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The Triphenylphosphine Adduct of a Copper(I) Complex involving an Incompletely Bound N_2S_2 Macrocyclic Ligand*

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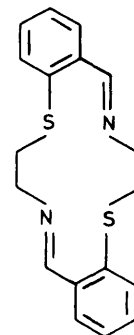
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The highly distorted tetrahedral copper(I) complex of the 14-membered *trans*- N_2S_2 macrocyclic ligand 6,7,15,16-tetrahydrodibenzo[*f,m*][1,8,4,11]dithiadiazacyclotetradecine (L) undergoes reaction with triphenylphosphine to form an adduct in which one of the two sulphur donors of the macrocycle has been displaced from the primary co-ordination sphere of the metal ion, resulting in tetrahedral co-ordination *via* an N_2PS donor array. The triphenylphosphine molecule is labile allowing the parent complex to be recovered upon recrystallization from an acetone-ethanol mixture. Crystal structures of both $[CuL]ClO_4$ (**1**) and $[CuL(PPh_3)]ClO_4 \cdot 0.5Me_2CO$ (**2**) are reported. For (**1**): space group $P6$, $a = 17.610(7)$, $c = 5.377(2)$ Å, $Z = 3$, $R = 0.061$ for 947 'observed' reflections. For (**2**): space group $P1$, $a = 15.74(2)$, $b = 12.29(1)$, $c = 9.91(1)$ Å, $\alpha = 82.07(9)$, $\beta = 84.88(8)$, $\gamma = 84.43(9)^\circ$, $Z = 2$, $R = 0.10$ for 1 796 'observed' reflections. The solid-state ^{31}P n.m.r. spectrum for (**2**) shows a quartet centred on 2.3 p.p.m. with line spacings of 1.41, 1.55, and 1.65 kHz.

In our investigations of the copper(I) complexes of the macrocyclic ligand 6,7,15,16-tetrahydrodibenzo[*f,m*][1,8,4,11]dithiadiazacyclotetradecine (L), we found that it was possible to add one molecule of triphenylphosphine to the cation and isolate the product as stable yellow crystals.¹ We considered this compound to be of interest from a variety of aspects but in particular the structural possibilities included the addition of the ligand to the cation to give a rare five-co-ordinate copper(I) geometry² or substitution to give an equally unlikely four-co-ordinate configuration with one donor atom of the macrocyclic ligand unco-ordinated. To explore these possibilities we have completed spectroscopic and X-ray diffraction studies on the perchlorate salts of both the parent cation $[CuL]^+$ and its PPh_3 adduct $[CuL(PPh_3)]^+$.



L

Experimental

Preparation of Compounds.—[6,7,15,16-Tetrahydrodibenzo[*f,m*][1,8,4,11]dithiadiazacyclotetradecine- S^5, S^{14}, N^8, N^{17}]-copper(I) perchlorate, $[CuL]ClO_4$ (**1**). The ligand (L) (0.25 g, 0.76 mmol) and tetrakis(acetonitrile)copper(I) perchlorate (0.25 g, 0.76 mmol) were added to dry deoxygenated ethanol (75 cm³). The resulting mixture was refluxed for 1 h yielding a solution which upon cooling precipitated orange crystals of the product. These were collected by filtration and recrystallised from ethanol giving the pure product: yield 0.32 g (86%) (Found: C, 43.9; H, 3.7; N, 5.5. Calc. for $C_{18}H_{18}ClCuN_2O_4S_2$: C, 44.2; H, 3.7; N, 5.7%). 1H N.m.r. [$(CD_3)_2SO$]: δ 8.77 (s, 2 H, CH=N), 8.12–7.79 (m, 8 H, benzo H), 3.60 (br s, 8 H, CH_2N , CH_2S). I.r.(Nujol): 1 660, 1 650 [$\nu(C=N)$] and 1 580 cm^{-1} [$\nu(C=C)$]. $\Lambda_m(MeOH)$: 125 $\Omega^{-1} cm^2 mol^{-1}$.

[6,7,15,16-Tetrahydrodibenzo[*f,m*][1,8,4,11]dithiadiazacyclotetradecine- S^5, N^8, N^{17}](triphenylphosphine)copper(I) perchlorate-acetone (1/0.5), $[CuL(PPh_3)]ClO_4 \cdot 0.5Me_2CO$ (**2**). Triphenylphosphine (0.19 g, 0.72 mmol) was added to a solution of (**1**) (0.25 g, 0.51 mmol) in dry deoxygenated acetone (50 cm³). The solution was refluxed for 30 min and then allowed to cool. Addition of hexane (50 cm³) brought about precipitation of the hemiacetone solvate of the pure product in the form of fine yellow needles: yield 0.36 g (91%) (Found: C, 57.6; H, 4.6; N, 3.3. Calc. for $C_{36}H_{33}ClCuN_2O_4PS_2 \cdot 0.5Me_2CO$: C, 57.7; H, 4.6; N, 3.6%). 1H N.m.r. [$(CD_3)_2CO$]: δ 8.98 (s, 2 H, CH=N), 8.03–6.89 (m, 23 H, aromatic H), 3.92 (t, 4 H, $^3J = 5.3$ Hz, CH_2N), 3.52 (br t, 4 H, $^3J = 5.3$ Hz, CH_2S). I.r.(Nujol): 1 711 [$\nu(C=O)$], 1 645, 1 620 [$\nu(C=N)$], and 1 580 cm^{-1} [$\nu(C=C)$]. $\Lambda_m(MeOH)$: 117 $\Omega^{-1} cm^2 mol^{-1}$.

Physical Measurements.—The solid-state ^{31}P n.m.r. spectrum of (**2**) was obtained at room temperature on a Bruker CXP-300 spectrometer at 121.47 MHz using 1H - ^{31}P cross polarization with radio frequency fields of 8 and 20 G respectively, as described previously.³ Chemical shifts were referenced to 85% H_3PO_4 *via* solid triphenylphosphine [$\delta(PPh_3) - 9.9$ p.p.m.].

* Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii–xx.

Non-S.I. unit employed: $G = 10^{-4} T$.

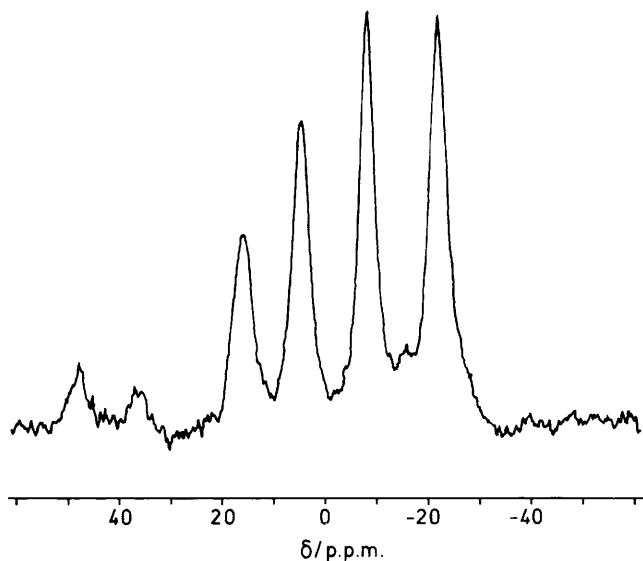


Figure 1. Cross-polarization magic angle spinning solid-state ^{31}P n.m.r. spectrum of (2)

A spectrum is presented in Figure 1. Solution ^1H n.m.r. spectra were recorded at 89.56 MHz using a JEOL FX90Q spectrometer. Chemical shifts are quoted on the δ scale relative to internal SiMe_4 . Molar conductivities were measured with a Phillips PW 9504 conductivity bridge on 10^{-3} mol dm^{-3} solutions at 20 °C. Elemental analyses were performed by the Australian Micro-analytical Service. Preparation of the ligand (L) was carried out as described previously.¹ Tetrakis(acetonitrile)copper(I) perchlorate was prepared by the literature method.⁴ Triphenylphosphine was recrystallized from ethanol before use.

Structure Determinations.—Unique data sets were measured at ca. 295 K within the specified $2\theta_{\text{max}}$ limits using a Syntex $P2_1$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode; monochromatic $\text{Mo-K}\alpha$ radiation ($\lambda = 0.710$ 6₉ Å) was employed. N Independent reflections were measured, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the large-block least-squares refinement with statistical weights derived from $\sigma^2(I) = [\sigma^2(I)_{\text{diff.}} + 0.000n\sigma^4(I)_{\text{diff.}}]$ after absorption correction (one only). Anisotropic thermal parameters were refined for the non-hydrogen atoms; (x, y, z, U_{iso})_H were included at estimated values, residuals R, R' on $|F|$ are quoted at convergence. Neutral atom complex scattering factors employed;⁵ computation used the XTAL program system⁶ implemented by S. R. Hall on a Perkin-Elmer 3241 computer. A trigonal data set was measured on (1); refinement in space group $P6$ using a unique hexagonal set was carried out in terms of a cation located with Cu on a crystallographic 2 axis and perchlorates were located about sites of $\bar{3}$ symmetry, implying disorder. Thermal motion on anion oxygen atoms was very high and anion geometries distorted with high e.s.d.s. In space group $P3$, refinement was achieved in terms of an ordered structure with R significantly but not greatly lower, but with thermal ellipsoid amplitudes much higher, and perchlorate geometries little improved. Data for the $P6$ model are recorded in the text, while those for the $P3$ model are deposited. Weak and limited data for (2), coupled with high thermal motion, and unidentified difference map residuals ('solvated acetone') modelled in terms of half-weighted carbon atoms, all contributed to the imprecision of this determination. Attempts to produce better material were unsuccessful.

Atom co-ordinates are given in Tables 1 and 2 and geometric

Table 1. Non-hydrogen atom co-ordinates for (1) (space group $P6$)

Atom	x	y	z
Cu	0.5000	0	0 ^a
S	0.613 4(2)	-0.018 8(2)	-0.078 4(6)
C(1)	0.694 2(7)	0.043 8(7)	0.156(2)
C(2)	0.675 1(8)	0.030 3(7)	0.162(2)
C(3)	0.831 7(8)	0.068 8(8)	0.339(3)
C(4)	0.826 5(8)	0.123 2(7)	0.510(3)
C(5)	0.759 0(7)	0.139 5(7)	0.503(3)
C(6)	0.689 8(7)	0.101 5(7)	0.327(2)
C(7)	0.625 6(8)	0.129 9(7)	0.352(2)
N	0.554 6(6)	0.102 5(5)	0.235(2)
C(8)	0.493 8(7)	0.137 7(7)	0.296(2)
C(9)	0.440 1(7)	0.127 7(7)	0.061(2)
Cl(1)		$-\frac{2}{3}$	0.095 6(10)
O(11)		$-\frac{1}{3}$	-0.183(2)
O(12)	0.684 4(7)	-0.731 5(6)	-0.171(2)
Cl(2)	0	0	-0.170(2)
O(21)	0	0	-0.437(7)
O(22) ^b	-0.069(16)	0.006(35)	-0.144(7)

^a Defines origin. ^b Population 0.5.

details in Table 3. The unit-cell contents of (1) are shown in Figure 2 and the cation and anion of (2) in Figure 3. The atom numbering scheme for the macrocycle (L) and the PPh_3 ligand is shown in Figure 3. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Crystal data for (1). $\text{C}_{18}\text{H}_{18}\text{ClCuN}_2\text{O}_4\text{S}_2$, $M = 489.5$, $a = 17.610(7)$, $c = 5.377(2)$ Å, $U = 1 444(1)$ Å³, $F(000) = 750$, D_c ($Z = 3$) = 1.69 g cm^{-3} , μ_{Mo} = 14.8 cm^{-1} . Specimen: 0.17 × 0.17 × 0.35 mm. $A_{\text{min...max}}^* = 1.24, 1.26$; $2\theta_{\text{max}} = 50^\circ$. Two refinements (residuals and data for the preferred chirality). (a) Hexagonal, space group $P6$ (C_6^1 , no. 168); $N = 1 332$, $N_o = 947$, $R = 0.061$, $R' = 0.054$ ($n = 1$). (b) Trigonal, space group $P3$ (C_3^1 , no. 143); $N = 2 199$, $N_o = 1 534$, $R = 0.058$, $R' = 0.053$ ($n = 1$).

Crystal data for (2). $\text{C}_{36}\text{H}_{33}\text{ClCuN}_2\text{O}_4\text{PS}_2$ (+ acetone solvent), $M = 751.8$ (+ solvent), triclinic space group $P\bar{1}$ (C_1^1 , no. 2), $a = 15.74(2)$, $b = 12.29(1)$, $c = 9.91(1)$ Å, $\alpha = 82.07(9)$, $\beta = 84.88(8)$, $\gamma = 84.43(9)^\circ$, $U = 1 882(2)$ Å³, D_c ($Z = 2$) = 1.33 g cm^{-3} , $F(000) = 776$ (+ solvent), μ_{Mo} = 8.2 cm^{-1} . $2\theta_{\text{max}} = 45^\circ$; $N = 4 830$, $N_o = 1 796$, $R = 0.10$, $R' = 0.095$ ($n = 6$).

Results and Discussion

The structure of the parent cation as its triflate salt has been reported previously¹ and the structural features of (1) are similar with an N_2S_2 donor array (Figure 2). The Cu-S and Cu-N distances of 2.222(4) and 2.009(9) Å respectively are within the range normally found for copper-thioether⁷ and copper-imino nitrogen⁸ compounds. The two sulphur atoms are held in an approximately *trans* relationship with S-Cu-S 158.1(1)° with the two nitrogens positioned in closer proximity [N-Cu-N 102.2(4)°]. This is a similar situation to that observed for the nickel(II) chloride complex of the same ligand,⁹ in which a *cis*-octahedral structure is adopted with the ligand folded from its planar conformation along the S-Ni-S axis. The reason for the folding along the S-S axis, rather than the N-N axis in both cases becomes obvious on inspection of molecular models and arises from the fact that the tetrahedral bond arrangement around the *trans* sulphur atoms readily accommodates a N-metal-N angle of $\ll 180^\circ$ whilst in the alternative situation,

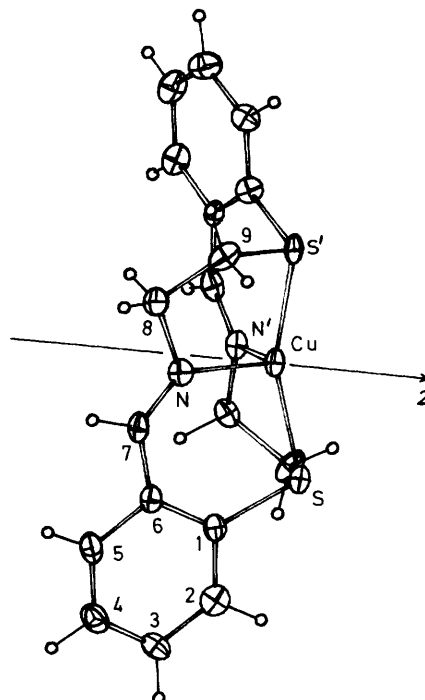
Table 2. Non-hydrogen atom co-ordinates for (2)

Atom	x	y	z	Atom	x	y	z
Cu(1)	0.183 0(2)	-0.326 0(3)	-0.084 5(3)				
Macrocyclic							
S(1)	0.370 5(5)	-0.302 9(6)	0.134 9(8)	S(2)	0.047 0(4)	-0.360 6(6)	0.038 8(7)
C(11)	0.411(1)	-0.346(2)	-0.016(3)	C(21)	0.008(2)	-0.237(2)	0.105(2)
C(12)	0.473(2)	-0.307(2)	-0.098(3)	C(22)	-0.079(2)	-0.229(2)	0.150(2)
C(13)	0.508(1)	-0.343(2)	-0.218(3)	C(23)	-0.119(2)	-0.129(2)	0.199(3)
C(14)	0.476(1)	-0.442(2)	-0.249(2)	C(24)	-0.068(2)	-0.052(2)	0.227(2)
C(15)	0.415(1)	-0.498(2)	-0.171(3)	C(25)	0.016(2)	-0.057(2)	0.183(3)
C(16)	0.380(1)	-0.447(2)	-0.055(2)	C(26)	0.055(2)	-0.152(2)	0.122(2)
C(17)	0.309(1)	-0.503(2)	0.030(2)	C(27)	0.147(2)	-0.129(2)	0.073(3)
N(1)	0.233(1)	-0.464(2)	0.032(2)	N(2)	0.198(1)	-0.194(1)	-0.009(2)
C(18)	0.166(2)	-0.525(2)	0.117(2)	C(28)	0.280(1)	-0.141(2)	-0.038(2)
C(19)	0.103(2)	-0.431(2)	0.181(2)	C(29)	0.340(2)	-0.157(2)	0.074(3)
Triphenylphosphine							
P	0.179 1(4)	-0.314 5(6)	-0.308 7(7)	C(123)	-0.074(2)	-0.220(2)	-0.325(3)
C(111)	0.226(1)	-0.434(2)	-0.384(2)	C(124)	-0.100(2)	-0.272(3)	-0.425(3)
C(112)	0.227(2)	-0.537(2)	-0.311(2)	C(125)	-0.040(2)	-0.339(2)	-0.497(2)
C(113)	0.262(2)	-0.630(2)	-0.358(2)	C(126)	0.044(1)	-0.347(2)	-0.456(2)
C(114)	0.297(2)	-0.627(2)	-0.496(3)	C(131)	0.228(2)	-0.204(2)	-0.411(2)
C(115)	0.298(1)	-0.524(2)	-0.567(2)	C(132)	0.315(2)	-0.197(2)	-0.403(3)
C(116)	0.264(2)	-0.430(2)	-0.518(2)	C(133)	0.352(2)	-0.104(2)	-0.468(4)
C(121)	0.069(2)	-0.302(2)	-0.359(2)	C(134)	0.317(3)	-0.024(3)	-0.558(4)
C(122)	0.008(2)	-0.232(2)	-0.282(2)	C(135)	0.233(2)	-0.036(3)	-0.568(3)
				C(136)	0.187(2)	-0.122(2)	-0.501(3)
Perchlorate							
Cl	-0.297 2(4)	-0.176 2(6)	-0.079 2(7)	O(3)	-0.374(1)	-0.107(3)	-0.048(3)
O(1)	-0.229(1)	-0.099(1)	-0.091(2)	O(4)	-0.303(1)	-0.225(2)	-0.194(2)
O(2)	-0.283(1)	-0.257(2)	0.034(2)				
Solvent							
C(1)*	0.472(4)	0.006(5)	0.761(7)	C(3)*	0.448(6)	0.155(8)	0.730(10)
C(2)*	0.409(6)	0.103(7)	0.657(9)	C(4)*	0.491(5)	0.233(6)	0.632(7)

* Population 0.5: isotropic thermal parameter refinement.

Table 3. Copper atom environment (distances in Å, angles in °) for (1) and (2). Values for the P3 model for (1) are given in square brackets; mean values for the previously determined cation are given in parentheses

Compound (1)			
Cu-S	2.222(4)	[2.216(6), 2.232(6)]	(2.21 ₂)
Cu-N	2.009(9)	[2.01(1), 2.00(1)]	(1.98 ₀)
S-Cu-S'	158.1(1)	[158.5(1)]	(152 ₂)
N-Cu-N'	102.2(4)	[101.6(4)]	(110 ₀)
S-Cu-N	101.0(3)	[101.2(4), 100.6(4)]	(102 ₀)
S-Cu-N'	92.7(3)	[92.9(4), 92.4(4)]	(92 ₀)
Compound (2)			
Cu-S(2)	2.412(7)		
Cu-N(1)	2.05(2)		
Cu-N(2)	1.92(2)		
Cu-P	2.212(8)		
S(2)-Cu-N(1)	86.7(5)		
S(2)-Cu-N(2)	96.6(5)		
S(2)-Cu-P	113.1(3)		
N(1)-Cu-N(2)	111.6(8)		
N(1)-Cu-P	122.9(6)		
N(2)-Cu-P	117.8(6)		

**Figure 2.** The cation of the P6 model of (1), with 20% thermal ellipsoids for the non-hydrogen atoms

the trigonal-planar bond arrangement around *trans* imino-nitrogen atoms will not sustain a reduction of the S-metal-S angle without incurring progressively increasing strain in the molecule. Overall, the structure of (1) is an unusual one for a copper(I) compound and can be best viewed as being based on that of an approximate trigonal bipyramid with one of the equatorial sites vacant (Scheme 1).

In the structure of the adduct (2), the close proximity of the nitrogen atoms observed in (1) is retained but with the N-Cu-N angle increasing to 111.6(8)°. However, bonding of the PPh₃ ligand to the copper results in the displacement of one of the sulphur atoms to give an N₂SP donor array (Figure 3). The non-bonded Cu...S(1) distance is 3.872(9) Å with the nearest intermolecular O...S(1) distance 5.483(9) Å. The Cu-P distance of 2.212(8) Å is very similar to the average value of 2.213(5) Å for other copper(I) complexes containing one triphenylphosphine ligand.¹⁰ The Cu-N(1) and Cu-N(2) distances of 2.05(2) and 1.92(2) Å are asymmetric by comparison with (1), with the Cu-N(2) distance quite short. The copper atom lies 0.33 Å out of the PN₂ plane with the P-Cu-N and N-Cu-N angles adding up to 352.3°. S(2)-Cu-N(1) and S(2)-Cu-N(2) are 86.7(5) and 96.6(5)°. However, the S(2)-Cu-P angle of 113.1(3)° is considerably greater than the 90° expected for an ideal trigonal-pyramidal geometry. The Cu-S(2) distance of 2.412(7) Å is also significantly longer than the Cu-S distance in (1). By analogy with the description of (1) as a trigonal bipyramid with one *equatorial* site vacant, the structure of (2) can be described as a trigonal bipyramid with one *axial* site vacant (Scheme 1). Again, this is quite an unusual co-ordination geometry for copper(I) complexes.

The solid-state ³¹P n.m.r. spectrum of (2) shows a single well resolved quartet of lines with an average chemical shift of *ca.* 2.3 p.p.m. For comparison, the solution ³¹P n.m.r. spectrum of the more soluble triflate salt shows a broad singlet band centred at 1.1 p.p.m.¹ The line spacings in the solid-state spectra are 1.41, 1.55, and 1.65 kHz which are comparable with values of 1.4–1.9 kHz recorded for other copper(I) complexes containing a singly bound triphenylphosphine ligand.¹⁰ The differences in the line spacings are consistent with the copper sited in a four-coordinate geometry distorted from ideal *T_d* symmetry as found in the X-ray structure. The chemical shifts in the solution and solid-state spectra provide good evidence that the structure of (2) does not differ greatly in the two states.

In solution, the PPh₃ ligand is quite labile. For example, recrystallization of (2) from an acetone-ethanol mixture gives crystals of both (1) and (2). Mechanistically, the formation of (2) from (1) can be envisaged as proceeding through the approach of triphenylphosphine towards the equatorial vacancy in (1), displacing S(1) as shown in Scheme 1. This displacement process proceeds *via* a twist of the macrocycle about the C(16)-C(17) aromatic-imino carbon bond resulting in the *p_z* orbitals of the exocyclic double bond becoming approximately orthogonal to the aromatic ring with a torsion angle N(1)-C(17)-C(16)-C(11) of 73° compared to 4° for the analogous N(2)-C(27)-C(26)-C(21) angle (Scheme 2, Figure 3).

The difference in the conformational structure around the two imino groups in (2) is also reflected in the considerable increase in the splitting of the C=N stretching mode in the i.r. spectrum and in the differences in the C(n7)-N(n) bond lengths with the unconjugated C(17)-N(1) distance of 1.24(3) Å shorter than the conjugated C(27)-N(2) distance of 1.38(3) Å.

Both the size and the steric profile of the PPh₃ ligand appear to be critical factors in this reaction sequence as other molecules of comparable Lewis-base strength such as carbon monoxide, oxygen, pyridine, or imidazole do not react at all with (1); the more sterically hindered phosphine, diphenyl-*o*-tolylphosphine also fails to give an isolable adduct under the same conditions. The three phenyl rings of the PPh₃ ligand and the C(11)-C(16)

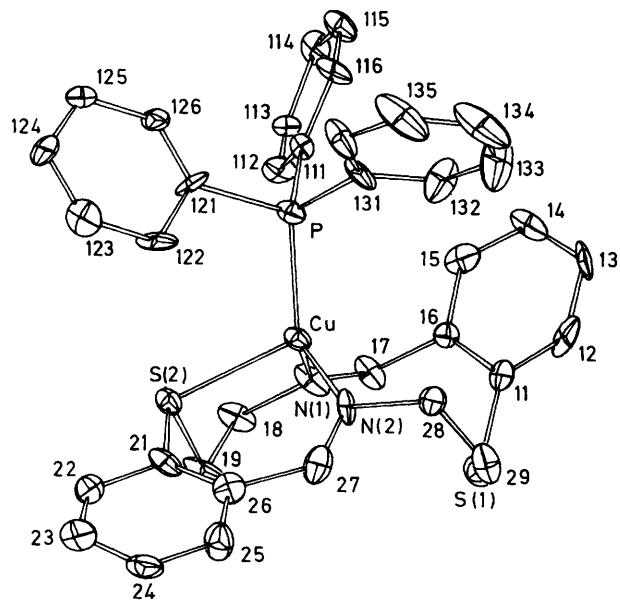
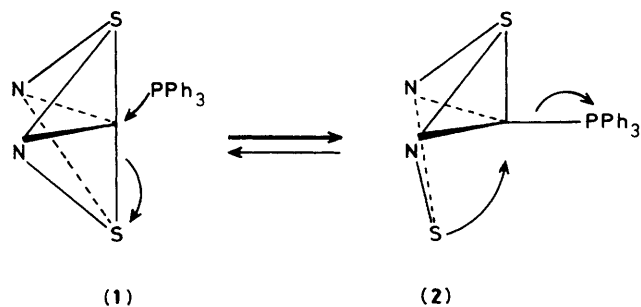
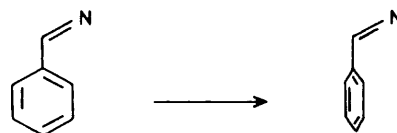


Figure 3. The cation of (2), with 20% thermal ellipsoids for the non-hydrogen atoms



Scheme 1.



Scheme 2.

phenyl ring of the macrocycle adopt a 'head-to-tail' conformational structure which is found for a wide range of triphenylphosphine complexes,¹¹ the dihedral angles between the planes ranging between 91 and 104°. In a fashion similar to that found in several copper(I) halide triphenylphosphine complexes,¹² the Cu-S(2) bond lies approximately coplanar with ring 2 of the PPh₃ ligand with a S(2)-Cu-P-C(121) torsion angle of 13° and a S(2)...H(122) contact distance of *ca.* 2.9 Å. It seems reasonable to infer that it is this interaction between the PPh₃ ligand and the macrocycle that is the cause of the observed increase in both the Cu-S(2) bond length and the P-Cu-S(2) bond angle.

Displacement of a single sulphur donor from the group of co-ordinating atoms in this macrocycle is not totally unexpected since although the failure of all four donors to co-ordinate to a single central copper ion is extremely rare amongst N₄ macrocycles, there being only one documented case in the literature,¹³ for S₄ macrocycles it is quite common to find the ligand in an *exo* configuration, that is contributing two sulphurs to each of

two different metal ions^{14,15} or contributing three sulphurs to one metal ion and one to another.¹⁶ The behaviour of this N₂S₂ macrocycle can therefore be viewed as being intermediate between the typical behaviour of N₄ and S₄ macrocycles: showing neither the reluctance of the N₄ systems to facilitate tetrahedral co-ordination by the expulsion of a donor atom from the primary co-ordination sphere nor the willingness of the S₄ system, which does so spontaneously. Instead, L will only behave in this way when induced to do so by a competing ligand.

It is plausible to argue that the co-ordination of the PPh₃ ligand, the displacement of S(1), the twisting of the macrocycle around C(16)–C(17), the orientation of the phenyl rings and the increase in the Cu–S(2) distance and the P–Cu–S(2) angle all occur as a concerted process. The fact that the PPh₃ ligand happens to be quite labile provides a convenient trigger for switching the geometry and charge-transfer characteristics of this system.

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