a strong, fairly sharp, band at 2105 cm^{-1} . A medium intensity band at 700 cm^{-1} is assigned to the ν_{sym} (mainly CS) stretching mode, while a pair of weak bands at 443, 462 cm^{-1} may be due to the NCS^- bending mode. The structure of (4) has been determined.

Crystal data: $\text{C}_{20}\text{H}_{20}\text{O}_2\text{N}_6\text{S}_2\text{Cu}_2$, $M = 567.6$, triclinic, space group $P\bar{1}$, $a = 8.016(7)$, $b = 9.618(9)$, $c = 8.692(8)$ Å, $\alpha = 121.3(4)$, $\beta = 75.1(6)$, $\gamma = 105.1(5)^\circ$, $U = 547.0$ Å³, $D_m = 1.70$ g cm^{-3} , $D_c = 1.72$ g cm^{-3} , $Z = 1$. 848 independent reflections with $2\theta < 50^\circ$ and $I > 2\sigma(I)$ were collected on a diffractometer and refined to $R = 0.081$. Heavy atoms were refined anisotropically and the hydrogen atoms isotropically.†

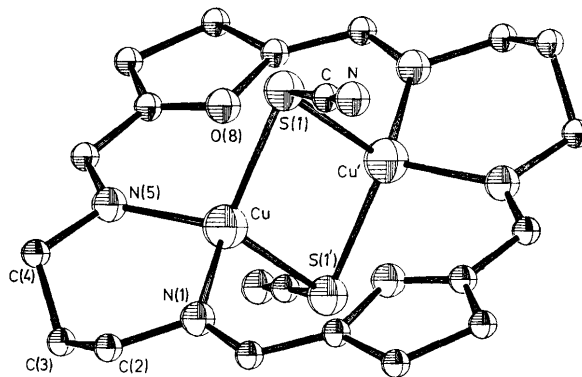
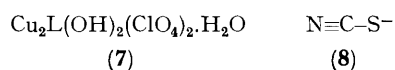


FIGURE. The structure of $[\text{Cu}_2\text{L}(\text{SCN})_2]$. Selected bond lengths are: $\text{Cu}-\text{N}(1)$ 2.04(3), $\text{Cu}-\text{N}(5)$ 2.05(2), $\text{Cu}-\text{S}(1)$ 2.37(1), $\text{Cu}-\text{S}(1')$ 2.39(1), $\text{Cu} \dots \text{Cu}'$ 2.796(8) Å.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The molecule has crystallographically imposed symmetry. The two copper atoms are each bonded to two nitrogen atoms of the macrocycle and to the two sulphur atoms of the bridging thiocyanate groups (Figure). The furan ring oxygen atoms are not bonded (Cu . . . O 2.95, 2.93 Å). The environment of the copper atoms is distorted tetrahedral with angles in the range 104—119°. The Cu . . . Cu separation is 2.796(8) Å. The macrocycle is approximately planar, least squares calculations showing that only C(3) and C(3') are displaced further than 0.23 Å from the mean plane of the 24 non-hydrogen atoms of the Cu₂L moiety. The Cu₂S₂ plane is nearly perpendicular (85.4°) to this macrocycle plane. The N—C and C—S bond distances in the thiocyanate groups are 1.13(5) and 1.70(4) Å while the Cu—S—C bond angles are 106.8, 109.2°. These observations are consistent, as are the i.r. data, with the predominance of the valence bond structure (8). The closest contact of the thiocyanate nitrogen atoms to another non-hydrogen atom is 3.52 Å.



It seems likely that the unique thiocyanate bridging mode found in [Cu₂L(SCN)₂] is a consequence of the nature of the

macrocyclic ligand which, unlike other larger and more flexible binucleating macrocycles,⁵ does not permit much variation in the metal . . . metal separation. In the present case the Cu . . . Cu separation is such as to preclude other than two single-atom bridges. The choice of sulphur rather than nitrogen as the bridging atom is presumably associated with the class b or 'soft' nature of the Cu^I ion. Molecular models indicate that, provided the Cu₂L moiety remains roughly planar, intramolecular steric interactions between the bridging groups and the furan oxygen atoms are minimised when the co-ordination geometry about the metal atoms is tetrahedral. Indeed, this is the probable reason for the stabilization of the Cu^I state. For a square-based co-ordination geometry to occur requires that the molecule be folded about the axis joining the two bridging atoms so that the M₂X₂ unit sits above the plane(s) containing the furan rings. This may be the structural arrangement existing in the antiferromagnetically coupled [μ_{eff} (293 K) 1.52 B.M., μ_{eff} (103 K) 1.13 B.M. per metal atom] di- μ -hydroxo-di-Cu^{II}-complex (7) for which electronic spectra (ν_{max} 16,500 cm⁻¹) suggest a square-based co-ordination geometry.

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¹ J. L. Burmeister, in 'The Chemistry and Biochemistry of Thiocyanic Acid and its Derivatives,' ed. A. A. Newman, Academic Press, London, 1975; K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Co-ordination Compounds,' Wiley, New York, 1977.

² F. A. Cotton, A. Davison, W. H. Isley, and H. S. Trop, *Inorg. Chem.*, 1979, **18**, 2719.

³ We exclude those structures in which it appears that the nitrogen atom of NCS⁻ is sited adjacent to two metal ions as a result of ionic packing in the crystal rather than covalent bond formation, as in the alkali metal crown-ether complex [K₂C₂₄H₃₂O₈] [NCS]₂, D. E. Fenton, M. Mercer, N. S. Poonia, and M. R. Truter, *J. Chem. Soc., Chem. Commun.*, 1972, 66.

⁴ K. Dehnicke, *Angew. Chem.*, 1967, **79**, 942; J. E. Förster, M. Vargas, and H. Müller, *J. Organomet. Chem.*, 1973, **59**, 97.

⁵ M. G. B. Drew, M. McCann, and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1979, 481; M. G. B. Drew, C. Cairns, A. Lavery, and S. M. Nelson, *ibid.*, 1980, 1122.