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Thiamacrocyclic chemistry: synthesis of a novel oxadithiacrown and its copper iodide complex†

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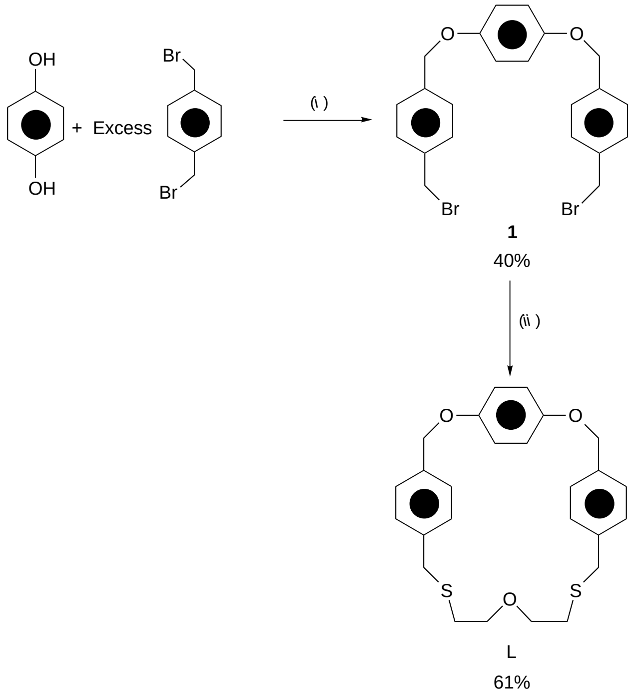
A mixed oxa–thia macrocycle incorporating a rigid ‘horseshoe-shaped’ aromatic moiety, 1,11,21-trioxa-8,14-dithia[2,9,2]paracyclophane, L, has been synthesised. The molecular structures of L and of its copper iodide complex have been determined by single-crystal X-ray diffraction methods. There are two independent conformations observed in the solid state for the macrocycle, L. Its copper iodide complex $[Cu_2I_2(L)]\cdot 1.25MeCN$, crystallises, in a 2 : 1 metal : crown ratio, as a one-dimensional infinite array of cubane-like units consisting of four copper atoms, four iodine atoms and four sulfur atoms from four different macrocycles.

Studies on thioether macrocycles have sparked off a great deal of interest[1] owing to the fact that these ligands: (1) stabilise unusual oxidation states in transition-metal complexes,[2] (2) form metal complexes which can bind and activate guest molecules for molecular recognition and/or catalysis,[3] and (3) provide a tool for the study of conformational effects in macrocycles owing to the substantial efforts which have been made to preorganise thiacrowns for metal-ion binding.[4,5] With these criteria and ideas in mind, we have designed a macrocycle containing an oxadithia chelate chain and a ‘horseshoe-shaped’ moiety containing three aromatic rings. The ligand was designed to incorporate a metal chelating site, in addition to a second site to interact with a substrate molecule bound to the metal centre,[6] within the same macrocyclic framework. For the purposes of metal-ion co-ordination, the oxadithia chelate, $-SCH_2CH_2OCH_2CH_2S-$, was chosen with the expectation that only the thioether donors would co-ordinate a copper(I) ion. Thus, this chain would provide only two donor atoms, leaving two labile co-ordination sites on the metal.

Results and Discussion

The macrocycle was synthesised (Scheme 1) by a two-step procedure. The first step was the preparation of the dibromide, **1**, from hydroquinone and an excess of 1,4-bis(bromomethyl)benzene. The solvent chosen for this reaction was a mixture of thf and MeCN, rather than pure MeCN which is more typical for a K_2CO_3-mediated ether synthesis. The thf is necessary to maintain the solubility of both the starting 1,4-bis(bromomethyl)benzene and the monoalkylated monobromo intermediate and, thus, the desired stoichiometry of the reaction. Although the yield for this procedure is only *ca.* 40%, depending upon the scale of the reaction, the product can be obtained analytically pure by successive recrystallisations from MeCN. The second reaction is a Cs_2CO_3-mediated cyclisation[7] between the dibromide **1** and 2,2′-oxydiethanethiol to give the oxadithiacrown L in a satisfactory yield (>60%). This product can also be purified without the need for column chromatography as white feathers formed upon concentration of an acetone solution of the crown.



Scheme 1 Synthetic route to the macrocycle L. (*i*) K_2CO_3, MeCN, tetrahydrofuran (thf), heat; (*ii*) Cs_2CO_3, dimethylformamide (dmf), $(HSCH_2CH_2)_2O$, heat

The X-ray analysis shows (Figs. 1 and 2 and Table 1) L to crystallise with two crystallographically independent molecules (A and B) in the asymmetric unit. Although both macrocycles have an open geometry, the conformations exhibit marked differences. In conformation A, the hydroquinone ring is inclined by *ca.* 53° and the two *p*-xylyl rings by 77 and 95°, respectively, to the mean plane of the macrocycle as defined by the four *p*-xylyl carbon atoms (coplanar to within 0.1 Å). The conformation of the S(1) to S(7) chain is that which one would predict based upon the 1,4-interactions in the chelate chain,[5] that is, with the sulfur donors adopting exodentate orientations with respect to the macrocyclic cavity and the oxygen donor of the chelate chain adopting an endodentate orien-

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† 1,11,21-Trioxa-8,14-dithia[2,9,2]paracyclophane = 9,15-dithia-3,5,12-trioxa-1(1,4), 4(1,4), 7(1,4)-tribenzenacyclohexadecaphane.

Table 1 Selected bond angles (°) for both conformations of L

A		B	
C(2)–S(1)–C(31)	100.0(4)	C(2′)–S(1′)–C(31′)	99.6(4)
S(1)–C(2)–C(3)	109.2(5)	C(2′)–C(3′)–O(4′)	109.8(5)
C(2)–C(3)–O(4)	109.8(6)	S(1′)–C(2′)–C(3′)	111.3(6)
C(3)–O(4)–C(5)	114.9(6)	C(3′)–O(4′)–C(5′)	114.9(6)
O(4)–C(5)–C(6)	113.0(6)	O(4′)–C(5′)–C(6′)	116.1(6)
C(5)–C(6)–S(7)	114.8(5)	C(5′)–C(6′)–S(7′)	109.4(6)
C(6)–S(7)–C(8)	103.9(4)	C(6′)–S(7′)–C(8′)	99.3(4)
S(7)–C(8)–C(9)	115.2(5)	S(7′)–C(8′)–C(9′)	114.6(5)
S(1)–C(31)–C(28)	115.2(6)	S(1′)–C(31′)–C(28′)	114.1(5)

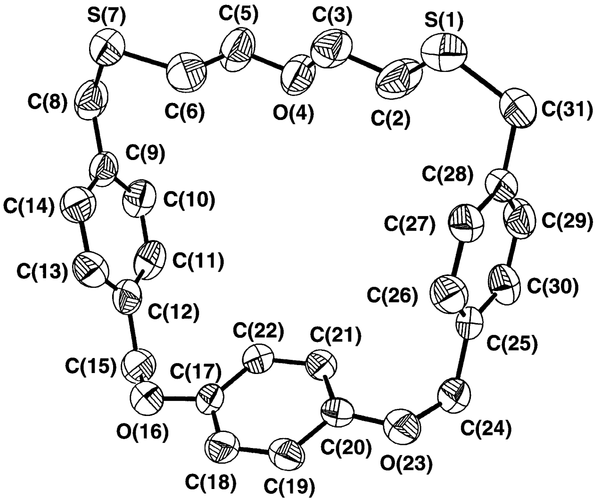

Fig. 1 The conformation A of the macrocycle L (50% probability ellipsoids)

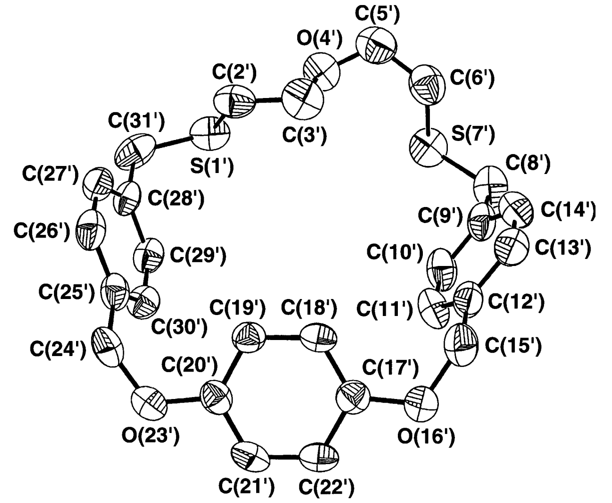

Fig. 2 The conformation B of the macrocycle L (50% probability ellipsoids)

tation. The cavity dimensions, as defined by the distance from the central polyether oxygen O(4) to the centroid of the hydroquinone ring and between the centres of the two *p*-xylyl rings, are 6.9 and 8.2 Å, respectively. In conformation B, the hydroquinone and *p*-xylyl rings are inclined to the mean plane by 53, 53 and 66°, respectively. The conformation of the S(1′) to S(7′) linkage is unusual in that the ether oxygen atom is directed outwards and is in a *gauche* geometry with respect to the two sulfur atoms, *cf.* an *anti* geometry in conformation A. The cavity dimensions are 8.1 and 7.6 Å for the O(4′)–hydroquinone separation and the xylyl–xylyl distance, respectively. It is notable that in both molecules there is a marked in-plane bending of the pairs of hydroquinone C–O bonds with respect to each other.

Table 2 Selected bond distances (Å) and angles (°) for $[Cu_2I_2(L)]\cdot 1.25MeCN$

Cu(1)–Cu(2)	2.731(1)	Cu(1)–I(1)	2.688(1)
Cu(1)–I(2)	2.704(1)	Cu(1)–S(1)	2.304(2)
Cu(2)–I(1)	2.720(1)	Cu(2)–S(7)	2.306(2)
Cu(2)–Cu(1)–I(1)	60.3(1)	Cu(2)–Cu(1)–I(2)	109.5(1)
I(1)–Cu(1)–I(2)	112.7(1)	Cu(2)–Cu(1)–S(1)	145.2(1)
I(1)–Cu(1)–S(1)	111.4(1)	I(2)–Cu(1)–S(1)	104.8(1)
Cu(1)–Cu(2)–I(1)	59.1(1)	Cu(1)–Cu(2)–S(7)	139.6(1)
I(1)–Cu(2)–S(7)	102.7(1)	Cu(1)–I(1)–Cu(2)	60.7(1)
Cu(1)–S(1)–C(2)	107.0(2)	Cu(1)–S(1)–C(31)	103.1(2)
C(2)–S(1)–C(31)	99.6(3)	S(1)–C(2)–C(3)	111.3(5)
C(2)–C(3)–O(4)	109.0(6)	C(3)–O(4)–C(5)	113.9(6)
O(4)–C(5)–C(6)	108.4(6)	C(5)–C(6)–S(7)	110.5(5)
C(6)–S(7)–C(8)	99.4(3)	S(7)–C(8)–C(9)	112.1(5)
C(8)–C(9)–C(10)	122.2(6)		

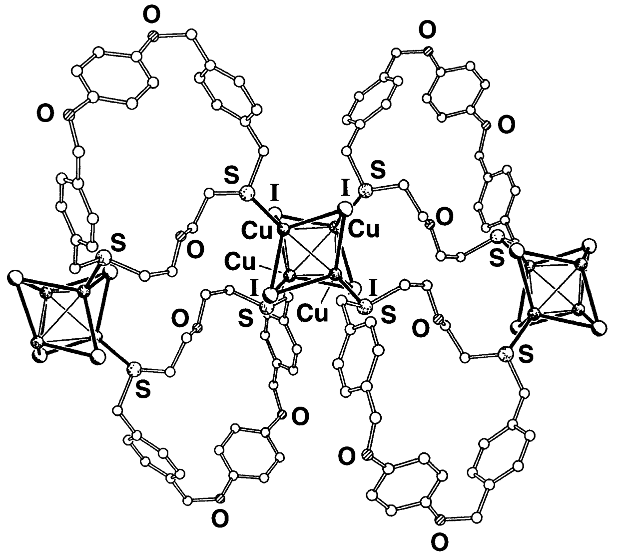

Fig. 3 Part of the array formed by the complex $[Cu_2I_2(L)]\cdot 1.25MeCN$

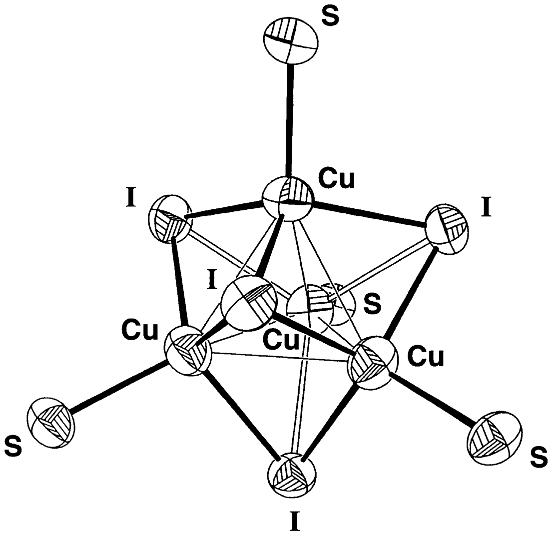

Fig. 4 The cubane-like core of $[Cu_2I_2(L)]\cdot 1.25MeCN$ (50% probability ellipsoids)

The copper iodide complex of L, which was formed by stirring the macrocycle and copper iodide in MeCN at room temperature, unexpectedly yielded the 2:1 CuI:L complex although the reactants were mixed in a 1:1 ratio. This outcome is possibly a consequence of the low σ-donor ability of thioethers[8] (*i.e.* they will not displace anions from the coordination sphere of a metal), coupled with the propensity of copper halide complexes to form aggregate structures.[9] The complex $[Cu_2I_2(L)]$ is readily isolable as an air-stable, white solid. It should be noted that the analogous procedure, employing 2 equivalents of copper iodide and 1 equivalent of L, yielded a compound which gave NMR and mass spectra identical to those obtained for the product of the 1:1 reaction.

The crystal structure shows (Figs. 3 and 4 and Table 2) the complex to contain two copper atoms, two iodine atoms and one dithia macrocycle in the asymmetric unit. The geometry of the macrocycle, although adopting an open conformation, still differs markedly from those observed for the two crystallographically independent uncomplexed forms. The *p*-xylyl rings are inclined by 80 and 84° to the mean plane of the macrocycle and the hydroquinone ring is inclined by 70°. The overall length and breadth of the cavity are 7.4 and 7.9 Å for the oxygen–hydroquinone and xylyl–xylyl spacings, respectively. The macrocycle is bound *via* one of the S atoms to one of the Cu centres [Cu(1)–S(1) 2.304(2) Å], whilst the other S atom, S(7), of a symmetry-related macrocycle, co-ordinates to the other independent Cu centre [Cu(2)–S(7) 2.306(2) Å]. In addition to being co-ordinated to a sulfur atom of a macrocycle, each pair of Cu atoms is bridged by two iodine atoms. The Cu–I distances are in the range 2.676–2.720 Å. The co-ordination geometry of each Cu centre is tetrahedral, the fourth co-ordination site being occupied by a symmetry-related iodine atom. Each I centre is, in turn, bound to three Cu atoms, producing a cubane-like core comprising interpenetrating tetrahedra of Cu and I atoms. Each cubane-like core is bridged *via* the S atoms of two macrocycles to form a polymeric chain that extends in the crystallographic *c* direction, the macrocycles being in an approximately tetrahedral geometry about each cubane centre.

Experimental

Materials and methods

All solvents were dried and degassed prior to use and all reactions were carried out under a nitrogen atmosphere. All starting materials were purchased from the Aldrich Chemical Company and used as received, with the exception of copper iodide, which was purchased from the Fluka Chemical Company. Proton and $^{13}C-\{^1H\}$ NMR spectra were run on a Bruker AC300 spectrometer and referenced to $SiMe_4$, ^{13}C NMR spectra were not obtained for the metal complex owing to its poor solubility in suitable solvents.

Preparations

1,4-Bis[(4-bromomethylphenyl)methoxy]benzene, 1. A solution of hydroquinone (11.5 g, 104 mmol) in dry MeCN (500 cm^3) was added over 24 h to a refluxing suspension of 1,4-bis(bromomethyl)benzene (83.0 g, 314 mmol) and K_2CO_3 (62.5 g, 630 mmol) in dry MeCN (900 cm^3) and dry thf (1.25 dm^3) under nitrogen with vigorous stirring. The reaction mixture was maintained under reflux for an additional 24 h and then it was cooled down to room temperature and concentrated *in vacuo*. The resulting solid was recrystallised three times from MeCN to yield 1,4-bis[(4-bromomethylphenyl)-methoxy]benzene as a white solid (20.2 g, 40%), m.p. 146–147.5 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.42 (8 H, s, $2 \times CH_2C_6H_4CH_2$), 6.90 (4 H, s, OC_6H_4O), 5.02 (4 H, s, 2 × aromatic CH_2O), 4.49 (4 H, s, 2 × aromatic CH_2Br). $^{13}C-\{^1H\}$ NMR (75.1 MHz, $CDCl_3$, 25 °C): δ 153.0, 137.2, 137.1, 129.0, 127.5, 115.7 (aromatic), 70.1 (CH_2O), 32.9 (CH_2Br). EI mass spectrum: *m*/*z* 474 (M^+).

1,11,21-Trioxa-8,14-dithia[2,9,2]paracyclophane, L. Caesium carbonate (32.26 g, 99.0 mmol) was stirred as a suspension in dmf (1500 cm^3) at 60 °C under N_2. A solution of the dibromide **1** (15.73 g, 33.0 mmol) and 2,2′-oxydiethanethiol (4.56 g, 33.0 mmol) in dmf (800 cm^3) was added dropwise to this mixture over a period of 4 d. Upon completion of addition, the dmf was removed *in vacuo* and the pale orange residue extracted with CH_2Cl_2 (300 cm^3) and filtered. The filtrate was washed with aqueous 0.1 mol dm^{-3} NaOH (200 cm^3) and deionised H_2O (2 × 200 cm^3) and then dried ($MgSO_4$). The CH_2Cl_2 was removed *in vacuo* to give an off-white solid which was recrystallised from acetone to give L as a feathery white precipitate (9.10 g, 61%), m.p. 102–103.5 °C. Crystals suitable for X-ray analysis were grown by the concentration of a MeCN solution of the macrocycle. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.18 (8 H, dd, $2 \times CH_2C_6H_4CH_2$), 6.67 (4 H, s, OC_6H_4O), 5.13 (4 H, s, 2 × aromatic CH_2O), 3.68 (4 H, s, 2 × aromatic CH_2S), 3.32 (4 H, t, $2 \times SCH_2CH_2O$), 2.41 (4 H, t, $2 \times SCH_2CH_2O$). $^{13}C-\{^1H\}$ NMR (75.1 MHz, $CDCl_3$, 25 °C): δ 152.2, 137.4, 136.6, 129.1, 126.9, 116.6 (aromatic), 70.1, 70.0 (CH_2O), 36.0 (aromatic CH_2S), 30.0 (SCH_2CH_2O). FAB mass spectrum: *m*/*z* 452 (M^+).

$[Cu_2I_2(L)]\cdot1.25MeCN$. The macrocycle L (0.095 g, 0.210 mmol) was dissolved in MeCN (30 cm^3) at room temperature. Copper(I) iodide (0.040 g, 0.210 mmol) was added as a solid and the solution stirred for 10 h. The CuI is sparingly soluble in MeCN but goes into solution as complexation occurs. The solution was concentrated to 10 cm^3 and Et_2O (25 cm^3) was added to precipitate the metal complex. The precipitate was filtered off and collected. The filtrate was stored at 5 °C overnight, resulting in further precipitation of the complex. The precipitates were combined and dried *in vacuo*. Yield: 0.091 g, 53%. The filtrates were combined, the solvent removed and the white residue dried *in vacuo* to give *ca.* 1 equivalent of L (0.044 g, 47%). Crystals of $[Cu_2I_2(L)]\cdot1.25MeCN$, suitable for X-ray analysis, were obtained by slow diffusion of Et_2O into a MeCN solution of the complex. ^1H NMR (300 MHz, CD_3CN, 25 °C): δ 7.22 (8 H, s, $2 \times CH_2C_6H_4CH_2$), 6.74 (4 H, s, OC_6H_4O), 5.13 (4 H, s, 2 × aromatic CH_2O), 3.71 (4 H, s, 2 × aromatic CH_2S), 3.48 (4 H, t, $2 \times SCH_2CH_2O$), 2.52 (4 H, t, $2 \times SCH_2CH_2O$). FAB mass spectrum: *m*/*z* 452 (L), 515 (L + Cu).

Crystallographic analyses

Crystal data for L and $[Cu_2I_2(L)]\cdot1.25MeCN$ and a summary of the crystallographic analyses are given in Table 3. The data were collected on a Siemens P4 diffractometer using ω scans and graphite-monochromated Mo-Kα radiation. The data were corrected for Lorentz and polarisation factors and, in the case of $[Cu_2I_2(L)]\cdot1.25MeCN$, for absorption (empirical). Both structures were solved by direct methods and all their non-hydrogen atoms refined anisotropically with the exception of the disordered solvent in $[Cu_2I_2(L)]\cdot1.25MeCN$ which was refined partially anisotropically and partially isotropically. The positions of all the hydrogen atoms were idealised, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbon atoms. Refinements were by full-matrix least squares based on *F*, and the polarity of L was determined by a η refinement. This parameter refined to a value of 1.2(6). Computations were carried out on 486 PCs using the SHELXTL PC system.[10]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instruction for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/436.

Acknowledgements

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Table 3 Crystallographic data for L and for $[Cu_2I_2(L)]\cdot 1.25MeCN$

Compound	L	$[Cu_2I_2(L)]\cdot 1.25MeCN$
Formula	$C_{26}H_{28}O_3S_2$	$C_{26}H_{28}Cu_2I_2O_3S_2\cdot C_{2.5}H_{3.75}N_{1.25}$
M	452.6	884.8
Colour, habit	Clear blocks	Pale yellow needles
Crystal size/mm	0.37 × 0.37 × 0.23	0.17 × 0.17 × 0.40
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$C2/c$
a/Å	11.654(2)	27.177(3)
b/Å	10.098(2)	12.381(2)
c/Å	20.278(2)	19.964(3)
β/°	90.27(2)	93.67(2)
U/Å^3	2386.4(4)	6704(1)
2θ Range/°	7.0–50.0	7.0–45.0
ρ (calc.)/g cm^{-3}	1.260	1.753
Z	4[a]	8
T/ °C	20	20
μ/cm^{-1}	2.48	32.64
λ/Å	0.710 73	0.710 73
F(000)	960	3452
hkl Ranges	0–13, 0–12, −24 to 24	0–32, 0–14, −23 to 23
Reflections collected	4684	6047
Independent reflections	4457 (R_{int} = 0.0627)	5910 (R_{int} = 0.0276)
Observed reflections	3135 ($F > 4.0\sigma\|F\|$)	3977 ($F > 4.0\sigma\|F\|$)
Parameters refined	560	335
Maximum, minimum residual electron density/e Å^{-3}	+0.57, −0.22	+0.56, −0.39
R[b]	0.0484	0.0318
R'[c]	0.0497	0.0334

[a] There are two crystallographically independent molecules in the asymmetric unit. [b] $R = \Sigma|F_o - F_c|/\Sigma|F_o|$. [c] $R' = \Sigma(|F_o - F_c|w^{\frac{1}{2}})/\Sigma(|F_o|w^{\frac{1}{2}})$; $w^{-1} = [\sigma^2(F_o) + 0.0007(F_o^{\,2})]$.

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