Copper(II) Complexes of the 14-Membered *cis*-N_2S_2 Macrocycle 14,14,16-Trimethyl-2,6-dithia-13,17-diazatricyclo[16.4.0.$0^{7,12}$]docosa-1(18),7(12),8,10,16,19,21-heptaene

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The ligand 14,14,16-trimethyl-2,6-dithia-13,17-diazatricyclo[16.4.0.$0^{7,12}$]docosa-1(18),7(12),8,10,16,19,21-heptaene (L) has been prepared by hydrolysis of the nickel(II) complex [$NiLBr_2$]. A variety of copper(II) complexes $CuL(ClO_4)_2$, $CuLBr_2$, $CuLCl_2$, $CuL(NO_3)_2{\cdot}H_2O$, and $CuL(O_2CMe)_2$ have been characterised and their spectroscopic properties studied. The complexes do not display a reversible Cu^{II}–Cu^{I} couple in acetonitrile solution, presumably as a result of the rigid nature of the macrocycle which does not readily adapt to the preferred tetrahedral stereochemistry of copper(I).

There has been continuing interest in the chemistry of quadridentate open-chain and macrocyclic ligands containing the N_2S_2 donor set.[1–9] Copper(II) complexes have atttracted particular attention due to the occurrence of the CuN_2S_2 chromophore in the type I or 'blue' copper(II) proteins such as plastocyanin.[10,11]

In a previous paper[1] we have described the preparation of the macrocyclic nickel(II) complex (**2**) by the reaction of acetone with the nickel complex (**1**). We have now found that refluxing aqueous suspensions of complex (**2**) leads to the displacement of nickel(II), and we have been able to isolate the free ligand L. The availability of the free ligand allows a variety of copper(II) complexes to be characterised and their chemistry is described below.

Table 1. Analytical data for the complexes*

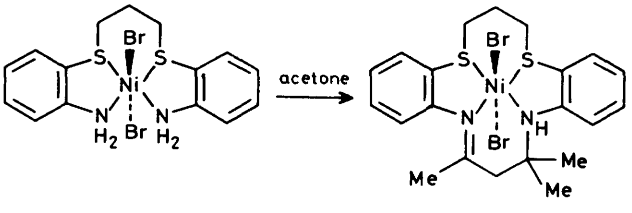
Complex	Formula	C	H	N
$CuL(ClO_4)_2$	$C_{21}H_{26}Cl_2CuN_2O_8S_2$	40.0 (39.8)	4.2 (4.1)	4.3 (4.4)
$CuLBr_2$	$C_{21}H_{26}Br_2CuN_2S_2$	42.8 (42.5)	4.2 (4.4)	5.0 (4.7)
$CuLCl_2$	$C_{21}H_{26}Cl_2CuN_2S_2$	50.0 (49.9)	5.2 (5.2)	5.4 (5.6)
$CuL(NO_3)_2{\cdot}H_2O$	$C_{21}H_{28}CuN_4O_7S_2$	43.9 (43.8)	4.9 (4.9)	9.7 (9.7)
$CuL(O_2CMe)_2$	$C_{25}H_{32}CuN_2O_4S_2$	54.2 (54.4)	5.9 (5.8)	5.3 (5.1)

* Required figures in parentheses.

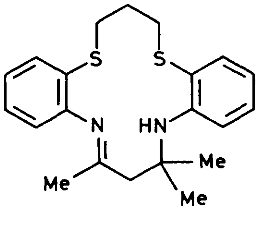
Experimental

The complex [$NiLBr_2$] was prepared essentially as previously described.[1] The pale blue complex can also be characterised as a monohydrate depending upon the degree of drying employed.

The free ligand (L) was prepared as follows. The complex [$NiLBr_2$] (*ca.* 10 g) was suspended in water (*ca.* 200 cm^3) and the mixture refluxed for 1 h. The complex slowly dissolved and the solution became milk-like in appearance. On cooling, the solution was filtered through Celite and the volume reduced to *ca.* 50 cm^3 on a rotary evaporator. The aqueous solution was extracted with diethyl ether (4 × 200 cm^3) and the ether layer dried with Na_2SO_4. Removal of the ether gave a viscous residue which was dissolved in ethanol (100 cm^3) and heated for *ca.* 30 min with activated charcoal. The solution was filtered and the ethanol removed on a rotary evaporator to give a very viscous liquid, $m/e = 370.1549$ ($C_{21}H_{26}N_2S_2$ 370.1538). The i.r. spectrum has ν(NH) at 3 300 and 3 420 (sh), ν(C=N) at 1 700, and *o*-substituted aromatic δ(CH) at 750 cm^{-1} determined as a thin film.



(**1**) (**2**)



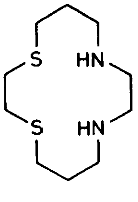
L

Preparation of Complexes.—The complex $CuL(ClO_4)_2$ was prepared as follows. The ligand (L) was dissolved in dry ethanol (10 cm^3) and to this solution was added copper(II) perchlorate hexahydrate in dry ethanol (10 cm^3) with constant stirring. Deep green crystals immediately formed, and were filtered off and dried *in vacuo*. The other complexes were prepared similarly using copper(II) bromide (0.06 g) to give $CuLBr_2$ (dull green), copper(II) chloride dihydrate (0.046 g) to give bright green crystals of $CuLCl_2$, and copper(II) nitrate hexahydrate (0.065 g) to give the deep green-violet $CuL(NO_3)_2{\cdot}H_2O$. In the case of $CuL(O_2CMe)_2$, copper(II) acetate monohydrate (0.054 g) was employed, and it was necessary to allow the solution to stand for several hours before green crystals of the complex slowly deposited as the ethanol evaporated. This complex is hygroscopic. Analytical data for the various complexes are summarised in Table 1.

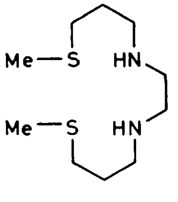
Physical Studies.—Infrared spectra of the complexes were recorded on a Perkin-Elmer 577 instrument using KBr discs. Electronic spectra were obtained using Nujol mulls on a Perkin-Elmer Lambda 5 instrument. Electrochemical studies were

Table 2. Electronic spectra in the solid state

Complex	$\lambda_{max.}$/nm
$CuL(ClO_4)_2$	612
$CuLBr_2$	600
$CuL(NO_3)_2 \cdot H_2O$	600
$CuLCl_2$	615
$CuL(O_2CMe)_2$	620



L^1



L^2

carried out using a PAR170 electrochemistry system. Measurements were made using 1×10^{-3} mol dm^{-3} solutions in acetonitrile with 0.1 mol dm^{-3} $[NBu^n_4][ClO_4]$ as supporting electrolyte.

Results and Discussion

The ligand L can be prepared in good yield by hydrolysis of $[NiLBr_2]$. Copper(II) complexes are readily prepared by reacting the free ligand with the appropriate copper(II) salt in dry ethanol. It seems likely that the present complexes have a tetragonally distorted octahedral structure in the solid state with the anionic ligands in the axial sites. Rigorously four-co-ordinate planar copper(II) complexes are relatively rare. The perchlorate complex $CuL(ClO_4)_2$ shows no significant splitting of the ν_3 band at 1 100 cm^{-1}, but a band at 933 cm^{-1} (ν_2) of medium intensity may be indicative of unidentate perchlorate.[12,13] The complexes have very limited solubility in the common solvents, but $CuL(ClO_4)_2$ is sufficiently soluble in nitromethane for conductivity studies. The complex has Λ_M = 182 S cm^2 mol^{-1} at 25 °C, consistent with a 2:1 electrolyte. In solution, the weakly co-ordinating perchlorate ions are replaced by solvent molecules.

All of the complexes exhibit a broad *d–d* band in the region 600—620 nm in the solid state, Table 2. Similar spectroscopic data have been reported recently for the copper(II) complexes of a range of N_2S_2 macrocycles which also display a *d–d* band at 620 nm in aqueous solution.[14] The solution spectra of the present complexes show time-dependent changes in hydroxylic solvents such as water and ethanol, probably due to the displacement of the sulphur donors by harder oxygen donors. Thioethers are known to co-ordinate very weakly to copper(II) in dipolar solvents;[15] however, if the thioether donor atoms are placed at the inner co-ordination positions of linear multidentate N_xS_y ($x = 2, y = 2$ or 3) systems, the sulphur donors are constrained to bond to copper(II) by virtue of the strong co-ordination of the terminal nitrogen donors. This effect is of course enhanced in a macrocyclic system.

Recent formation constant studies[14] using the ligands L^1 and L^2 have indicated a significant 'macrocyclic effect' with log $K_{CuL^1} = 15.96$ and log $K_{CuL^2} = 11.41$. The Δ log K term of 4.55 is mainly due to the entropic term ($T\Delta S$ = 17.6 kJ mol^{-1}) and only partially to the enthalpic term ($-\Delta H$ = 8.4 kJ mol^{-1}).

The band at 620 nm observed in the present complexes occurs at slightly lower energies when compared with the planar CuN_4 chromophore (due to the weaker ligand field of sulphur) and can be assigned to *d–d* transitions essentially localised on Cu^{II}.[15] The intense band at *ca.* 600 nm observed in the type I blue copper proteins has a quite different origin, arising from an $RS^-(\sigma) \longrightarrow Cu^{II}$ transition in tetrahedral co-ordination.[15]

In addition to the band at 620 nm, the present complexes also display a strong band near 330 nm which can be assigned to an $S \longrightarrow d_{x^2-y^2}$ charge-transfer excitation.[15]

Kaden and co-workers[4,5] have studied the electrochemistry of a number of Cu^{II}–N_2S_2 macrocycles. Generally tetra-aza macrocycles stabilise Cu^{II}, while the corresponding tetrathia analogues form only weak Cu^{II} complexes and stabilise Cu^I. For a series of 12-, 14-, and 16-membered N_2S_2 macrocycles the Cu^{II}–Cu^I redox potentials span a range of 340 mV or six orders of magnitude in relative stability, a result attributable to subtle differences in steric requirements. The present complexes do not display a reversible Cu^{II}–Cu^I couple in solvents such as acetonitrile. This effect almost certainly arises due to the very rigid nature of L which does does not favour the tetrahedral stereochemistry commonly observed with Cu^I. Crystallographic studies[16] on related dibenzo-substituted N_2S_2 macrocycles suggest that the Cu^{II} ion will be insignificantly displaced from the best plane defined by the two nitrogen and two sulphur donors and that any form of distortion leading to tetrahedral stereochemistry will be difficult.

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