Ditopic Crown Thioethers. Synthesis and Structures of *anti*-$[\mathrm{Cu_2(L^1)(PPh_2Me)_2}][\mathrm{ClO_4}]_2$ and *syn*-$[\mathrm{Cu_2(L^1)(\mu\text{-}PPh_2CH_2CH_2PPh_2)}][\mathrm{PF_6}]_2$, ($\mathrm{L^1}$ = 2,5,8,17,20,23-hexathia[9](1,2)[9](6,5)cyclophane)

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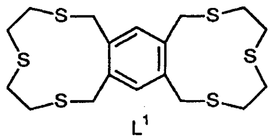
The ditopic crown thioether, 2,5,8,17,20,23-hexathia[9](1,2)[9](6,5)cyclophane contains two $\mathrm{S_3}$ coordination sites separated by an *o*-xylyl spacing unit which allows coordination of two metal ions in either an *anti* or *syn* arrangement as demonstrated by the structures of *anti*-$[\mathrm{Cu_2(L^1)(PPh_2Me)_2}][\mathrm{ClO_4}]_2$ and *syn*-$[\mathrm{Cu_2(L^1)(\mu\text{-}PPh_2CH_2CH_2PPh_2)}][\mathrm{PF_6}]_2$.

Crown thioether ligands containing six or more S donor atoms have the potential to coordinate two metal centres.[1,2] However, the only structurally characterized binuclear complexes of crown thioethers† are $[\mathrm{Cu_2(MeCN)_2([18]aneS_6)}][\mathrm{ClO_4}]_2$,[3] $[\mathrm{Cu_2([24]aneS_8)}][\mathrm{BF_4}]_2$,[4] $[\mathrm{Cu_2([28]aneS_8)}][\mathrm{ClO_4}]_2$,[4] $[\mathrm{Rh_2(Me_5Cp)_2Cl_2([18]aneS_6)}][\mathrm{BPh_4}]_2$[5] and $[\mathrm{Rh_2(1,5\text{-}cod)_2([20]aneS_6)}][\mathrm{BF_4}]_2$.[6] The major problems associated with preparing binuclear complexes of these ligands are that (*i*) this



$\mathrm{L^1}$

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† Abbreviations used are: $[9]\mathrm{aneS_3}$, 1,4,7-trithiacyclononane; $[18]\mathrm{aneS_6}$, 1,4,7,10,13,16-hexathiacyclooctadecane; $[20]\mathrm{aneS_6}$, 1,4,7,11,14,17-hexathiacycloicosane; $[24]\mathrm{aneS_8}$, 1,4,7,10,13,16,19,22-octathiacyclotetracosane; $[28]\mathrm{aneS_8}$, 1,4,8,11,15,18,22,25-octathiacyclooctacosane; $\mathrm{L^2}$, 2,5,8-trithia[9]-*o*-cyclophane, abbreviated to TT[9]OB in ref. 8.

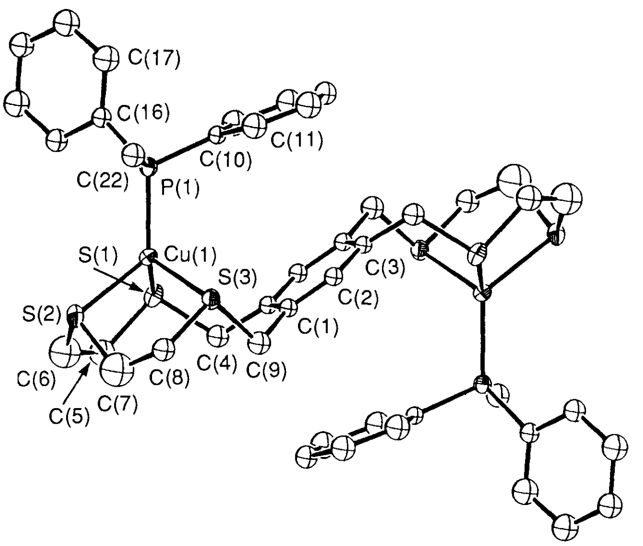

Fig. 1 Perspective ORTEP drawing of the *anti*-[Cu$_2$(L^1)(PPh$_2$Me)$_2$]$^{2+}$ cation, (molecule 1), showing the atom numbering scheme. Significant bond lengths (Å) and angles (°): Cu(1)–S(1) 2.294(6), Cu(1)–S(2) 2.328(7), Cu(1)–S(3) 2.341(5), Cu(1)–P(1) 2.209(5), Cu(1)···Cu(1)′ 8.502(4); S(1)–Cu(1)–S(2) 92.7(2), S(1)–Cu(1)–S(3) 112.7(2), S(1)–Cu(1)–P(1) 126.0(2), S(2)–Cu(1)–S(3) 92.6(2), S(2)–Cu(1)–P(1) 122.2(2), S(3)–Cu(1)–P(1) 106.0(2).

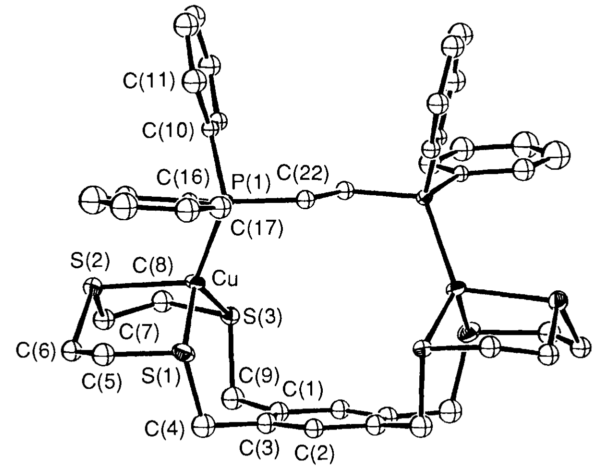

Fig. 2 Perspective ORTEP drawing of the *syn*-[Cu$_2$(L^1)(μ-Ph$_2$PCH$_2$CH$_2$PPh$_2$)]$^{2+}$ cation showing the atom numbering scheme. Significant bonding lengths (Å) and angles (°): Cu–S(1) 2.330(8), Cu–S(2) 2.341(5), Cu–S(3) 2.297(7), Cu–P(1) 2.222(6) Cu···Cu′ 5.886(7), P(1)···P(1)′ 4.432(9); S(1)–Cu–S(2) 93.0(2), S(1)–Cu–S(3) 117.0(2), S(1)–Cu–P(1) 103.5(3), S(2)–Cu–S(3) 93.7(2), S(2)–Cu–P(1) 117.9(2), S(3)–Cu–P(1) 126.9(2).

type of flexible macrocycle with a large central cavity will often prefer to encapsulate a single metal ion[1,2] and (*ii*) there is little control over the relative orientation of the metal atoms. We report herein the synthesis and coordination chemistry of 2,5,8,17,20,23-hexathia[9](1,2)[9](6,5)cyclophane, (L^1), the first example of a crown thioether ligand designed specifically for binuclear coordination.

L^1 was prepared *via* the template reaction of 1,2,4,5-tetrabromodurene with [Me$_4$N]$_2$[Mo(CO)$_3$(SCH$_2$CH$_2$SCH$_2$CH$_2$S)] employing the method used by Sellmann[7] for the preparation of 1,4,7-trithiacyclononane, ([9]aneS$_3$).‡ The reaction of one equivalent of L^1 with two equivalents of [Cu(MeCN)$_4$][X] (X = ClO$_4$, PF$_6$), in MeCN, followed by the addition of either two equivalents of PPh$_2$Me or one equivalent of Ph$_2$PCH$_2$CH$_2$PPh$_2$ gave, in good yield, the complexes *anti*-[Cu$_2$(L^1)(PPh$_2$Me)$_2$][X]$_2$, and *syn*-[Cu$_2$(L^1)(μ-PPh$_2$CH$_2$CH$_2$PPh$_2$)][X]$_2$. Recrystallization from CHCl$_3$ or acetone afforded colourless X-ray quality crystals of *anti*-[Cu$_2$(L^1)(PPh$_2$Me)$_2$][ClO$_4$]$_2$, **1** and *syn*-[Cu$_2$(L^1)(μ-PPh$_2$CH$_2$CH$_2$PPh$_2$)][PF$_6$]$_2$, **2**, respectively.

The X-ray structure of **1**§ verifies (Fig. 1)¶ that L^1 acts as a ditopic ligand coordinating to two Cu atoms *via* two sets of S$_3$ donors with the fourth site on each Cu atom occupied by a PPh$_2$Me ligand. The Cu atoms are in identical,¶ distorted tetrahedral environments bonded to three S atoms, Cu(1)–S(1) 2.294(6), Cu(1)–S(2) 2.328(7), Cu(1)–S(3) 2.341(5) Å and a P atom, Cu(1)–P(1) 2.209(5) Å. The S(1)–Cu(1)–S(2) and S(2)–Cu(1)–S(3) angles involving the five-membered chelate rings are 92.7(2) and 92.6(2)°, respectively and the S(1)–Cu(1)–S(3) angle associated with the seven-membered chelate ring spanning the *o*-xylyl unit is 112.7(2)°. Overall, the ligand adopts an *anti*-conformation that places the two coordination sites on opposite sides of the central aromatic ring thereby excluding any possibility of intramolecular interaction between coordination sites. The X-ray structure of **2**§ demonstrates (Fig. 2)‖ that L^1 can also accommodate a coordination mode that places the two Cu atoms on the same side of the *o*-xylyl ring. Most significantly, this coordination mode allows for the incorporation of bridging ligands or substrate molecules. As in **1**, each Cu atom is coordinated by a set of S$_3$ donors with the fourth site occupied by a phosphine ligand. Again, the Cu atoms are in identical,‖ distorted tetrahedral environments bonded to three S atoms, Cu–S(1) 2.330(8), Cu–S(2) 2.341(5), Cu–S(3) 2.297(6) Å and a P atom, Cu(1)–P(1) 2.209(5) Å. The S(1)–Cu–S(2) and S(2)–Cu–S(3) angles involving the five-membered chelate rings are 93.0(2) and 93.7(2)°, respectively and the S(1)–Cu(1)–S(3) angle associated with the seven-membered chelate ring is 117.0(2)°. The coordination about Cu in both **1** and **2** compares well to that found for [Cu(PPh$_2$Me)(L^2)][ClO$_4$],[8] which has the same structural features as one of the S$_3$ coordination sites of L^1.

The compartmentalized nature of L^1 separates the S$_6$ donor set into two equivalent S$_3$ binding sites which can each coordinate *facially* to a metal centre. The use of a simple monodentate ligand such as PPh$_2$Me results in the formation of **1** in which the ligand adopts an *anti*-conformation. This conformation maximizes the separation between the two coordination sites and is probably the favoured conformation on steric grounds. The use of a bidentate ligand such as Ph$_2$PCH$_2$CH$_2$PPh$_2$ yields **2** in which L^1 adopts a *syn*-conformation. It appears that intramolecular bridging between adjacent metal atoms in the *syn*-conformation of the ligand is favoured over intermolecular linking of the fragments in the *anti*-conformation. In **2**, the *syn*-conformation places the Cu atoms at a distance of 5.886(7) Å and the P(1)···P(1)′

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‡ Two equivalents of [NMe$_4$]$_2$[Mo(CO)$_3$(SCH$_2$CH$_2$SCH$_2$CH$_2$S)] were reacted with one equivalent of 1,2,4,5-tetrakis(bromomethyl)benzene under the conditions outlined in ref. 7 for the synthesis of [9]aneS$_3$. A reaction time of 20 h followed by identical workup and recrystallisation from CHCl$_3$–hexanes gave L^1 in 15% yield.

§ *Crystal data* for **1**: [C$_{44}$H$_{52}$Cu$_2$P$_2$S$_6$][ClO$_4$]$_2$·(CHCl$_3$) triclinic $P\bar{1}$, a = 15.192(7), b = 16.943(8), c = 11.725(6) Å, α = 96.86(5), β = 112.34(4), γ = 92.73(5)°, U = 2757(2) Å^3, Z = 2, D_c = 1.542 g cm^{-3}, μ(Mo-Kα) = 13.40 cm^{-1}. Rigaku AFC6 diffractometer; 2732 unique reflections with $F_o^2 > 3\sigma F_o^2$, R = 7.94, R_w = 7.63%. *Crystal data* for **2**: [C$_{44}$H$_{50}$Cu$_2$P$_2$S$_6$][PF$_6$]$_2$, monoclinic, *C*2/*c*, a = 26.33(2), b = 12.658(2), c = 17.771(9) Å, β = 117.74(3)°, U = 5241(5) Å^3, Z = 4, D_c = 1.584 g cm^{-3}, μ(Mo-Kα) = 12.37 cm^{-1}. Rigaku AFC6 diffractometer; 1282 unique reflections with $F_o^2 > 3\sigma F_o^2$, R = 7.42, R_w = 7.45%. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ Complex **1** crystallizes with two independent molecules in the asymmetric unit. Both molecules sit on a centre of inversion and are essentially identical. For simplicity, the structure of only one of these molecules is described.

‖ Complex **2** has crystallographically imposed twofold symmetry.

separation is 4.432(9) Å. Thus, this conformation produces a relatively large cavity into which $PPh_2CH_2CH_2PPh_2$ or some other similar sized, substrate molecule could coordinate. The flexibility of L^1 and the dependence of the metal–metal separation and cavity size on metal and bridging ligand type are currently being investigated. The resemblance of a single S_3 binding site of L^1 to the S_3 set of L^2 or [9]aneS_3 is notable and it may be possible to develop binuclear chemistry with L^1, based on the known chemistry of these ligands.[1,2]

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