Three-, Four-, and Five-co-ordination Modes of a Potentially Quinquedentate ' Nitrogen–Sulphur ' Macrocyclic Ligand: The Crystal and Molecular Structures of Two Copper(II) Complexes

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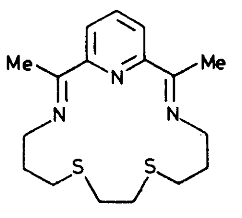
The 17-membered Schiff-base ' N_3S_2 ' macrocycle (L) derived from the cyclic condensation of 2,6-diacetylpyridine with 1,10-diamino-4,7-dithiadecane forms complexes with Cu^{II} of formulae CuLXY and $CuLY_2$ where X = Cl, Br, or NCS and Y = ClO_4, BPh_4, or NCS. The crystal and molecular structures of two of the complexes have been determined: $[CuL][ClO_4]_2$ is orthorhombic, space group $P2_1cn$ (no. 33), with a = 11.934(5), b = 13.528(6), c = 14.581(7) Å, and Z = 4; $[CuL(NCS)][ClO_4]\cdot0.5H_2O$ is monoclinic, space group $C2/c$, with a = 37.831(30), b = 8.187(5), c = 16.364(11) Å, β = 102.9(1)°, and Z = 8. Diffraction data for both crystals have been refined by full-matrix least squares (1 364 reflections to R 0.068 and 1 196 reflections to R 0.082, respectively). Both structures have a distorted square-pyramidal structure in which the trimethine unit of the macrocycle occupies three positions of the square plane [Cu–N 1.93—2.08 Å]. In $[CuL][ClO_4]_2$ the fourth position is occupied by one sulphur atom of the macrocycle [Cu–S 2.377(4) Å], the other sulphur atom being axially sited at 2.470(4) Å. In $[CuL(NCS)][ClO_4]\cdot0.5H_2O$ the square plane is completed by the thiocyanate group [Cu–N 1.854(19) Å], the axial position being occupied by one ligand sulphur atom at 2.745(5) Å, the other sulphur atom being unco-ordinated. In both structures there is a weak interaction with a perchlorate oxygen in the axial position *trans* to the sulphur atom. Infrared and e.s.r. spectra suggest that $[CuL(NCS)][BPh_4]$ has a dimeric (NCS-bridged) structure in the solid state whereas solid $[CuL(NCS)_2]$ appears to contain both bridging and terminally *N*-bonded NCS groups, with neither of the macrocycle sulphur atoms co-ordinated.

SOME copper(I) and silver(I) complexes of the ' nitrogen–sulphur ' Schiff-base macrocycle (L) derived from the cyclic condensation of 2,6-diacetylpyridine with 1,10-diamino-4,7-dithiadecane have been described.[1] *X*-Ray analysis has established that for both metal ions the macrocycle uses all five potential donor atoms in co-ordination to give distorted trigonal-bipyramidal structures. In this paper we describe some copper(II) complexes of L and show by means of physical properties and two structure determinations that the potentially quinquedentate macrocycle may use both, one only, or neither of the sulphur atoms in co-ordination.



L

RESULTS AND DISCUSSION

The copper(II) complexes to be considered are listed in Table 1 along with analytical and selected physical data. The preparation of the complex $[CuL][ClO_4]_2$ has been described;[1] the remainder of the complexes were prepared from the diperchlorate as described in the Experimental section.

Analytical data (Table 1) and i.r. spectra clearly establish the occurrence of the macrocycle (L) in all the complexes. However, the information derived from the i.r. spectra and other physical properties, to be considered later, was insufficient to define the nature of the co-ordination of the macrocycle in the different complexes. For this reason the crystal and molecular structures of two of the complexes were determined by *X*-ray diffraction methods.

Crystal data.—(1) $[CuL][ClO_4]_2$, $C_{17}H_{25}Cl_2CuN_3O_8S_2$, M = 597.8, Orthorhombic, a = 11.934(5), b = 13.528(6),

TABLE 1

Analytical and physical data for the copper(II) complexes

	Analysis (%)								
	Found			Calc.			$\Lambda^a/S\ cm^2\ mol^{-1}$		
Complex	C	H	N	C	H	N	MeCN	H_2O	$\mu_{eff.}{}^b$/B.M.
$[CuL][ClO_4]_2$	34.2	4.3	7.0	34.2	4.2	7.0	297	225	1.88
$[CuL][BPh_4]_2$	75.0	6.4	4.2	75.2	6.3	4.1	222	*c*	1.75
$[CuLCl][ClO_4]$	38.2	4.6	8.0	38.2	4.7	7.9	163	269	1.90
$[CuLBr][ClO_4]$	35.6	4.4	7.1	35.3	4.4	7.3	168	251	1.92
$[CuLBr][PF_6]$	32.9	4.0	6.9	32.7	4.0	6.1	164	214	2.06
$[CuL(NCS)][ClO_4]\cdot0.5H_2O$	38.3	4.7	9.9	38.2	4.6	9.9	180	*c*	1.90
$[CuL(NCS)][BPh_4]$	64.8	5.9	7.5	65.0	5.8	7.2	104	*c*	1.96
$[CuL(NCS)_2]$	44.2	5.0	13.7	44.3	4.9	13.6	163	*c*	1.94

[a] For 10^{-3} mol dm^{-3} solutions at 25 °C. [b] Corrected for diamagnetism of ligands. [c] Insoluble.

$c = 14.581(7)$ Å, $U = 2\,354.1$ Å^3, $D_m = 1.67$ g cm^{-3}, $Z = 4$, $D_c = 1.69$ g cm^{-3}, $F(000) = 1\,228$, λ(Cu-K_α) $= 1.541\,78$ Å, $\mu = 55.1$ cm^{-1}, space group $P2_1cn$ (no. 33) from systematic absences $hk0$, $h + k = 2n + 1$, $h0l$, $l = 2n + 1$ and the successful structure determination.

(2) [CuL(NCS)][ClO$_4$]·0.5H$_2$O, $C_{18}H_{26}ClCuN_4O_{4.5}S_3$, $M = 565.4$, Monoclinic, $a = 37.831(30)$, $b = 8.187(5)$, $c = 16.364(11)$ Å, $\beta = 102.9(1)°$, $U = 4\,941.0$ Å^3, $D_m = 1.55$ g cm^{-3}, $Z = 8$, $D_c = 1.52$ g cm^{-3}, $F(000) = 2\,200$, λ(Mo-K_α) $= 0.710\,7$ Å, $\mu = 13.0$ cm^{-1}, space group $C2/c$ from systematic absences $hkl, h + k = 2n + 1$, $h0l, l = 2n + 1$ and the structure determination.

For (1) a crystal with dimensions $0.2 \times 0.2 \times 0.5$ mm was mounted on an Enraf–Nonius CAD-4 diffractometer and 2 106 reflections with $2\theta < 130°$ were measured by the θ—2θ scan technique. The w scan width was $0.80 + 0.15 \tan\theta$ and the horizontal aperture 4.0 mm. 1 364 Reflections with $I > 1.56\sigma(I)$ were used in subsequent calculations. An absorption correction was made.

For (2) a crystal with dimensions $0.2 \times 0.55 \times 1.00$ mm was mounted around c^* on a GE XRD5 diffractometer and 1 956 reflections with $2\theta < 35°$ were measured by the stationary-crystal–stationary counter method. Of these, 1 196 with $I > 2\sigma(I)$ were used in subsequent calculations. An absorption correction was not deemed necessary. For both crystals, cell dimensions were calculated by least-squares refinement of high angle reflections.

In both structures, it was possible to locate the copper atoms from the Patterson map and subsequent Fourier maps permitted all non-hydrogen atoms to be located. In (1) all atoms were refined anisotropically. Hydrogen atoms were positioned in trigonal or tetrahedral positions and their thermal parameters fixed at the value of the carbon atoms to which they were bonded. The positions of the hydrogens in the two methyl groups were located by rigid body refinement. The correct signs of the co-ordinates were located by the lowest R value 0.067 9 *vs.* 0.068 6.

In (2) the metal, chlorine, and sulphur atoms were refined anisotropically and the others isotropically. The hydrogen atoms were treated as in (1). A water molecule was located in the lattice and refined with occupancy $\frac{1}{2}$ which was deemed appropriate. The perchlorate anion was clearly disordered but the electron density was very much smeared and we were not able to refine successfully two or more tetrahedra of low occupancy. We found that the most successful treatment of the perchlorates was to refine one tetrahedron with all oxygens given anisotropic thermal parameters. Values for O(3) and O(4) were very high in particular directions but this procedure did account for the electron density. The final R was 0.082.

In both structures, a weighting scheme was employed to give constant values for $w\Delta^2$ over ranges of F_o and $\sin\theta/\lambda$. In (1) it was $w = 1/[0.003F^2 + \sigma(F)]^2$. In (2) it was $\sqrt{w} = 1$ for $F_o < 140$ and $140/F_o$ for $F_o > 140$. Both structures were refined by full-matrix least squares using the SHELX-76 package [2] at the University of Manchester Computer Centre. Scattering factors and dispersion corrections were taken from ref. 3.

In the final cycles of refinement no shift was $>0.2\sigma$.

TABLE 2

Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*X*	*Y*	*Z*
(*a*) Complex (1)			
Cu(1)	5 000(0)	−685(1)	2 797(1)
Cl(1)	209(4)	1 077(3)	1 697(2)
O(11)	1 142(12)	1 529(10)	2 155(9)
O(12)	527(22)	308(12)	1 166(11)
O(13)	−386(12)	1 778(10)	1 206(9)
O(14)	−477(20)	721(11)	2 418(12)
Cl(2)	330(3)	−1 832(3)	5 633(2)
O(21)	117(10)	−1 206(9)	4 872(6)
O(22)	803(12)	−1 260(10)	6 348(8)
O(23)	1 233(13)	−2 505(10)	5 379(9)
O(24)	−583(13)	−2 278(20)	5 897(12)
S(2)	3 856(4)	−1 766(3)	1 804(2)
C(3)	2 575(20)	−1 911(19)	2 415(19)
C(4)	2 016(16)	−1 313(15)	3 002(12)
C(5)	2 573(13)	−369(13)	3 438(11)
N(6)	3 733(9)	−598(8)	3 714(6)
C(7)	3 978(11)	−823(9)	4 533(7)
C(8)	5 149(15)	−1 146(9)	4 646(7)
N(9)	5 759(9)	−1 135(7)	3 889(6)
C(10)	6 807(11)	−1 434(9)	3 827(9)
C(11)	7 259(13)	−1 281(11)	2 892(9)
N(12)	6 621(10)	−911(8)	2 318(7)
C(13)	6 969(17)	−615(13)	1 393(10)
C(14)	6 717(24)	483(18)	1 276(20)
C(15)	5 710(20)	841(16)	1 081(14)
S(16)	4 522(4)	630(3)	1 789(2)
C(17)	3 554(26)	71(15)	1 036(13)
C(18)	3 573(23)	−954(13)	872(10)
C(20)	3 269(14)	−802(13)	5 363(9)
C(21)	5 670(13)	−1 499(10)	5 464(8)
C(22)	6 765(14)	−1 811(11)	5 421(9)
C(23)	7 345(13)	−1 810(11)	4 584(9)
C(24)	8 495(14)	−1 550(14)	2 727(12)
(*b*) Complex (2)			
Cu	3 744(1)	2 093(3)	6 402(2)
Cl(1)	706(3)	3 266(14)	1 195(7)
O(1)	455(6)	2 414(27)	591(14)
O(2)	577(7)	4 855(35)	1 337(16)
O(3)	682(12)	1 883(42)	1 943(15)
O(4)	1 026(8)	3 530(49)	843(28)
N(1)	3 433(5)	3 617(20)	6 702(10)
C(1)	3 193(6)	4 093(24)	6 988(12)
S(1)	2 862(2)	4 712(9)	7 421(4)
S(2)	3 371(1)	1 857(7)	4 763(3)
C(3)	3 290(6)	4 087(24)	4 579(13)
C(4)	3 633(5)	5 001(24)	4 598(12)
C(5)	3 907(5)	5 172(23)	5 418(12)
N(6)	4 034(4)	3 581(18)	5 761(9)
C(7)	4 314(5)	2 898(24)	5 619(11)
C(8)	4 403(5)	1 276(23)	5 952(11)
N(9)	4 148(4)	680(18)	6 360(9)
C(10)	4 175(5)	−729(22)	6 748(11)
C(11)	3 859(6)	−1 030(24)	7 154(12)
N(12)	3 623(4)	117(19)	7 041(9)
C(13)	3 268(6)	81(26)	7 403(13)
C(14)	2 925(7)	250(31)	6 683(17)
C(15)	2 812(7)	−1 157(30)	6 185(15)
S(16)	3 083(2)	−1 723(7)	5 454(4)
C(17)	2 863(6)	−639(25)	4 536(14)
C(18)	2 902(6)	1 226(26)	4 550(14)
C(20)	4 560(6)	3 643(27)	5 108(14)
C(21)	4 706(6)	248(26)	5 981(13)
C(22)	4 731(6)	−1 205(26)	6 365(13)
C(23)	4 470(5)	−1 763(26)	6 763(12)
C(24)	3 851(6)	−2 570(26)	7 660(14)
O(10)	197(13)	300(59)	2 202(31)

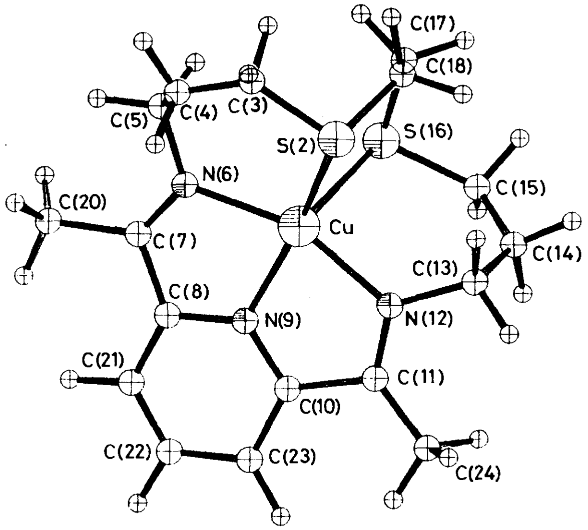


FIGURE 1 The structure of $[CuL]^{2+}$ together with the atom-numbering scheme

In the final difference-Fourier maps there were no significant peaks and none of the zero-weighted peaks showed any serious discrepancies.

Final positional parameters for (1) and (2) are given in Table 2. Dimensions are given in Table 3. Thermal parameters, hydrogen-atom positions, and observed and calculated structure factors are given in Supplementary Publication No. SUP 22874 (23 pp.).*

Discussion of the Structures.—Both structures contain discrete complex cations, $[CuL]^{2+}$ and $[CuL(NCS)]^+$, shown in Figures 1 and 2 together with a common atomic numbering scheme. In both complexes the metal atom is strongly bonded to the three nitrogens of

TABLE 3

Molecular dimensions [bond lengths (Å) and angles (°)] in (1) and (2) with estimated standard deviations in parentheses

(*a*) Geometry of the co-ordination sphere in $[CuL]^{2+}$ (1)

Cu–S(2)	2.470(4)	S(2)–Cu–N(6)	90.5(3)
Cu–N(6)	2.022(11)	S(2)–Cu–N(9)	123.8(3)
Cu–N(9)	1.930(11)	S(2)–Cu–N(12)	103.3(3)
Cu–N(12)	2.079(13)	S(2)–Cu–S(16)	87.0(1)
Cu–S(16)	2.377(4)	N(6)–Cu–N(9)	79.9(5)
		N(6)–Cu–N(12)	157.9(5)
		N(6)–Cu–S(16)	100.7(3)
		N(9)–Cu–N(12)	78.1(5)
		N(9)–Cu–S(16)	149.2(3)
		N(12)–Cu–S(16)	97.2(4)

(*b*) Geometry of the co-ordination sphere in $[CuL(\dot{N}CS)]^+$ (2)

Cu–S(2)	2.745(5)	S(2)–Cu–N(6)	76.2(4)
Cu–N(6)	2.074(16)	S(2)–Cu–N(9)	99.3(4)
Cu–N(9)	1.930(16)	S(2)–Cu–N(12)	108.7(4)
Cu–N(12)	2.033(16)	S(2)–Cu–N(1)	95.0(5)
Cu–N(1)	1.854(19)	N(6)–Cu–N(9)	79.7(6)
		N(6)–Cu–N(12)	158.9(6)
		N(9)–Cu–N(12)	79.2(7)
		N(9)–Cu–N(1)	165.2(6)
		N(6)–Cu–N(1)	100.2(7)
		N(12)–Cu–N(1)	99.8(7)

(*c*) Geometry of the macrocycle in (1) and (2)

TABLE 3 (*continued*)

	(1)	(2)
S(2)–C(3)	1.78(3)	1.86(2)
S(2)–C(18)	1.78(2)	1.80(2)
C(3)–C(4)	1.35(3)	1.49(3)
C(4)–C(5)	1.57(3)	1.51(2)
C(5)–N(6)	1.47(2)	1.46(2)
N(6)–C(7)	1.27(2)	1.26(3)
C(7)–C(8)	1.47(2)	1.45(3)
C(7)–C(20)	1.48(2)	1.51(3)
C(8)–N(9)	1.32(2)	1.38(3)
C(8)–C(21)	1.43(2)	1.41(3)
N(9)–C(10)	1.32(2)	1.31(2)
C(10)–C(11)	1.48(2)	1.51(3)
C(10)–C(23)	1.37(2)	1.40(3)
C(11)–C(12)	1.24(2)	1.28(3)
C(11)–C(24)	1.53(2)	1.51(3)
N(12)–C(13)	1.47(2)	1.52(3)
C(13)–C(14)	1.53(3)	1.60(3)
C(14)–C(15)	1.33(4)	1.42(3)
C(15)–S(16)	1.78(2)	1.80(3)
S(16)–C(17)	1.76(3)	1.78(2)
C(17)–C(18)	1.41(3)	1.53(3)
C(21)–C(22)	1.37(2)	1.34(3)
C(22)–C(23)	1.40(2)	1.38(3)
Cu–S(2)–C(3)	104.3(9)	96.8(6)
Cu–S(2)–C(18)	100.8(7)	118.6(8)
C(3)–S(2)–C(18)	106.7(18)	97.5(10)
S(2)–C(3)–C(4)	132.4(20)	112.1(15)
C(3)–C(4)–C(5)	122.2(19)	119.2(17)
C(4)–C(5)–N(6)	109.7(14)	111.2(15)
C(5)–N(6)–C(7)	121.6(12)	122.9(17)
Cu–N(6)–C(7)	115.9(10)	113.1(13)
Cu–N(6)–C(5)	122.3(9)	123.6(12)
N(6)–C(7)–C(20)	129.5(14)	124.6(18)
N(6)–C(7)–C(8)	113.3(11)	118.1(18)
C(8)–C(7)–C(20)	117.2(11)	117.3(18)
C(7)–C(8)–C(21)	127.3(12)	132.7(19)
C(7)–C(8)–N(9)	115.2(11)	112.2(17)
C(21)–C(8)–N(9)	117.5(15)	121.2(19)
Cu–N(9)–C(10)	119.0(9)	119.2(14)
Cu–N(9)–C(8)	115.7(10)	116.7(12)
C(8)–N(9)–C(10)	125.2(12)	124.0(16)
N(9)–C(10)–C(11)	111.5(12)	111.9(16)
N(9)–C(10)–C(23)	120.1(13)	121.2(19)
C(11)–C(10)–C(23)	128.4(14)	126.9(17)
C(10)–C(11)–C(24)	117.4(13)	119.4(18)
C(10)–C(11)–N(12)	117.1(14)	114.3(17)
N(12)–C(11)–C(24)	125.5(14)	126.3(21)
Cu–N(12)–C(11)	113.9(10)	115.4(14)
Cu–N(12)–C(13)	122.1(11)	121.3(12)
C(11)–N(12)–C(13)	123.9(15)	123.2(17)
N(12)–C(13)–C(14)	108.2(17)	111.3(18)
C(13)–C(14)–C(15)	123.9(24)	116.8(20)
C(14)–C(15)–S(16)	122.7(20)	116.5(21)
C(15)–S(16)–C(17)	103.3(11)	101.7(11)
Cu–S(16)–C(15)	106.7(8)	
Cu–S(16)–C(17)	102.8(7)	
S(16)–C(17)–C(18)	121.2(20)	117.2(15)
S(2)–C(18)–C(17)	118.8(13)	112.0(15)
C(8)–C(21)–C(22)	118.6(13)	121.1(22)
C(21)–C(22)–C(23)	120.6(14)	122.3(21)
C(22)–C(23)–C(10)	117.9(15)	116.4(19)

(*d*) Geometry of the perchlorate anions in (1) and (2)

	(1) $n = 1$	(1) $n = 2$	(2)
Cl(*n*)–O(*n*1)	1.44(1)	1.42(1)	1.40(2)
Cl(*n*)–O(*n*2)	1.35(1)	1.41(1)	1.43(3)
Cl(*n*)–O(*n*3)	1.38(1)	1.46(1)	1.68(3)
Cl(*n*)–O(*n*4)	1.42(1)	1.30(2)	1.47(3)
O(*n*1)–Cl(*n*)–O(*n*2)	112(1)	109(1)	112(1)
O(*n*1)–Cl(*n*)–O(*n*3)	110(1)	108(1)	92(2)
O(*n*1)–Cl(*n*)–O(*n*4)	105(1)	111(1)	107(2)
O(*n*2)–Cl(*n*)–O(*n*3)	112(1)	104(1)	115(2)
O(*n*2)–Cl(*n*)–O(*n*4)	109(1)	112(1)	106(2)
O(*n*3)–Cl(*n*)–O(*n*4)	109(1)	114(1)	124(2)

(*e*) Dimensions of the isothiocyanate anion in (2)

Cu–N(1)–C(1)	156.8(16)	C(1)–S(1)	1.65(2)
N(1)–C(1)	1.18(3)	N(1)–C(1)–S(1)	177.7(18)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

the planar trimethine group. The Cu–N distances [2.022(11), 1.930(11), 2.079(13); 2.074(16), 1.930(16), 2.033(16) Å] are as expected from estimates of the Cu^{2+} ion radius and Cu–N bond lengths in comparable copper(II) structures.[4] However, apart from the Cu–trimethine moiety there is little in common between the two structures.

In [CuL]$^{2+}$ the metal atom is also bonded to the two sulphur atoms in the macrocycle [Cu–S(2) 2.470(4), Cu–S(16) 2.377(4) Å] giving a five-co-ordinate environment as found previously for [Cu$^{\text{I}}$L]$^{+}$ and [Ag$^{\text{I}}$L]$^{+}$.[1] In all three complexes the co-ordination geometry is distorted between the two idealized five-co-ordinate polyhedra, the trigonal bipyramidal and the square pyramid. In the complexes of the d^{10} ions the geometries are closer to the trigonal bipyramidal with both sulphur atoms in equatorial positions. In the copper(II) complex, on the other hand, the geometry is closer to the square pyramid with S(2) in the axial position, lying 2.07 Å above the CuN$_3$ plane. Angles subtended at the metal atom by S(2) and the nitrogen atoms range from 90.5(3) to 123.8(3)° while the S(2)–Cu–S(16) angle is 87.0(1)°. The 'equatorial' sulphur atom S(16) lies 1.17 Å below the CuN$_3$ plane and is 0.093 Å closer to the metal than S(2). In the axial position *trans* to S(2) is a perchlorate oxygen atom at 3.07 Å from the metal atom [O(22) ($\frac{1}{2}+x$, $-y$, $1-z$)], the S(2)–Cu–O(22) angle being 156.9°. We doubt whether this can be considered more than the weakest of interactions; clearly, there is a space on this side of the square plane of the cation which can be approached by other ions in the crystal. However, it is worth noting that in nearly all previously determined structures of this class of macrocyclic complex the perchlorate anions are disorded.[5] This perchlorate anion is not, suggesting that the preferred orientation of the tetrahedron may be due to a weak Cu ··· O interaction.

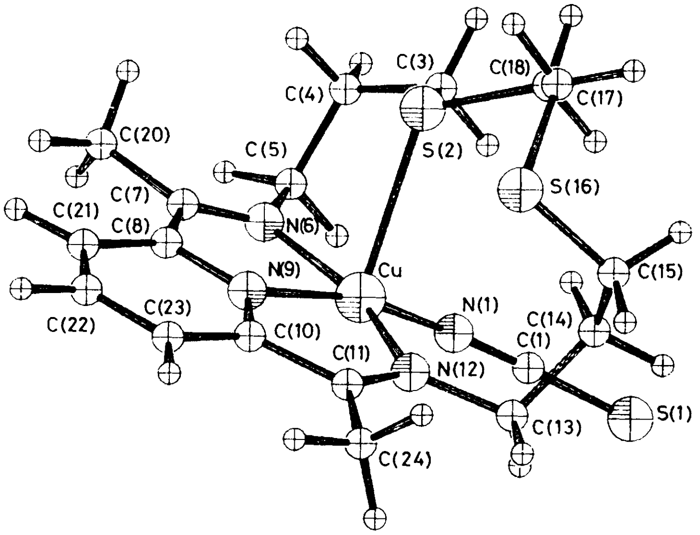

FIGURE 2 The structure of [CuL(NCS)]$^{+}$ together with the atom-numbering scheme

In [CuL(NCS)]$^{+}$ the metal is strongly bonded to the nitrogen of the thiocyanate anion *trans* to N(9), completing the square plane of nitrogen atoms around the metal. The Cu–N(NCS) distance is very short at 1.85(2) Å, a fact which suggests that the other Cu–N distances are lengthened by the constraints of the trimethine segment of the ring. The co-ordination sphere is completed by one sulphur atom S(2) of the macrocycle in an approximately axial position. The Cu–S(2) bond length is long at 2.745(5) Å and indicates a much weaker axial interaction than occurs in [CuL]$^{2+}$. Indeed, the sulphur atom is rather asymmetrically placed with respect to the four nitrogens of the square plane as shown by the S(2)–Cu–N angles which range from 76.2 to 108.7 ° and by the very different Cu–S–C angles of 96.8(6) and 118.6(8)°. As in [CuL][ClO$_4$]$_2$ there is a perchlorate oxygen in the axial position *trans* to the sulphur; this is O(3) ($\frac{1}{2}-x$, $\frac{1}{2}-y$, $1-z$) at 3.18 Å with a S(2)–Cu–O(3) angle of 162.7°.

Apart from the long distance Cu$^{2+}\cdots$OClO$_3^-$ interactions there are no contacts between cations and anions in the unit cells of either (1) or (2) of less than the sum of the van der Waals radii. The water molecule in (2) was refined with occupancy $\frac{1}{2}$, consistent with the assumption that the two sites at x, y, z and $-x, y, \frac{1}{2}-z$ at 2.18 Å apart are not occupied at the same time.

The conformation of the macrocycle in [CuL(NCS)]$^{+}$ is much more stable than in [CuL]$^{2+}$ as judged by a comparison of torsion angles (Table 4). In [CuL(NCS)]$^{+}$ the torsion angles are all close to 60° or 180° whereas in [CuL]$^{2+}$ there are considerable variations, the most extreme being a C(5)–C(4)–C(3)–S(2) torsion angle of −13.4° indicating severe repulsions. Also, it is clear from the least-squares planes calculations (Table 5) that planes 1 and 3 are very flat and do not show any of the puckering usually found in such six-membered rings.

TABLE 4

Torsion angles (°) in (1) and (2)

	(1)	(2)
C(7)–N(6)–C(5)–C(4)	−97.7	92.7
N(6)–C(5)–C(4)–C(3)	−41.8	60.1
C(5)–C(4)–C(3)–S(2)	−13.4	−68.8
C(4)–C(3)–S(2)–C(18)	−75.8	−172.7
C(3)–S(2)–C(18)–C(17)	81.2	172.8
S(2)–C(18)–C(17)–S(16)	38.8	57.3
C(18)–C(17)–S(16)–C(15)	85.0	70.4
C(17)–S(16)–C(15)–C(14)	−123.0	−90.9
S(16)–C(15)–C(14)–C(13)	58.5	−71.5
C(15)–C(14)–C(13)–N(12)	−80.2	76.0
C(11)–N(12)–C(13)–C(14)	−121.9	−123.0

TABLE 5

Least-squares planes in (1) and (2) with distances (Å) from these planes in square brackets

Plane 1: Cu, S(2), N(6)
(I) [C(3) * −0.03, C(4) * 0.45, C(5) * 0.94]
(II) [C(3) * 1.52, C(4) * 1.32, C(5) * 1.15]
Plane 2: Cu, S(2), S(16)
(I) [C(17) * −0.17, C(18) * 0.26]
Plane 3: Cu, S(16), N(12)
(I) [C(13) * −0.49, C(14) * 0.27, C(15) * −0.01]
Plane 4:
(I) [Cu −0.02, N(6) 0.01, N(9) −0.01, N(12) 0.01, S(2) * −2.07, S(16) * 1.17]
(II) [Cu −0.13, N(1) 0.11, C(1) * 0.18, S(1) * 0.32, N(6) −0.05, N(9) 0.12, N(12) −0.05, S(2) * −2.79]

* Distances of atoms not contributing to the planes are marked with an asterisk.

Physical Properties of the Complexes.—It remains to consider the structures of the other complexes. As mentioned above the relatively minor variations in the i.r. spectra of the different complexes were not sufficiently distinctive to be identified with a particular co-ordination mode of the macrocycle. Some information of structural value was obtained from the i.r. spectral bands due to the anions, however. No splitting of the ν_3 and ν_4 modes of the ClO_4^- ion, occurring at *ca.* 1 090 and *ca.* 620 cm^{-1}, respectively, was apparent in any of the spectra. However, the ν_3 mode in $[CuL][ClO_4]_2$ is somewhat broadened suggesting, as confirmed by the *X*-ray structure determination, that at least one of the two ClO_4^- ions interacts weakly with the metal ion. The structural analysis of $[CuL(NCS)][ClO_4]\cdot 0.5H_2O$ has shown that the NCS^- ion is terminally bonded to the metal ion *via* the nitrogen atom. Consistent with this is the observation of $\nu_{asym.}$ at 2 085 cm^{-1}. In $[CuL(NCS)][BPh_4]$, however, $\nu_{asym.}$ occurs at 2 102 cm^{-1}, whereas in $[CuL(NCS)_2]$ this mode is split into two peaks at 2 080 and 2 102 cm^{-1}. These observations suggest that in the tetraphenylborate salt the NCS^- ion occurs as a bridge between two different metal centres and that in the dithiocyanate one NCS is terminally *N*-bonded and the other is bridging. In an attempt to obtain further evidence for or against this hypothesis the magnetic susceptibilities of the complexes were measured as a function of temperature over the range 90—293 K.

The 293 K magnetic moments (Table 1) fall in the range 1.75—2.06 B.M.* The temperature variation of the susceptibilities conforms to the Curie–Weiss law with small Weiss constants (0 to −10°). Thus, the magnetic measurements, in the limited temperature range available, do not furnish positive evidence for spin–spin superexchange coupling in the thiocyanato-complexes. However, clear evidence for the occurrence of coupled dimers in solid $[CuL(NCS)][BPh_4]$ was obtained from the *X*-band e.s.r. spectra. Data for polycrystalline solids and MeCN solutions (*ca.* 10^{-2} mol dm^{-3}) are given in Table 6 for all three thiocyanate-containing complexes and for $[CuL][BPh_4]_2$. All four complexes gave axial spectra but for the solids the hyperfine splitting was observed only in the case of the tetraphenylborate salts. A well resolved seven-line pattern (relative intensity 1 : 2 : 3 : 4 : 3 : 2 : 1) in the parallel component was obtained for the powder spectrum of $[CuL(NCS)][BPh_4]$ (Figure 3). In contrast, the powder spectrum of $[CuL][BPh_4]_2$, presumed to have the same mononuclear distorted square-pyramidal structure found for the diperchlorate, gave a well resolved four-line spectrum (Figure 3). As expected [6] for coupled pairs of copper(II) ions, the hyperfine spacing in $[CuL(NCS)][BPh_4]$ is about one-half, *i.e.* $A_{\parallel} = 80$ G, the value observed for the mononuclear complex $[CuL][BPh_4]_2$, *i.e.* $A_{\parallel} = 178$ G.† The weak NCS bridges occurring in solid $[CuL(NCS)][BPh_4]$ are broken in solution as judged by the appearance of four lines ($A_{av.} = 58$ G) in the acetonitrile solution spectrum. Electron spin resonance confirmation for the presence of NCS bridging units in solid $[CuL(NCS)_2]$ was not obtained since hyperfine splitting was not observed in the powder spectrum yet the i.r. and e.s.r. data for the three thiocyanato-complexes, considered collectively, leave little doubt that this complex contains one bridging and one terminally *N*-bonded NCS^- group. The solution e.s.r. spectrum of $[CuL(NCS)_2]$ is, within experimental uncertainty, identical to that of $[CuL(NCS)][BPh_4]$ and $[CuL(NCS)][ClO_4]$ indicating rupture of the NCS^- bridges and dissociation of one NCS^- group (see, also, conductance data in Table 1).

Since the trimethine unit together with the NCS^- groups account for six co-ordination sites in $[CuL(NCS)_2]$ we conclude that neither of the sulphur atoms of the macrocycle is bonded to the metal. On this assump-

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* Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2.

† *Note added at proof:* A seven-line splitting pattern, $[2(2I) + 1$ where $I = \frac{3}{2}]$ in the $\Delta M = 1$ transition at *g ca.* 2 is also to be expected for a Cu^I, Cu^{II} system wherein one unpaired electron interacts with two copper nuclei. However, a mixed-valence formulation is inconsistent with the properties of $[CuL(NCS)][BPh_4]$ (chemical analysis, magnetism, electronic spectra) and with the results of an *X*-ray analysis. The structure consists of discrete BPh_4^- anions together with centrosymmetric $[\{CuL(NCS)\}_2]^{2+}$ dimers. The crystallographically equivalent copper atoms are each strongly bound in a square plane to a trimethine unit [Cu–N 2.23(4), 1.90(4), 1.80(4) Å] and to the nitrogen atom of a thiocyanate group [Cu–N 1.87(4) Å]. Two sulphur atoms are weakly bonded in axial positions, one from the macrocycle at 2.99(3) Å and one from the other thiocyanate group of the dimeric unit at 2.98(3) Å. The conformation of the macrocycle is thus similar to that in $[CuL(NCS)][ClO_4]$. The Cu ··· Cu distance is 5.80 Å.

TABLE 6

E.s.r. parameters [a] for the copper(II) complexes

Complex	State	$g_{av.}$	$g_{\parallel}$	$g_{\perp}$	$A_{av.}$/G	$A_{\parallel}$/G
$[CuL][BPh_4]_2$	Solid		2.18	2.02		178
	MeCN [b]	2.09			62	
$[CuL(NCS)][BPh_4]$	Solid		2.32	2.06		80
	MeCN [b]	2.10			58	
$[CuL(NCS)][ClO_4]$	Solid	2.08				
	MeCN [b]	2.10			58	
$[CuL(NCS)_2]$	Solid		2.16	2.05		
	MeCN [b]	2.03			57	

[a] At 20 °C. [b] 10^{-2} mol dm^{-3} solutions.

tion, the requirement that one NCS^- ion is terminally bound and one is bridging can best be met by a di-μ-thiocyanato-dimer. The alternative formulation in which one sulphur of the macrocycle is also co-ordinated would render the copper(II) atom seven-co-ordinate. While a few seven-co-ordinate copper(II) complexes are known [7] this seems a most unlikely geometry for the present complex in view of the steric crowding that would result.

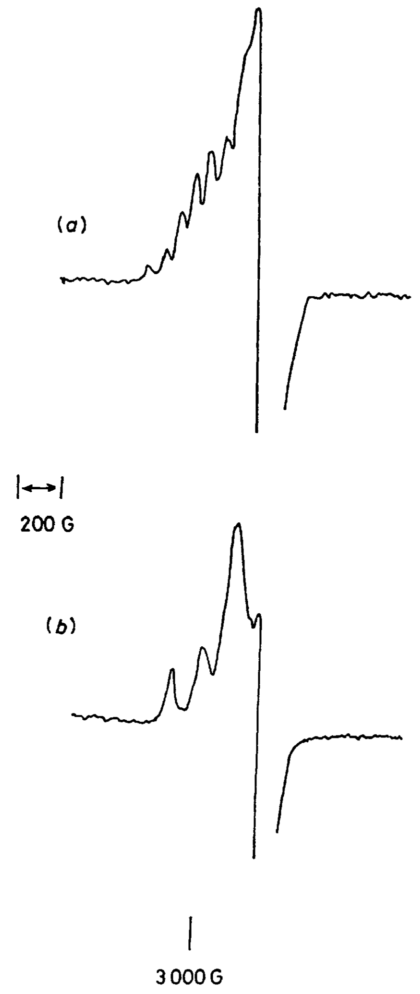

FIGURE 3 E.s.r. powder spectra at ambient temperature of (*a*) $[CuL(NCS)][BPh_4]$ and (*b*) $[CuL][BPh_4]$

Electronic spectra (Table 7) were measured for both solids and solutions in acetonitrile and in water. Two types of ligand field spectra were obtained. Those for $[CuL]Y_2$ ($Y = ClO_4$ or BPh_4) consisted of two well resolved bands at 16 000—17 000 cm^{-1} and 11 000—12 000 cm^{-1}. The spectra did not alter significantly on change of phase or solvent so it is concluded that the same absorbing species is present, namely, $[CuL]^{2+}$, in which all five potential donor atoms are co-ordinated. Uni-bivalent electrolyte behaviour was observed for solutions in both solvents (Table 1).

TABLE 7

Electronic spectral data (10^3 cm^{-1}) for the complexes

Complex	Solid	MeCN [a]	H_2O [a]
$[CuL][ClO_4]_2$	16.3, 11.2	16.0 (160) 11.6 (95)	16.1 (155) 11.6 (85)
$[CuL][BPh_4]_2$	16.6, 11.2	16.4 (180) 11.5 (120)	*b*
$[CuLCl][ClO_4]$	13.0	13.8 (140)	16.0 (150) 11.7 (100)
$[CuLBr][ClO_4]$	14.2	13.8 (155)	16.0 (145) 11.6 (80)
$[CuLBr][PF_6]$	14.1	13.8 (175)	
$[CuL(NCS)][ClO_4]$	14.6	14.4 (170)	*b*
$[CuL(NCS)_2]$	15.2	14.3 (150)	*b*

[a] ε/dm^3 mol^{-1} cm^{-1} is given in parentheses. [b] Insoluble.

Spectra of the remaining complexes, which are 1 : 1 electrolytes in acetonitrile (Table 1), showed a single broad band at 14 000—15 000 cm^{-1} (Table 7). Except for $[CuL(NCS)_2]$, a good correspondence between the solid state and acetonitrile solution spectra was found. These observations are fully consistent with conclusions reached from other properties, namely, that in the solid state the halide or thiocyanate ions are co-ordinated and that one sulphur atom of the macrocycle {both sulphur atoms in the case of $[CuL(NCS)_2]$} is unco-ordinated, and that, in acetonitrile, the complexes occur as solvated five-co-ordinate $[CuLX]^+$ cations. In water, solubility permitting, these complexes are 2 : 1 electrolytes and give the same spectrum as solid $[CuL]Y_2$ ($Y = ClO_4$ or BPh_4) indicating that the co-ordinated anions (X^-) are displaced by the second sulphur atom of the macrocycle which in the solid is unco-ordinated.

Conclusions.—The results described in this and in an earlier paper [1] have revealed a versatility in the co-ordinating properties of the potentially quinquedentate, 17-membered, 'N_3S_2' macrocyclic ligand L. In its complexes with Cu^{II}, Cu^I, and Ag^I this macrocycle may use all five donor atoms but with marked differences in the macrocycle conformation. In $[Cu^IL]^+$ the metal is strongly bonded to the two sulphur atoms and only weakly to two of the nitrogen donors, whereas in $[Cu^{II}L]^{2+}$ the sulphur atoms are the more weakly bound. In both structures there is evidence for macrocycle strain. In $[AgL]^+$ there appears to be a better overall fit between metal ion and macrocycle but here, too, there are significant Ag–N and Ag–S bond length inequivalences.

When co-ordinating anions such as halide or thiocyanate are present one or both of the macrocycle sulphur donors are displaced from the metal in $[Cu^{II}L]^{2+}$, but not in $[Cu^{I}L]^+$ or $[AgL]^+$. In $[CuL(NCS)]^+$ it is the equatorially bonded sulphur which is displaced by NCS^-, leaving one sulphur atom weakly bonded in an axial position. As judged by torsion angles (Table 4) this appears to be the least strained conformation so far found for this macrocycle. In this distorted square-pyramidal environment the copper(II) ion retains some bonding capacity for a sixth ligand in the second axial position as shown by the weak $Cu^{2+} \cdots OClO_3^-$ interaction in $[CuL(NCS)][ClO_4]$, and by the dimerization *via* NCS^- bridges in $[CuL(NCS)][BPh_4]$ in the solid state. In $[CuL(NCS)_2]$, in the solid state, both sulphur atoms of the macrocycle are displaced from the metal ion which achieves a six-co-ordinate structure by means of both bridging and terminally bonded NCS^- groups.

EXPERIMENTAL

Preparation of the Complexes.—The preparation of $[CuL][ClO_4]_2$ has been described previously;[1] the other complexes were prepared from the diperchlorate as outlined below.

$[CuLX][ClO_4]$ (X = Cl *or* Br). To a hot methanol solution of $[CuL][ClO_4]_2$ (0.001 mol) was added a two-fold excess of LiX (X = Cl or Br, as appropriate). The solution, which changed in colour from blue to green, was refluxed for 15 min. It was then cooled and concentrated to yield a green crystalline solid in 65—70% yield.

$[CuLBr][PF_6]$. This was prepared from the corresponding perchlorate salt by treatment of a methanolic solution with a three-fold excess of $K[PF_6]$. The mixture was refluxed for 15 min, filtered, and allowed to stand. The green crystalline product separated in 75% yield.

$[CuL(NCS)_2]$. To a methanol solution of $[CuL][ClO_4]_2$ (0.001 mol) was added a methanolic solution of Na[NCS] (0.003 mol). The solution, which turned green, was refluxed for 20 min and filtered hot to remove a small amount of brown impurity. The green product separated on cooling and concentrating in 60% yield.

$[CuL(NCS)][ClO_4]$. This compound was prepared from the dithiocyanate by addition of an excess of $Na[ClO_4]\cdot H_2O$ in hot methanol. Yield *ca.* 80%.

$[CuL(NCS)][BPh_4]$. This compound was prepared similarly, in 65% yield, except that the reaction was carried out at room temperature.

Physical Measurements.—E.s.r. spectra of polycrystalline powders and acetonitrile solutions (10^{-2} mol dm^{-3}) were measured with a Decca XI spectrometer operated at 9 270 MHz with a magnet field modulation of 100 kHz.

Other physical measurements were carried out as described in earlier papers.[1]

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