Dinucleating Macrocyclic Schiff Bases derived from Thiophene and Their Metal Complexes: The Crystal Structures † of a Free Macrocycle and of a Disilver Complex

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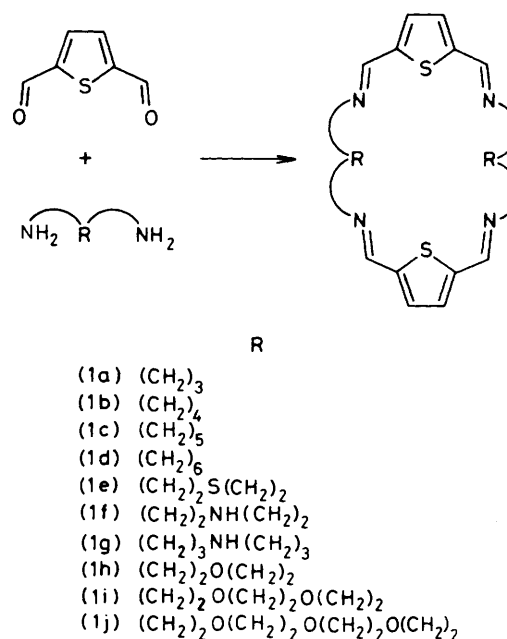*ICI Ltd., Pharmaceuticals Division, Mereside, Alderley Park, Macclesfield, Cheshire SK10 4TG*

Dinucleating macrocyclic Schiff bases derived from the condensation of thiophene-2,5-dicarbaldehyde and a number of α,ω-alkanediamines are reported together with their barium and silver complexes. The crystal structure of the macrocycle derived from 3-oxapentane-1,5-diamine, 6,19-dioxa-27,28-dithia-3,9,16,22-tetra-azatricyclo[22.2.1.1 [11,14]]-octacosa-2,9,11,13,15,22,24,26-octaene, has been determined. Crystals are orthorhombic of space group $P2_12_12_1$, with $a = 25.820(13)$, $b = 14.275(6)$, $c = 5.938(2)$ Å, and $Z = 4$. 1 629 Independent reflections with $I/\sigma(I) > 3.0$ gave $R = 0.0442$. The crystal structure of the dinuclear silver complex of the macrocycle derived from 3,6-dioxaoctane-1,8-diamine, [6,9,22,25-tetraoxa-33,34-dithia-3,12,19,28-tetra-azatricyclo[28.2.1.1 [14,17]]tetratriaconta-2,12,14,16,18,28,30,32-octaene-N^3N^{12} : $N^{19}N^{28}$]-bis[aquaperchloratosilver(i)], has also been determined. Crystals are monoclinic of space group $C2/c$, with $a = 27.941(16)$, $b = 8.612(6)$, $c = 15.359(9)$ Å, $\beta = 102.92(5)°$, and $Z = 4$. 855 Independent reflections with $I/\sigma(I) > 2.0$ gave $R = 0.1227$. In the latter structure the silver atoms are strongly co-ordinated by a pair of imine nitrogen atoms (2.27 and 2.17 Å) and by a water molecule (2.72 Å).

Macrocyclic tetraimine ligands derived from the cyclic (2 + 2) condensation of pyridine-2,6-dicarbaldehyde, or furan-2,5-dicarbaldehyde, with a range of α,ω-alkanediamines have generally been synthesised from their metal complexes using template methods involving Group 1A, 2A, or Main Group metal ions.[1] We report here the synthesis of free macrocyclic ligands generated from thiophene-2,5-dicarbaldehyde and α,ω-alkanediamines in the absence of metal ions. The synthesis and properties of barium and silver complexes of the macrocycles are also described together with the crystal structures of 6,19-dioxa-27,28-dithia-3,9,16,22-tetra-azatricyclo-[22.2.1.1 [11,14]]octacosa-2,9,11,13,15,22,24,26-octaene and [6,9,22,25-tetraoxa-33,34-dithia-3,12,19,28-tetra-azatricyclo-[28.2.1.1 [14,17]]tetratriaconta-2,12,14,16,18,28,30,32-octaene-N^3N^{12} : $N^{19}N^{28}$]-bis[aquaperchloratosilver(i)]. A preliminary account of this work has been published.[2]

Results and Discussion

The Free Macrocycles.—In 1939 Steinkopf *et al.*[3] reported the preparation of Schiff-base macrocycles derived from 3,4-dibromothiophene-2,5-dicarbaldehyde and some primary diamines (*e.g.* 1,2-diaminoethane, 1,2-diaminobenzene, 2,2′-diaminobiphenyl, and 4,4′-diaminobiphenyl). The products were highly coloured and high-melting amorphous solids insoluble in most solvents. The assignment of (2 + 2) macrocyclic structures to these compounds has been questioned by Meth-Cohn[4] who has suggested that the properties of the products are more consistent with polymers than with discrete molecular species.

When equimolar quantities of thiophene-2,5-dicarbaldehyde (tdc) and an α,ω-primary diamine are allowed to react in

	R
(1a)	$(CH_2)_3$
(1b)	$(CH_2)_4$
(1c)	$(CH_2)_5$
(1d)	$(CH_2)_6$
(1e)	$(CH_2)_2S(CH_2)_2$
(1f)	$(CH_2)_2NH(CH_2)_2$
(1g)	$(CH_2)_3NH(CH_2)_3$
(1h)	$(CH_2)_2O(CH_2)_2$
(1i)	$(CH_2)_2O(CH_2)_2O(CH_2)_2$
(1j)	$(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2$

Scheme 1.

methanol or ethanol, white or pale yellow powders, or crystals, of (2 + 2) macrocycles (1) are obtained (Scheme 1). The products are formed either on stirring the reactants together in methanol at room temperature (r.t.) for *ca.* 2.5 h, or by heating at reflux in ethanol for 0.5 h. The tetraimine macrocycles were characterised by microanalysis, m.s., i.r., and where possible by ^1H n.m.r. spectra. In one case, (1h), an X-ray structure was solved confirming the discrete nature of the compound.

The i.r. spectra of the free macrocycles all exhibit single,

Table 1. Infrared bands (cm^{-1}, KBr discs) for the free macrocycles and mass-spectral parent peaks

Macrocycle	$v(C=N)$	$v(N-H)$	Other bands	P^+
(1a)	1 630		2 920, 2 830, 1 465, 1 450, 1 330, 1 230, 1 208, 1 035, 990, 948, 810, 780, 700	356
(1b)	1 628		2 930, 2 850, 2 820, 1 460, 1 432, 1 330, 1 220, 1 210, 1 045, 995, 955, 815, 780, 700	384
(1c)	1 625		2 910, 2 850, 1 460, 1 335, 1 240, 1 055, 962, 930, 820, 810, 780, 735, 700	412
(1d)	1 628		2 920, 2 850, 1 465, 1 340, 1 320, 1 230, 1 210, 1 020, 938, 820, 778, 730, 700	440
(1h)	1 638		2 880, 2 855, 1 470, 1 450, 1 438, 1 340, 1 242, 1 225, 1 135, 1 060, 915, 830, 815, 792, 705	416
(1i)	1 633		2 860br, 1 470, 1 450, 1 330, 1 300, 1 238, 1 220, 1 125, 1 095, 1 045, 1 070, 930, 820, 780, 700	504
(1j)	1 637		2 870br, 1 470, 1 450, 1 335, 1 250, 1 200, 1 120, 1 080, 1 000, 940, 850, 770, 700	592
(1e)	1 630		2 910, 2 860, 2 825, 1 465, 1 430, 1 328, 1 230, 1 212, 1 030, 1 020, 940, 928, 822, 770, 720, 695	448
(1f)	1 635	3 270	2 925, 2 860, 2 810, 1 430, 1 345, 1 330, 1 225, 1 200, 1 178, 1 162, 1 055, 930, 915, 892, 880, 805, 772, 682	414
(1g)	1 632	3 250	2 935, 2 920, 2 840, 1 458, 1 434, 1 345, 1 234, 1 185, 1 150, 1 119, 1 092, 1 055, 890, 832, 745	470

**Table 2.** Proton n.m.r. spectral data for the free macrocycles [a]

Macrocycle	Chemical shift/p.p.m. relative to internal SiMe₄		
	(thiophene)	(CH=N)	CH₂
(1c) [b]	7.18 (s)	8.28 (s)	3.58 (s, NCH₂), 1.66 (m, (NCH₂CH_2), 1.38 (m, NCH₂CH₂CH_2)
(1d) [b]	7.23 (s)	8.30 (s)	3.54 (s, NCH₂), 1.65 (m, NCH₂CH_2), 1.39 (m, NCH₂CH₂CH_2)
(1h)	7.12 (s)	8.22 (s)	3.67 (s)
(1i)	7.23 (s)	8.29 (s)	3.71 (s, NCH₂), 3.57 (s, OCH₂)
(1j)	7.24 (s)	8.29 (s)	3.74 (s, NCH₂CH₂O), 3.58 (s, OCH₂CH₂O)
(1e) [c]	7.22 (s)	8.28 (s)	3.79 (t, NCH₂), 2.89 (t, SCH₂)
(1f) (1g) } See discussion			

[a] Solvent = CDCl₃ unless stated otherwise. [b] Solvent = CDCl₃–Me₂SO. [c] 400 MHz Proton n.m.r. spectrum.

(2)

(3)

(4)

sharp absorptions in the region 1 625—1 640 cm^{-1} which are attributed to the imine bond $v(C=N)$; no bands could be found between 1 650 and 1 700 or 3 300 and 3 500 cm^{-1} attributable to free carbonyl and free amine bands respectively. The single band at 3 270 of (1f) and at 3 250 cm^{-1} of (1g) is assigned to the secondary amine stretch. Thiophene ring absorptions occur in the region 700—900 cm^{-1} for all the macrocycles and differences in the lateral diamine-derived chains give rise to the characteristic absorptions of, for example, the C–O or C–N stretching vibrations at ca. 1 100 cm^{-1}.

The ^{1}H n.m.r. spectra of the soluble tetraimine macrocycles all show a singlet at ca. 8.3 p.p.m. corresponding to the four equivalent carboximine protons, and a further singlet at ca. 7.2 p.p.m. assigned to the thiophene ring protons; no signal is detected for the free carbaldehyde proton. This information together with the i.r. data and the observation that for each product the highest peak in the m.s. corresponds to the (2 + 2) macrocycle led to the assignment of the structures. The spectral data are summarised in Tables 1 and 2.
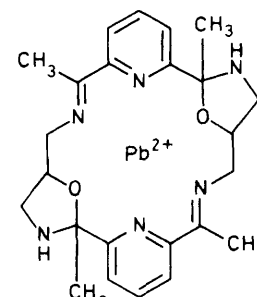
The macrocycles (1f) and (1g) have more complicated n.m.r. spectra which indicate the presence of more than one solution species. For example, the spectrum of (1f) is comprised of a
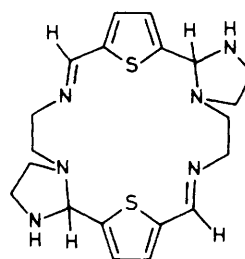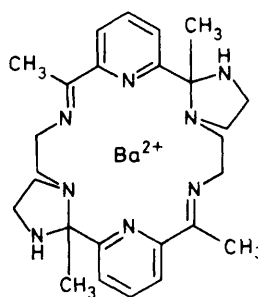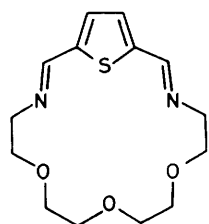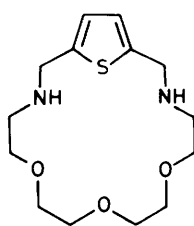
set of signals corresponding to the tetraimine macrocycle (8.26, 7.15, 3.82, and 2.93 p.p.m.) and a further set corresponding to the macrocycle (2) in which a ring contraction has occurred to give imidazolidine rings (8.34, 7.11, 7.06, 4.45, and 2.5—3.5 p.p.m.). There is also a broad band at 4.20 p.p.m. which slowly disappears on shaking with D₂O and so is assigned to the NH protons in each structure.

The second isomer is the result of nucleophilic addition of the two secondary amine groups of the tetraimine macrocycle across the adjacent imine bonds. Similar processes have been reported to produce imidazolidines in the formation of a barium complex, (3), of a pyridine-containing analogue,[5] and oxazolidine rings in the preparation of a lead(II) derivative, (4), from 2,6-diacetylpyridine and 1,3-diamino-2-propanol.[6] The ^{1}H n.m.r. of compound (1g) is similar to that of (1f) and so it is probable that a similar situation pertains in this case.
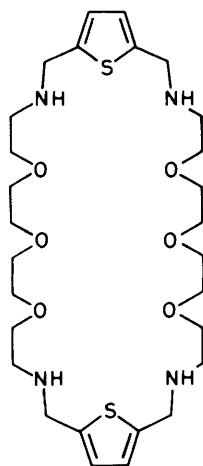
The Metal Complexes.—Silver complexes of the (2 + 2) macrocycles derived from the facultative primary diamines

(5)

Figure 1. Schematic representation of the proposed structure for 2 (5)·AgClO₄

(6)

(7)

M	R
(a) Ag^1	H
(b) Ag^1	Me
(c) Cu^1	H

Figure 2. Binuclear complexes of an acyclic Schiff base

(1e)—(1j) were prepared both from template procedures and from the free macrocycles. The complexes were characterised by their analyses, i.r. spectra, and where possible by their m.s. and ^{1}H n.m.r. spectra. The X-ray structure of (1i)· 2AgClO₄·2H₂O was solved and confirmed the binucleating capability of the macrocycles.

The i.r. spectra of the metal complexes show strong absorptions at ca. 1 620 cm⁻¹ attributable to the imine v(C=N) but no bands for the free carbonyls or primary di-amines. For each complex there is a slight lowering (5—10 cm⁻¹) of the v(C=N) relative to the free macrocycle. The spectra of compounds (1f) and (1g) show single sharp absorptions at ca. 3 300 cm⁻¹ which are assigned to the secondary amine NH stretching vibration. For the perchlorato-complexes the bands at ca. 1 100 and 625 cm⁻¹ are largely unsplit indicating that these are most probably due to ionic and so tetrahedral ClO₄⁻.[7] Mass spectra were obtained only for the silver complexes of (1h), (1i), and (1j). The remainder proved too involatile for spectra to be recorded. The spectra gave highest-molecular-weight peaks corresponding to the free macrocycle in each case. Due to the slight solubility of the complexes a representative ^{1}H n.m.r. spectrum was run in CD₃OD at 400 MHz. The spectrum of (1i)·2AgClO₄·2H₂O showed two singlets, at 8.80 (imine protons) and 7.70 p.p.m. (thiophene ring protons), and two triplets at 3.80 and 3.90 p.p.m. (ethylenic bridge protons).

Interestingly two compounds can be recovered from the reaction of AgNO₃, tdc, and 3,6,9-trioxaundecane-1,11-di-amine. After refluxing overnight in ethanol and filtration into an excess of NaClO₄ in methanol two products are recovered: the first deposits are plate-like crystals of 2 (5)·AgClO₄ and then after removal of these crystals by filtration pale yellow bricks of (1j)·AgClO₄ are deposited. The formulation as (1 + 1) and (2 + 2) complexes can be made on the basis of m.s. as for the other spectral techniques nearly identical results
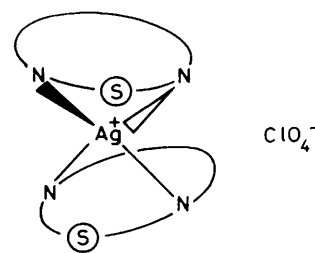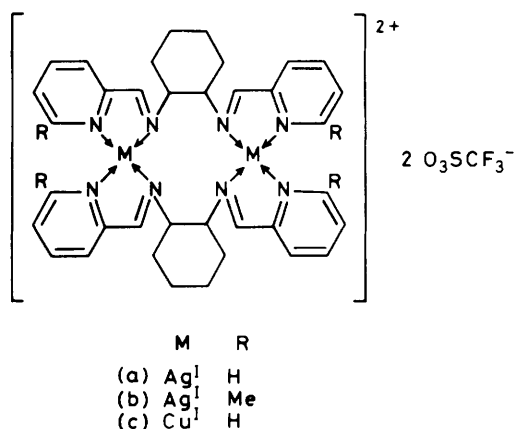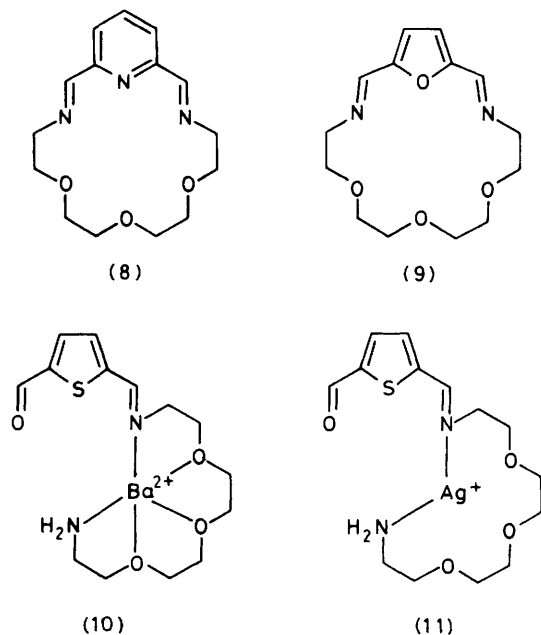
are obtained. The highest-molecular-weight peaks are at 296 and 592 respectively corresponding to the free macrocycles. Further evidence for the two forms is obtained on reduction of the complexes using NaBH₄ where mass spectra corresponding to the fully reduced free macrocycles (6) and (7) are obtained in each case (300 and 600 respectively). The metal-free macrocycles are recovered on reduction together with silver metal, and the detection of v(NH) and the absence of v(C=N) in the i.r. shows that it is these bonds which are reduced and not the thiophene rings.

The i.r. spectrum of 2 (5)·AgClO₄ shows only one sharp peak at 1 628 cm⁻¹ indicating that both of the imine nitrogens of the (1 + 1) macrocycle are bonded to the metal. It is likely that a sandwich complex occurs for this compound in which a tetrahedral or distorted geometry is found for the metal ion (Figure 1). Such a geometry has been found recently for a dimeric binuclear complex of an acyclic Schiff-base ligand (Figure 2).[8] Although there are no comparable examples from macrocyclic Schiff-base chemistry, an analogy can also be made with the cyclic polyether complex 2 (benzo-15-crown-5)*·KI in which a sandwich structure is established by X-ray diffraction analysis.[9]

Binuclear Ba(NCS)₂ complexes of the macrocycles (1f), (1h), and (1i) were prepared using metal template procedures and characterised by their analyses, i.r., and m.s. The reaction of Ba(NCS)₂, tdc, and 3-thiapentane-1,5-diamine gave, in contrast, only the free (2 + 2) macrocycle (1e) and 3,6,9-trioxaundecane-1,11-diamine gave oily solids which eluded characterisation.

The i.r. spectra of the barium complexes show single sharp peaks at ca. 1 620 cm⁻¹ attributed to v(C=N). The complex

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* 2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclo-pentadecine.

Figure 3. The structure of the cation [(1i)·2Ag(H₂O)]²⁺ showing the atom labelling. ⁿ Atoms related to C(1) and C(12) respectively by the C₂ symmetry

(1f)·2Ba(NCS)₂ has a band at 3 245 cm⁻¹ assigned to the secondary amine v(NH), but no bands are detected for free carbonyls or free primary diamines. The thiocyanate v(C=N) absorptions occur in the region 1 990—2 050 cm⁻¹ associated with terminally N-bonded thiocyanates.[10] All the complexes show peaks corresponding to the free (2 + 2) macrocycles as the highest-molecular-weight peak. The ¹H n.m.r. spectrum of (1h)·2Ba(NCS)₂, run in CD₃OD, shows singlets at 8.25 (imine protons), 7.16 (thiophene ring protons), and 3.68 p.p.m. (ethylenic bridge protons).

It has not been possible to grow crystals of the barium complexes which are suitable for structure determination. Consequently the precise nature of the metal co-ordination and the origin of the two thiocyanate bands in the i.r. remain obscure. It is probable that the co-ordination environment is dominated by the terminal heterocyclic di-imine units, with further co-ordination from the side-chain donor atoms. The presence of two v(C−N) bands also suggests different environments for the thiocyanate anions.

The reaction of tdc and 3,6,9-trioxaundecane-1,11-diamine in the presence of Ba(NCS)₂ gave only intractable oily solids. It is not immediately obvious why this diamine did not condense to give isolable products, either (2 + 2) as with the smaller diamines or (1 + 1) as with this diamine and furan-2,5-dicarbaldehyde [11] or pyridine-2,6-dicarbaldehyde,[12] (8) and (9), especially as 2 (5)·AgClO₄ was readily available. A possible explanation can be found by considering the intermediate steps in the formation of the putative complex. Assuming that the barium ions complex most strongly with the diaminoether chain and that the thiophene sulphur atom does not co-ordinate [as expected from hard–soft acid–base theory and by analogy with the known structure of (1i)·2AgClO₄·2H₂O] then a 'half-macrocyclic' intermediate (10) can be envisaged.[13] Intramolecular imine formation would lead to the (1 + 1) macrocycle but would involve considerable reorganisation of the diamine chain; in the furan-derived analogue where the furan oxygen atom also complexes the barium [14] the position of the metal would sufficiently alter the conformation to facilitate ring closure by bringing the secondary amine unit into close proximity with the aldehyde unit. In structure (11) the interaction of the silver cation would be with the nitrogen donors and so also give an increased
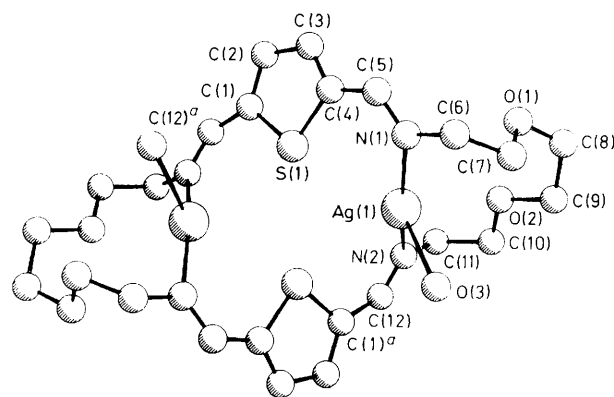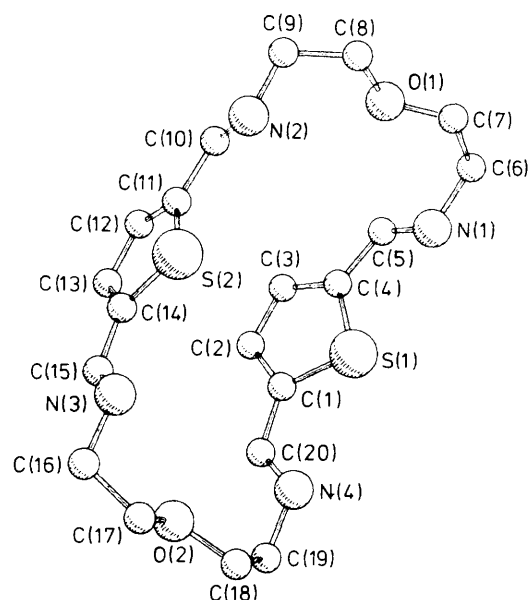
Figure 4. The molecular structure and atom labelling of the macrocycle (1h)

freedom to the ethyleneoxy-chain allowing the amine to move closer to the aldehyde. Similar processes could also inhibit (2 + 2) formation via intermolecular condensations.

The reluctance of sulphur atoms to co-ordinate with Ba²⁺ is advanced as a reason for the formation of free (1e) rather than its barium complex in the attempted template reaction. An alternative explanation may arise from the relative solubilities of (1e) and any barium complexes that might exist in solution. The free ligand is quite insoluble in the reaction solvents and so could precipitate preferentially from them.

The Crystal Structures of (1h) and (1i)·2AgClO₄·2H₂O.— The structures of the silver complex and of the macrocycle are illustrated in Figures 3 and 4 respectively, in each case with the atom labelling used in the corresponding Tables. Bond lengths and angles (together with estimated standard deviations) and details of planar fragments are given in Tables 3—6.

The structure of the disilver complex cation possesses crystallographically imposed C₂ symmetry and has a twisted-loop configuration for the macrocycle. The two symmetry-

Table 3. Bond lengths (Å) and angles (°) with estimated standard deviations for (1i)·2AgClO₄·2H₂O

Ag(1) · · · S(1)	3.100(13)	S(1)–C(4)	1.77(5)	N(1)–C(6)	1.40(7)	C(10)–C(11)	1.55(8)
Ag(1) · · · S(1) ᵃ	3.188(13)	C(1)–C(12) ᵃ	1.40(6)	C(6)–C(7)	1.53(8)	N(2)–C(11)	1.42(7)
Ag(1) · · · O(1)	3.55(4)	C(1)–C(2)	1.38(7)	O(1)–C(7)	1.43(7)	N(2)–C(12)	1.25(6)
Ag(1)–O(2)	2.92(3)	C(2)–C(3)	1.42(7)	O(1)–C(8)	1.43(7)	Cl–O (all)	1.38
Ag(1)–O(3)	2.72(7)	C(3)–C(4)	1.36(7)	C(8)–C(9)	1.53(8)	O(3) · · · O(4)	3.04(14)
Ag(1)–N(1)	2.27(4)	C(4)–C(5)	1.38(7)	O(2)–C(9)	1.46(7)	O(3) · · · O(6) ᵇ	2.81(14)
Ag(1)–N(2)	2.17(4)	N(1)–C(5)	1.27(6)	O(2)–C(10)	1.35(6)	O(3) · · · O(8)	3.07(8)
S(1)–C(1)	1.80(4)						

S(1)–Ag(1)–S(1) ᵃ	66.3(3)	Ag(1)–O(3) · · · O(6) ᵇ	128(4)	Ag(1)–N(1)–C(6)	115(3)
S(1)–Ag(1)–O(2)	133.7(7)	Ag(1)–O(3) · · · O(8)	93(2)	C(5)–N(1)–C(6)	122(4)
S(1)–Ag(1)–O(3)	127.9(15)	O(4) · · · O(3) · · · O(8)	134(3)	N(1)–C(6)–C(7)	118(5)
S(1)–Ag(1)–N(1)	71.3(11)	O(6) ᵇ · · · O(3) · · · O(8)	135(4)	O(1)–C(7)–C(6)	104(4)
S(1)–Ag(1)–N(2)	106.9(10)	C(1)–S(1)–C(4)	94(2)	C(7)–O(1)–C(8)	107(4)
S(1) ᵃ–Ag(1)–O(2)	136.2(7)	S(1)–C(1)–C(2)	107(3)	O(1)–C(8)–C(9)	117(5)
S(1) ᵃ–Ag(1)–O(3)	82.5(15)	S(1)–C(1)–C(12) ᵃ	118(3)	O(2)–C(9)–C(8)	108(4)
S(1) ᵃ–Ag(1)–N(1)	121.2(11)	C(2)–C(1)–C(12) ᵃ	135(4)	C(9)–O(2)–C(10)	113(4)
S(1) ᵃ–Ag(1)–N(2)	70.4(10)	C(1)–C(2)–C(3)	115(4)	O(2)–C(10)–C(11)	110(4)
O(2)–Ag(1)–O(3)	97.9(16)	C(2)–C(3)–C(4)	117(5)	N(2)–C(11)–C(10)	104(4)
O(2)–Ag(1)–N(1)	102.6(12)	S(1)–C(4)–C(3)	107(4)	Ag(1)–N(2)–C(11)	121(3)
O(2)–Ag(1)–N(2)	66.3(12)	S(1)–C(4)–C(5)	125(4)	Ag(1)–N(2)–C(12)	124(3)
O(3)–Ag(1)–N(1)	93.7(18)	C(3)–C(4)–C(5)	128(5)	C(11)–N(2)–C(12)	115(4)
O(3)–Ag(1)–N(2)	99.7(18)	N(1)–C(5)–C(4)	127(5)	N(2)–C(12)–C(1) ᵃ	132(4)
N(1)–Ag(1)–N(2)	163.5(15)	Ag(1)–N(1)–C(5)	121(3)	O–Cl–O (all)	109.5
Ag(1)–O(3) · · · O(4)	106(3)				

ᵃ At −x, y, ½ − z. ᵇ At ½ − x, ½ − y, 1 − z.

Table 4. Bond lengths (Å) and angles (°) with estimated standard deviations for the macrocycle (1h)

S(1)–C(1)	1.730(6)	S(2)–C(11)	1.731(6)	C(6)–C(7)	1.535(9)	C(16)–C(17)	1.467(10)
S(1)–C(4)	1.732(6)	S(2)–C(14)	1.737(6)	O(1)–C(7)	1.408(8)	O(2)–C(17)	1.376(9)
C(1)–C(2)	1.350(8)	C(11)–C(12)	1.351(9)	O(1)–C(8)	1.420(8)	O(2)–C(18)	1.465(9)
C(2)–C(3)	1.416(8)	C(12)–C(13)	1.419(10)	C(8)–C(9)	1.503(10)	C(18)–C(19)	1.508(10)
C(3)–C(4)	1.353(8)	C(13)–C(14)	1.355(10)	N(2)–C(9)	1.456(9)	N(4)–C(19)	1.483(8)
C(4)–C(5)	1.442(8)	C(14)–C(15)	1.439(9)	N(2)–C(10)	1.264(8)	N(4)–C(20)	1.255(8)
N(1)–C(5)	1.267(8)	N(3)–C(15)	1.245(8)	C(10)–C(11)	1.444(9)	C(1)–C(20)	1.461(8)
N(1)–C(6)	1.480(8)	N(3)–C(16)	1.466(9)				

C(1)–S(1)–C(4)	90.9(3)	C(11)–S(2)–C(14)	90.4(3)	N(1)–C(5)–C(4)	122.4(5)	N(3)–C(15)–C(14)	124.0(6)
S(1)–C(1)–C(20)	121.5(4)	S(2)–C(11)–C(10)	121.4(5)	C(5)–N(1)–C(6)	115.8(5)	C(15)–N(3)–C(16)	116.8(6)
S(1)–C(1)–C(2)	111.7(4)	S(2)–C(11)–C(12)	112.8(5)	N(1)–C(6)–C(7)	109.0(5)	N(3)–C(16)–C(17)	111.1(6)
C(20)–C(1)–C(2)	126.9(5)	C(10)–C(11)–C(12)	125.7(6)	O(1)–C(7)–C(6)	107.5(5)	O(2)–C(17)–C(16)	108.6(6)
C(1)–C(2)–C(3)	113.0(5)	C(11)–C(12)–C(13)	111.7(6)	C(7)–O(1)–C(8)	112.3(5)	C(17)–O(2)–C(18)	111.3(5)
C(2)–C(3)–C(4)	112.8(5)	C(12)–C(13)–C(14)	113.6(6)	O(1)–C(8)–C(9)	106.5(5)	O(2)–C(18)–C(19)	106.0(6)
S(1)–C(4)–C(3)	111.6(4)	S(2)–C(14)–C(13)	111.4(5)	N(2)–C(9)–C(8)	111.0(6)	N(4)–C(19)–C(18)	108.9(5)
S(1)–C(4)–C(5)	121.5(4)	S(2)–C(14)–C(15)	120.8(5)	C(9)–N(2)–C(10)	117.3(6)	C(19)–N(4)–C(20)	117.0(5)
C(3)–C(4)–C(5)	126.9(5)	C(13)–C(14)–C(15)	127.8(6)	N(2)–C(10)–C(11)	124.5(6)	N(4)–C(20)–C(1)	121.8(5)

related silver ions are accommodated at opposite ends of the macrocycle, each being co-ordinated most strongly by a pair of imine nitrogen atoms at very short Ag–N distances (2.27 and 2.17 Å) and by a water molecule (Ag–O 2.72 Å). Longer contacts to one of the ether oxygen atoms and to the two symmetry-related sulphur atoms of the thiophene fragments give rise to a co-ordination number between 3 and 6: the remaining ether oxygen atom is distant and pointing away from the metal. The empty site opposite to the co-ordinated water ligand is blocked (at 3.08 Å) by a hydrogen atom [H(2)] of a centrosymmetrically related cation. The co-ordinated water forms hydrogen bonds to two perchlorate anions: to one near the inversion centre (one to each disorder component) which therefore bridges two cations related by that inversion symmetry, and to a second disordered across the same C₂ axis that passes through the cation. The disorder model for this latter perchlorate shows it to be hydrogen bonded to one or the other water ligand but not in bridging mode. The limited precision of this crystal structure precludes any discussion of bond lengths within the macrocycle but the thiophene frag-

ment is planar and the torsion angles seem unexceptional.

The free macrocycle (1h) possesses approximate Cₛ symmetry through the two sulphur atoms and perpendicular to the thiophene rings; these latter are each planar and, although not parallel (24.7°), are aligned and approximately eclipsed with the minimum separations of 3.49 Å [C(2) to C(13) and C(3) to C(12)]. Bond lengths and angles and torsion angles within the macrocycle are generally unexceptional. Substantial changes in this conformation will be necessary to allow the co-ordination of a metal ion in, for example, the silver complex of (1h). There are no significant intermolecular contacts in the crystal structure of (1h).

Silver complexes of macrocyclic Schiff-base ligands derived from pyridine dicarbonyls have been reported by Drew et al.[15,16] These include two complexes which are related to the (2 + 2) thiophene-derived ligands. The 2AgClO₄ complex of the macrocycle arising from a (2 + 2) condensation reaction between 2,6-diacetylpyridine and 3-thiapentane-1,5-diamine has been prepared using the template procedure and the corresponding complex of the (2 + 2) macrocycle from

Table 5. Details of planar fragments of $[(1i)\cdot 2Ag(H_2O)]^{2+}$. Equations of least-squares planes in the form $pX + qY + rZ = d$ where p, q, and r are direction cosines referred to orthogonal crystal axes a, b, c^*. Deviations (Å) of atoms are given in parentheses

	p	q	r	d
Plane A: S(1),C(1)—C(4)			r.m.s. deviation 0.020 Å	
	0.6279	−0.7782	−0.0124	−1.7212

[S(1) 0.009, C(1) 0.005, C(2) −0.021, C(3) 0.030, C(4) −0.023, N(1) 0.352, N(2) ^{a} −0.493, C(5) 0.021, C(12) ^{a} −0.052]

Plane B: O(3),N(1),N(2)				
	0.9512	−0.1087	−0.2889	0.6923

[Ag(1) −0.167, S(1) −2.490, O(2) 2.561]

Plane C: Ag(1),C(5),C(6)				
	0.6059	−0.6139	−0.5059	−1.5435

[N(1) −0.122]

Plane D: Ag(1),C(11),C(12)				
	−0.7884	−0.4520	−0.4173	−3.4003

[N(2) 0.031]

Selected angles (°) between planes: ^{b} A–A′ 77.8, A–C 30.2, A′–D 32.7, C–D 89.4

Torsion angles (°)

C(5)–N(1)–C(6)–C(7)	−126.4	C(8)–C(9)–O(2)–C(10)	+172.0
N(1)–C(6)–C(7)–O(1)	+56.9	C(9)–O(2)–C(10)–C(11)	+174.4
C(6)–C(7)–O(1)–C(8)	−172.9	O(2)–C(10)–C(11)–N(2)	−73.6
C(7)–O(1)–C(8)–C(9)	+66.3	C(10)–C(11)–N(2)–C(12)	−117.1
O(1)–C(8)–C(9)–O(2)	+45.2		

^{a} At $-x$, y, $\frac{1}{2} - z$. ^{b} A′ is the plane of the C_2 symmetry-related thiophene ring, the orientation of which is related to plane A as: $p' = -p$, $q' = q$, and $r' = -r$.

(a)   (b)
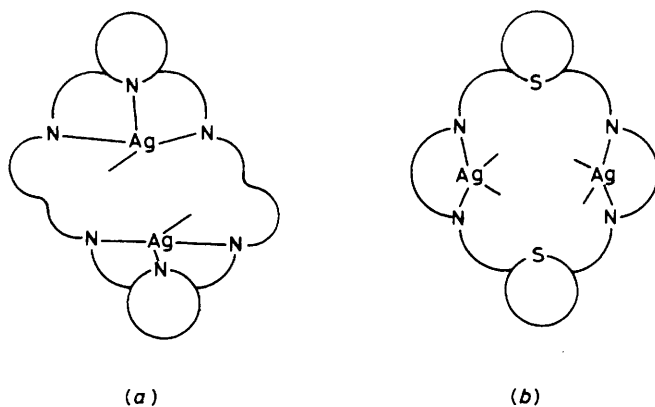
Figure 5. Schematic representations of the modes of disilver bonding in the (2 + 2) macrocycles

2,6-diacetylpyridine and 4-azaheptane-1,7-diamine was also prepared by template procedures and converted into its tetraphenylborate by metathesis. An X-ray crystal structure analysis of the latter complex shows an irregular four-co-ordination around each silver cation which is bound to the pyridine, imine, and secondary amine nitrogen donors as shown schematically in Figure 5(a).[16] A related structure of interest is that of the 2Pb(NCS)$_2$ complex of the (2 + 2) macrocycle derived from 2,6-diacetylpyridine and 1,8-di-amino-3,6-dioxaoctane.[17] The lead atoms are again terminally co-ordinated by the pyridine nitrogens and by one nitrogen and one oxygen from each of the diamine-derived chains. The

Table 6. Details of planar fragments of the macrocycle (1h). Equations of least-squares planes in the form $pX + qY + rZ = d$ where p, q, and r are direction cosines referred to orthogonal crystal axes a, b, c. Deviations (Å) of atoms are given in parentheses

|	p	q	r	d
Plane A: S(1),C(1)—C(4)			r.m.s. deviation 0.002 Å	
	−0.0842	0.9927	−0.0867	4.9379

[S(1) 0.002, C(1) −0.001, C(2) −0.001, C(3) 0.003, C(4) −0.003, C(5) −0.006, C(20) −0.006, S(2) −4.045, C(11) −3.481, C(12) −2.981, C(13) −3.061, C(14) −3.600]

Plane B: S(2),C(11)—C(14)			r.m.s. deviation 0.003 Å	
	−0.0596	0.9398	0.3365	0.7013

[S(2) 0.001, C(11) −0.003, C(12) 0.004, C(13) −0.003, C(14) 0.001, C(10) −0.027, C(15) 0.021, S(1) 4.478, C(1) 3.977, C(2) 3.455, C(3) 3.447, C(4) 3.958]

Angle (°) between planes: A–B 24.7

Torsion angles (°)

C(4)–C(5)–N(1)–C(6)	−176.3	C(14)–C(15)–N(3)–C(16)	+179.2
C(5)–N(1)–C(6)–C(7)	+95.8	C(15)–N(3)–C(16)–C(17)	+117.2
N(1)–C(6)–C(7)–O(1)	−64.5	N(3)–C(16)–C(17)–O(2)	−60.8
C(6)–C(7)–O(1)–C(8)	+176.0	C(16)–C(17)–O(2)–C(18)	+170.4
C(7)–O(1)–C(8)–C(9)	−171.0	C(17)–O(2)–C(18)–C(19)	−176.0
O(1)–C(8)–C(9)–N(2)	+69.5	O(2)–C(18)–C(19)–N(4)	+70.6
C(8)–C(9)–N(2)–C(10)	−128.1	C(18)–C(19)–N(4)–C(20)	−104.7
C(9)–N(2)–C(10)–C(11)	−178.6	C(19)–N(4)–C(20)–C(1)	+178.5

principal difference between these structures and that of the thiophene-derived complex is in the siting of the metal ions. In the latter complex the metals are co-ordinated to the lateral functions of the macrocycle [Figure 5(b)], whereas in the former two structures the metals are held by the terminal functions. This is a consequence of the thiophene imposing a constraint on the environment of the metal because of its poor donor ability.

Experimental

Microanalyses were carried out by the University of Sheffield microanalytical service and are recorded in Table 7. Infrared spectra were recorded for KBr discs in the region 4 000—600 cm^{-1} using a Perkin-Elmer 297 spectrometer. Proton n.m.r. spectra were run using a Perkin-Elmer 220-MHz or a Bruker 400-MHz spectrometer. Mass spectra were recorded using a Kratos MS25 spectrometer.

Thiophene-2,5-dicarbaldehyde was prepared by the method of Chadwick and Wilbe.[18] The diamines were used as supplied.

Preparation of the Free Macrocycles.—The α,ω-diamine (0.001 mol) in ethanol (5 cm^3) was added to a solution of thiophene-2,5-dicarbaldehyde (0.001 mol) in ethanol (15 cm^3) and the mixture refluxed for 0.5 h. The solution was allowed to cool slowly and the products were deposited as white or off-white powders, or pale yellow crystals. Some reduction in solvent volume by rotary evaporation was necessary for the more soluble products. The yields varied from 50 to 90%.

Preparation of the Macrocyclic Disilver Complexes.—The following general method was used. Thiophene-2,5-dicarb-aldehyde (0.01 mol), dissolved in methanol (50 cm^3), and the required diamine (0.01 mol), dissolved in methanol (50 cm^3), were added to a warm solution of silver(I) nitrate (0.01 mol) in methanol (200 cm^3). The mixture was heated at reflux overnight and then filtered hot through Hyflosupercel, to

Table 7. Microanalytical data

	Found (%)				Required (%)			
M.p. (°C)	C	H	N	S	C	H	N	S
(a) Ligands								
(1a) 220 (decomp.)	59.5	5.6	14.8	18.1	60.6	5.7	15.7	18.0
(1b) 202—204	60.1	6.4	13.7	16.6	59.7	6.5	13.9	16.7
(1c) 148—150	64.0	6.6	13.3	16.5	64.1	6.8	13.6	15.5
(1d) 168—170	65.1	7.3	12.5	14.3	65.4	7.3	12.7	14.6
(1e) 219—221	53.2	5.3	12.1	28.6	53.5	5.4	12.5	28.6
(1f) 169—170	57.8	6.2	20.3	16.2	57.9	6.3	20.3	15.5
(1g) 170—173	60.2	7.2	17.1	13.4	61.2	7.3	17.8	13.6
(1h) 214—216	57.3	5.3	14.0	15.2	57.7	5.8	13.5	15.4
(1i) 136—138	57.5	6.2	11.9	12.0	57.1	6.4	11.1	12.7
(1j) 84—86	56.3	6.6	9.1	10.2	56.7	6.8	9.5	10.8
(b) Disilver complexes								
(1e)·2AgClO₄	30.5	3.2	7.2	15.3	27.8	2.8	6.5	14.9
(1f)·2AgClO₄	29.6	3.6	10.9	6.4	29.0	3.2	10.1	10.1
(1g)·2AgClO₄	32.3	3.9	9.7	5.7	32.6	3.9	9.5	7.2
(1h)·2AgClO₄	30.0	2.9	7.4	6.9	28.9	2.9	6.7	7.7
(1i)·2AgBPh₄	63.5	5.2	3.9	3.9	63.6	5.3	4.1	4.7
(1i)·2AgClO₄·2H₂O	30.4	3.7	6.0	6.5	30.2	3.8	5.9	6.7
(1j)·2AgClO₄	33.6	4.6	5.5	5.9	33.4	4.0	5.6	6.4
2 (5)·AgClO₄	41.1	5.2	6.2	7.4	42.0	5.0	7.0	8.0
(c) Dibarium complexes								
(1i)·2Ba(NCS)₂	30.0	2.8	11.6	15.3	30.4	2.6	11.8	20.3
(1j)·2Ba(NCS)₂	33.3	3.6	9.9	14.7	33.2	3.2	11.1	19.0
(1f)·2Ba(NCS)₂	31.2	2.9	14.8	17.1	31.3	2.8	15.2	20.9

Problems with interference in the analyses of some of the samples, and particularly the barium samples, has given poor sulphur analyses in these instances.

remove any deposited silver metal, into a methanolic solution of NaClO₄·H₂O (3 g in 30 cm³). The disilver complexes were deposited on cooling as white crystals or pale yellow powders and were dried *in vacuo* over silica gel.

When this reaction was carried out using 3,6,9-trioxa-undecane-1,11-diamine two products were recovered; on first cooling, white plates of 2 (5)·AgClO₄ were obtained and after their removal by filtration yellow crystals of (1j)·2AgClO₄ were formed overnight.

The complex (1i)·2AgBH₄ was prepared from (1i)·2AgClO₄·2H₂O by metathesis with sodium tetraphenylborate in refluxing methanol.

The complexes could also be prepared by reaction of silver(ı) nitrate with the free ligand in ethanolic solution followed by metathesis with sodium perchlorate.

Preparation of the Macrocyclic Dibarium Complexes.—The following general method was used. The α,ω-diamine (0.001 mol), dissolved in ethanol (5 cm³), was added to a solution of thiophene-2,5-dicarbaldehyde (0.001 mol) and barium thiocyanate (0.001 mol) dissolved in ethanol (25 cm³). The mixture was refluxed for 1 h and off-white solids precipitated on cooling. These were filtered off, washed with ethanol, and dried over silica gel.

Structural Determinations.—*Crystal data for* (1i)·2AgClO₄·2H₂O. C₂₄H₃₆Ag₂Cl₂N₄O₁₄S₂, $M = 955.32$, crystallises from methanol–ethanol as colourless, very fine needles, crystal dimensions $0.51 \times 0.07 \times 0.04$ mm, monoclinic, $a = 27.941(16)$, $b = 8.612(6)$, $c = 15.359(9)$ Å, $\beta = 102.92(5)°$, $U = 3\,602(4)$ Å³, $D_m = 1.78$, $Z = 4$, $D_c = 1.762$ g cm⁻³, space group $C2/c$ (C_{2h}^6, no. 15; confirmed by the analysis), Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 14.02 cm⁻¹, $F(000) = 1\,920$.

Three-dimensional X-ray diffraction data of limited quality and quantity were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet/Syntex R3 diffractometer by the ω-scan method. 855 Independent reflections for which $I/\sigma(I) > 2.0$ were corrected for Lorentz and polarisation effects. The structure was solved, with some difficulty, by Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were placed in calculated positions (C–H 0.97 and O–H 0.93 Å, Ag–O–H 110°); their contributions were included in structure-factor calculations ($B = 10.0$ Å²) but no refinement of positional parameters was permitted. The two perchlorate anions were found to be disordered, one about an inversion centre at (0.25, 0.25, 0.5) and the other about the C_2 axis at (0, y, 0.25). They were each refined with constrained T_d symmetry (Cl–O 1.38 Å), and with group isotropic thermal parameters, in a simple disorder model which adequately accounted for the electron density; although it is probable that disorder is more extensive about these two sites in the lattice, the quality of the data precluded any further elaboration. Refinement converged at R 0.1227 with allowance for anisotropic thermal motion of silver and sulphur and for the anomalous scattering of silver, chlorine, and sulphur. Table 8 lists the atomic positional parameters with estimated standard deviations.

Crystal data for (1h). C₂₀H₂₄N₄O₂S₂, $M = 416.55$, crystallises from methanol as colourless irregular bricks, crystal dimensions $0.70 \times 0.62 \times 0.48$ mm, orthorhombic, $a = 25.820(13)$, $b = 14.275(6)$, $c = 5.938(2)$ Å, $U = 2\,188.7(16)$ Å³, $D_m = 1.26$, $Z = 4$, $D_c = 1.264$ g cm⁻³, space group $P2_12_12_1$ (D_2^4, no. 19), Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 2.54 cm⁻¹, $F(000) = 880$.

The data were collected and processed [1 629 independent reflections with $I/\sigma(I) > 3.0$] as for the silver complex above. A correction for 6.2% crystal-decay during data collection was

Table 8. Atomic positional parameters with estimated standard deviations for (Ii)·2AgClO₄·2H₂O

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Ag(1)	0.088 14(14)	0.177 0(5)	0.217 5(3)	C(9)	0.217 4(20)	0.117(7)	0.171(4)
S(1)	-0.023 5(4)	0.146 3(14)	0.136 5(7)	C(10)	0.185 0(18)	-0.066(6)	0.255(3)
O(1)	0.156 9(13)	0.267(4)	0.056(2)	C(11)	0.137 6(21)	-0.149(8)	0.268(4)
O(2)	0.175 2(11)	0.025(4)	0.182(2)	C(12)	0.102 8(16)	-0.049(6)	0.374(3)
O(3)	0.134 8(24)	0.398(8)	0.332(5)	Cl(1)	0.250(2)	0.250(8)	0.492(5)
N(1)	0.067 2(14)	0.345(5)	0.102(3)	O(4)	0.201(3)	0.221(18)	0.484(9)
N(2)	0.110 1(13)	-0.029(5)	0.298(2)	O(5)	0.260(5)	0.264(17)	0.409(6)
C(1)	-0.074 7(15)	0.034(5)	0.077(3)	O(6)	0.277(5)	0.130(13)	0.538(9)
C(2)	-0.077 9(18)	0.061(6)	-0.013(3)	O(7)	0.263(5)	0.387(11)	0.539(9)
C(3)	-0.040 4(17)	0.158(7)	-0.032(3)	Cl(2)	0.000 0(0)	0.634(2)	0.250(0)
C(4)	-0.008 9(18)	0.223(6)	0.039(3)	O(8)	0.040 9(12)	0.592(5)	0.314(3)
C(5)	0.030 3(15)	0.320(7)	0.038(3)	O(9)	-0.003 4(19)	0.541(5)	0.176(2)
C(6)	0.103 9(20)	0.452(7)	0.094(4)	O(10)	-0.041 5(12)	0.615(6)	0.284(4)
C(7)	0.157 2(21)	0.395(7)	0.116(4)	O(11)	0.004 0(17)	0.787(3)	0.226(3)
C(8)	0.204 2(20)	0.196(7)	0.080(4)				

Atoms Cl(1), O(4)—O(7) and Cl(2), O(8)—O(11) comprise the two disordered perchlorate groups. They were assigned occupancy factors of 0.5 and their estimated standard deviations were derived from the group parameters which were used to refine their positions.

Table 9. Atomic positional parameters with estimated standard deviations for the macrocycle (Ih)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
S(1)	0.359 93(6)	0.408 42(11)	0.126 94(25)	C(7)	0.175 79(23)	0.267 0(5)	0.274 5(13)
S(2)	0.378 19(6)	0.116 09(11)	-0.136 73(27)	C(8)	0.181 40(23)	0.121 9(4)	0.089 4(14)
O(1)	0.187 40(16)	0.220 5(3)	0.071 6(8)	C(9)	0.203 09(24)	0.080 8(5)	-0.123 5(14)
O(2)	0.550 08(16)	0.274 8(3)	0.105 1(9)	C(10)	0.278 36(25)	0.127 8(4)	-0.306 3(11)
N(1)	0.243 59(17)	0.383 4(3)	0.200 3(9)	C(11)	0.333 10(24)	0.141 5(4)	-0.343 5(12)
N(2)	0.259 15(18)	0.091 2(3)	-0.131 3(10)	C(12)	0.354 98(30)	0.173 1(5)	-0.535 8(11)
N(3)	0.495 00(18)	0.120 1(4)	-0.051 6(10)	C(13)	0.409 75(30)	0.176 4(5)	-0.519 5(12)
N(4)	0.477 38(16)	0.426 7(3)	0.167 0(9)	C(14)	0.428 13(24)	0.148 6(4)	-0.316 4(11)
C(1)	0.406 36(21)	0.407 7(4)	-0.083 1(9)	C(15)	0.481 21(23)	0.145 3(4)	-0.243 1(12)
C(2)	0.384 94(24)	0.397 0(4)	-0.288 8(9)	C(16)	0.550 81(25)	0.119 7(5)	-0.006 0(14)
C(3)	0.330 31(22)	0.389 1(4)	-0.281 9(10)	C(17)	0.564 05(25)	0.186 2(5)	0.173 4(14)
C(4)	0.311 16(20)	0.393 5(4)	-0.070 0(9)	C(18)	0.554 12(24)	0.342 1(5)	0.290 4(14)
C(5)	0.257 51(22)	0.387 4(4)	-0.004 1(11)	C(19)	0.534 20(22)	0.433 9(5)	0.199 1(14)
C(6)	0.187 40(23)	0.371 5(4)	0.239 7(12)	C(20)	0.461 40(21)	0.417 7(4)	-0.031 4(11)

made based on the monitoring of two reflections. The structure was solved by Patterson and multiple-solution, direct methods techniques, and refined by block-diagonal, least-squares methods. Hydrogen atoms were detected and placed in calculated positions (C–H 0.95 Å); their contributions were included in structure-factor calculations ($B = 8.0$ Å²) but no refinement of positional parameters was permitted. Refinement converged at R 0.0442 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of sulphur. A slight difference in R (of 0.0002) was noted on reversing the chirality of the molecule and the enantiomer giving the lower value was accepted. Table 9 lists atomic positions and estimated standard deviations.

Scattering factors were taken from ref. 19; unit weights were used throughout both refinements. Computer programs used were MULTAN and those of the Sheffield X-ray system.

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