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## Ditopic Crown Thioethers. Synthesis and Structures of anti-[Cu<sub>2</sub>(L<sup>1</sup>)(PPh<sub>2</sub>Me)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub> and syn-[Cu<sub>2</sub>(L<sup>1</sup>)( $\mu$ -PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)][PF<sub>6</sub>]<sub>2</sub>, (L<sup>1</sup> = 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 S<sub>3</sub> 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*-[Cu<sub>2</sub>(L<sup>1</sup>)(PPh<sub>2</sub>Me)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub> and *syn*-[Cu<sub>2</sub>(L<sup>1</sup>)( $\mu$ -PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)][PF<sub>6</sub>]<sub>2</sub>.

Crown thioether ligands containing six or more S donor atoms have the potential to coordinate two metal centres.<sup>1,2</sup> However, the only structurally characterized binuclear complexes of crown thioethers<sup>†</sup> are  $[Cu_2(MeCN)_2([18]aneS_6]$ -

 $\begin{array}{l} [ClO_4]_{2,3} \ [Cu_2([24]aneS_8)][BF_4]_{2,4} \ [Cu_2([28]aneS_8)][ClO_4]_{2,4} \\ [Rh_2(Me_5Cp)_2Cl_2([18]aneS_6)][BPh_4]_{2,5} \ and \ [Rh_2(1,5-cod)_{2-} \\ ([20]aneS_6)][BF_4]_{2,6} \ The major problems associated with \\ preparing binuclear complexes of these ligands are that (i) this \\ \end{array}$ 



<sup>†</sup> Abbreviations used are: [9]aneS<sub>3</sub>, 1,4,7-trithiacyclononane; [18]aneS<sub>6</sub>, 1,4,7,10,13,16-hexathiacyclooctadecane; [20]aneS<sub>6</sub>, 1,4,7,11,14,17-hexathiacycloicosane; [24]aneS<sub>8</sub>, 1,4,7,10,13,16,19,22-octathiacyclotetracosane; [28]aneS<sub>8</sub>, 1,4,8,11,15,18,22,25-octathiacyclooctacosane; L<sup>2</sup>, 2,5,8-trithia[9]-o-cyclophane, abbreviated to TT[9]OB in ref. 8.



Fig. 1 Perspective ORTEP drawing of the *anti*- $[Cu_2(L^1)(PPh_2Me)_2]^{2+}$  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)–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<sub>2</sub>(L<sup>1</sup>)- $(\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)]<sup>2+</sup> 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<sup>1</sup>), the first example of a crown thioether ligand designed specifically for binuclear coordination.

 $L^{1}$  was prepared *via* the template reaction of 1,2,4,5tetrabromodurene with  $[Me_4N]_2[Mo(CO)_3(SCH_2CH_2SCH_2 CH_2S)]$  employing the method used by Sellmann<sup>7</sup> for the preparation of 1,4,7-trithiacyclononane, ([9]aneS<sub>3</sub>).‡ The

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reaction of one equivalent of L<sup>1</sup> 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<sub>2</sub>Me or one equivalent of Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> gave, in good yield, the complexes *anti*-[Cu<sub>2</sub>(L<sup>1</sup>)(PPh<sub>2</sub>Me)<sub>2</sub>][X]<sub>2</sub>, and *syn*-[Cu<sub>2</sub>(L<sup>1</sup>)-( $\mu$ -PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)][X]<sub>2</sub>. Recrystallization from CHCl<sub>3</sub> or acetone afforded colourless X-ray quality crystals of *anti*-[Cu<sub>2</sub>(L<sup>1</sup>)( $\mu$ -PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)][ClO<sub>4</sub>]<sub>2</sub>, **1** and *syn*-[Cu<sub>2</sub>(L<sup>1</sup>)-( $\mu$ -PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)][PF<sub>6</sub>]<sub>2</sub>, **2**, respectively.

The X-ray structure of 1§ verifies (Fig. 1)¶ that L1 acts as a ditopic ligand coordinating to two Cu atoms via two sets of S3 donors with the fourth site on each Cu atom occupied by a PPh<sub>2</sub>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<sub>3</sub> 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  $93.7(2)^\circ$ , respectively and the S(1)-Cu(1)-S(3) angle associated with the seven-membered chelate ring is  $117.0(2)^{\circ}$ . The coordination about Cu in both 1 and 2 compares well to that found for  $[Cu(PPh_2Me)(L^2)][ClO_4]$ ,<sup>8</sup> which has the same structural features as one of the  $S_3$  coordination sites of  $L^1$ .

The compartmentalized nature of L<sup>1</sup> separates the S<sub>6</sub> donor set into two equivalent S<sub>3</sub> binding sites which can each coordinate *facially* to a metal centre. The use of a simple monodentate ligand such as PPh<sub>2</sub>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<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> yields **2** in which L<sup>1</sup> 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)'

§ *Crystal data* for 1: [C<sub>44</sub>H<sub>52</sub>Cu<sub>2</sub>P<sub>2</sub>S<sub>6</sub>][ClO<sub>4</sub>]<sub>2</sub> (CHCl<sub>3</sub>) triclinic *P*I, *a* = 15.192(7), *b* = 16.943(8), *c* = 11.725(6) Å, *α* = 96.86(5), *β* = 112.34(4),  $\gamma = 92.73(5)^{\circ}$ , *U* = 2757(2) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.542 g cm<sup>-3</sup>,  $\mu$ (Mo-K*α*) = 13.40 cm<sup>-1</sup>. Rigaku AFC6 diffractometer; 2732 unique reflections with  $F_0^2 > 3\sigma F_0^2$ , *R* = 7.94, *R<sub>w</sub>* = 7.63%. *Crystal data* for 2: [C<sub>44</sub>H<sub>50</sub>Cu<sub>2</sub>P<sub>2</sub>S<sub>6</sub>][PF<sub>6</sub>]<sub>2</sub>, monoclinic, *C2/c*, *a* = 26.33(2), *b* = 12.658(2), *c* = 17.771(9) Å, *β* = 117.74(3)°, *U* = 5241(5) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.584 g cm<sup>-3</sup>,  $\mu$ (Mo-K*α*) = 12.37 cm<sup>-1</sup>. Rigaku AFC6 diffractometer; 1282 unique reflections with  $F_0^2 > 3\sigma F_0^2$ , *R* = 7.42, *R<sub>w</sub>* = 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.

 $\P$  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.

 $<sup>\</sup>ddagger$  Two equivalents of [NMe<sub>4</sub>]<sub>2</sub>[Mo(CO)<sub>3</sub>(SCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>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<sub>3</sub>. A reaction time of 20 h followed by identical workup and recrystallisation from CHCl<sub>3</sub>-hexanes gave L<sup>1</sup> in 15% yield.

separation is 4.432(9) Å. Thus, this conformation produces a relatively large cavity into which PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> 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<sub>3</sub> binding site of  $L^1$  to the S<sub>3</sub> set of  $L^2$  or [9]aneS<sub>3</sub> is notable and it may be possible to develop binuclear chemistry with  $L^1$ , based on the known chemistry of these ligands.<sup>1.2</sup>

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