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Mercury macrocyclic complexes: synthesis and crystal structures of $\{[HgCl(\mu\text{-}Cl)(L^1)][Hg(\mu\text{-}Cl)_2]\}_n$ (L^1 = 1,4,7,10-tetraoxa-13-azacyclopentadecane), $[Hg(L^2)Cl_2]$ (L^2 = 1,4,7,10,13-pentaoxa-16-azacyclooctadecane) and $[Hg(L^3)Cl_2]$ (L^3 = 16-methyl-1,4,7,10,13-pentaoxa-16-azacyclooctadecane)

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Abstract

The mercury(II) complexes of the fifteen- and eighteen-membered ring macrocycles 1,4,7,10,-tetraoxa-13-azacyclopentadecane (L^1); 1,4,7,10,13-pentaoxa-16-azacyclooctadecane (L^2) and 16-methyl-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (L^3) have been prepared. The complexes $\{[HgCl(\mu\text{-}Cl)(L^1)][Hg(\mu\text{-}Cl)_2]\}_n$, $[Hg(L^2)Cl_2]$ and $[Hg(L^3)Cl_2]$ have been characterised by single crystal X-ray structural analysis. $\{[HgCl(\mu\text{-}Cl)(L^1)][Hg(\mu\text{-}Cl)_2]\}_n$ crystallises in the orthorhombic space group *Pbca*, with a = 7.498(1), b = 15.201(1), c = 32.575(2) Å, U = 3713(2) Å^3, Z = 8, D_c = 2.727 g cm^{-3}, with R 0.039, R_w 0.040. The structure consists of a polymeric chain of five-coordinate mercury atoms $[Hg(\mu\text{-}Cl)_2]$ bearing $[HgCl(\mu\text{-}Cl)(L^1)]$ substituents. One mercury atom is located above the plane of the macrocyclic ligand L^1; bond lengths Hg–N 2.145(10), Hg–O 2.664(10)–2.806(9) Å. Two Cl ligands are located on the same side of the folded macrocyclic ring, Hg(1)–Cl(1) and Hg(1)–Cl(2) 2.291(4) and 3.129(4) Å, respectively, Cl(1)–Hg(1)–Cl(2) 102.37(13)°. $[Hg(L^2)Cl_2]$ crystallises in the monoclinic space group $P2_1/c$, with a = 7.648(1), b = 7.858(1), c = 15.366(3) Å, β = 92.462(8)°, U = 922.6(3) Å^3, Z = 2, D_c = 1.925 g cm^{-3} with R 0.029, R_w 0.032. The mercury atom is eight-coordinate and is located at an inversion centre; bond lengths Hg–Cl 2.327(2), Hg–N/O(1) 2.748(8), av. Hg–O distance 2.856 Å; the Cl(1)–Hg–Cl(1a) angle was 180°. $[Hg(L^3)Cl_2]$ crystallises in the monoclinic space group $C2/c$, with a = 11.751(4), b = 10.504(3), c = 31.38(2) Å, β = 91.92°, U = 3871(2) Å^3, Z = 8, D_c = 1.884 g cm^{-3} and R 0.027, R_w 0.031. The metal ion is eight-coordinate (five oxygen, one tertiary amine and two chloride donors); there are two short (2.767(5), 2.753(6) Å), and three longer (2.961(6), 2.968(6), 2.922(6) Å) Hg–O bond lengths, with Hg–N 2.739(6) and Hg–Cl 2.327(2) Å. The Cl(1)–Hg(1)–Cl(2) angle was 174.07(8)°.

Introduction

The macrocyclic ligands 1,4,7,10-tetraoxa-13-azacyclopentadecane (L^1) and 1,4,7,10,13-pentaoxa-16-azacyclooctadecane (L^2) are examples of 15- and 18-membered ring oxa-monoaza-coronands, ligands which are of interest because they are structurally similar to the polyoxacoronands but the presence of the nitrogen donor atoms has been shown to result in stronger complexes with some cations [1, 2]. We have previously characterised the Pb(II) complexes with L^1 and L^2 as part of an investigation of the chemistry of these ligands with Group 12 and 14 elements [3]. We report herein the syntheses and single crystal X-ray structure determinations for the mercury(II) complexes of these ligands. In addition, the Hg(II) complex of the N-methylated analogue of L^2, 16-methyl-1,4,7,10,13-pentaoxa-16-azacyclooctadecane [4] (L^3) has been prepared and characterised.

Experimental

$^{13}C\{^1H\}$ NMR spectra were recorded with a JEOL GX400 FT spectrometer, TMS being the internal reference. Microanalyses were determined by the National Analytical Service, Victoria, Australia.

Ligand synthesis and characterisation

The ligands 1,4,7,10-tetraoxa-13-azacyclopentadecane (L^1) and 1,4,7,10,13-pentaoxa-16-azacyclooctadecane (L^2) were prepared as described previously [4]. 16-

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Methyl-1,4,7,10,13-pentaoxa-16-azacyclooctadecane [3] (L^3) was prepared from L^2, formaldehyde and formic acid by a modification of a reported method [5–7].

Synthesis of [Hg(L^3)Cl$_2$]

Mercuric chloride (0.283 g, 1.04 mmol) in methanol (10 ml) was added to a solution of L^3 (0.289 g, 1.04 mmol) in methanol (5 ml). A white suspension formed immediately. The suspension was heated to reflux and methanol was added until almost complete dissolution of the precipitate. The solution was filtered and the filtrate permitted to cool to 4 °C. Colourless crystals formed on standing. The mother liquor was decanted and the colourless crystals washed with a minimum of cold methanol and dried in air resulting in $[Hg(L^3)Cl_2]$ (0.397 g, 0.72 mmol, 70%). ^{13}C NMR (dmso-D_6): δ 69.8, 69.4 (br), 69.3 (br), 69.2, 69.1, 69.0 (OCH_2CH_2O); 65.5 (OCH_2CH_2N); 58.2 (NCH_2CH_2O); 38.3 (NCH_3). *Anal.* Found: C, 28.4; H, 4.9; N, 2.3. Calc. for $C_{13}H_{27}Cl_2HgNO_5$: C, 28.4; H, 5.0; N, 2.6%.

$\{[HgCl(\mu\text{-}Cl)(L^1)][Hg(\mu\text{-}Cl)_2]\}_n$ and $[Hg(L^2)Cl_2]$ were prepared similarly. $\{[HgCl(\mu\text{-}Cl)(L^1)][Hg(\mu\text{-}Cl)_2]\}_n$: ^{13}C NMR (dmso-D_6): δ 69.5, 69.0, 67.6, 66.6 (OCH_2); 50.8 (NCH_2). *Anal.* Found: C, 16.0; H, 2.9; N, 1.9. Calc. for $C_{10}H_{21}Cl_4Hg_2NO_4$: C, 15.8; H, 2.8; N, 1.8%. $[Hg(L^2)Cl_2]$: ^{13}C NMR (dmso-D_6): δ 69.7, 69.6, 69.4, 69.0 (OCH_2CH_2O); 67.8 (OCH_2CH_2N); 49.5 (NCH_2CH_2O). *Anal.* Found: C, 26.9; H, 4.5; N, 2.6. Calc. for $C_{12}H_{25}Cl_2HgNO_5$: C, 27.0; H, 4.7; N, 2.6%.

Single crystal X-ray structure determinations

Crystal data

$\{[HgCl(\mu\text{-}Cl)(L^1)][Hg(\mu\text{-}Cl)_2]\}_n$: $(C_{10}H_{21}Cl_4Hg_2NO_4)_n$, $M = 762.3$, orthorhombic, space group *Pbca*, $a = 7.498(1)$, $b = 15.201(1)$, $c = 32.575(2)$ Å, $U = 3713(2)$ Å^3. $Z = 8$, $D_c = 2.73$ g cm^{-3}, $F(000) = 2784.0$ electrons. Specimen $0.04 \times 0.29 \times 0.22$ mm, temperature 296 K, μ(Mo Kα) = 17.45 mm^{-1}.

$[Hg(L^2)Cl_2]$: $C_{12}H_{25}Cl_2HgNO_5$, $M = 534.8$, monoclinic, space group $P2_1/c$, $a = 7.648(1)$, $b = 7.858(1)$, $c = 15.366(3)$ Å, $\beta = 92.462(8)°$, $U = 922.6(3)$ Å^3, $Z = 2$, $D_c = 1.925$ g cm^{-3}, $F(000) = 516.0$ electrons. Specimen $0.14 \times 0.22 \times 0.34$ mm, temperature 296 K, μ(Mo Kα) = 8.82 mm^{-1}.

$[Hg(L^3)Cl_2]$: $C_{13}H_{27}Cl_2HgNO_5$, $M = 548.9$, monoclinic, space group $C2/c$, $a = 11.751(4)$, $b = 10.504(3)$, $c = 31.38(2)$ Å, $\beta = 91.92°$, $U = 3871(2)$ Å^3, $Z = 8$, $D_c = 1.884$ g cm^{-3}, $F(000) = 2128.0$ electrons. Specimen $0.24 \times 0.14 \times 0.28$ mm, temperature 296 K, μ(Mo Kα) = 8.41 mm^{-1}.

Data collection and processing

Data were collected using Mo Kα graphite monochromatised radiation ($\lambda = 0.71069$ Å) with an Enraf-Nonius CAD4 diffractometer. The scan technique, maximum scan time and ω-scan width were $2\theta/\omega$, 45 s, 0.38°; $2\theta/\omega$, 45 s, 0.40° and $2\theta/\omega$, 30 s, 0.40° for $\{[HgCl(\mu\text{-}Cl)(L^1)][Hg(\mu\text{-}Cl)_2]\}_n$, $[Hg(L^2)Cl_2]$ and $[Hg(L^3)Cl_2]$, respectively. The structures were solved by the Patterson heavy-atom method for $[Hg(L^2)Cl_2]$ and direct methods for $\{[HgCl(\mu\text{-}Cl)(L^1)][Hg(\mu\text{-}Cl)_2]\}_n$ and $[Hg(L^3)Cl_2]$ using SHELXS86 [8]. Positional and anisotropic thermal parameters for non-hydrogen atoms were refined by full matrix least-squares using SHELX76 [9]. Hydrogen atoms were calculated. Figures were drawn with PLATON [10].

Structure analysis and refinement

[Hg(L^2)Cl$_2$]. Unit cell dimensions were obtained by a least-squares fit to 24 reflections ($17 < 2\theta < 28°$). Data were collected for 19.4 h, during which 16.9% decomposition occurred. Reflections $0 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 9$,

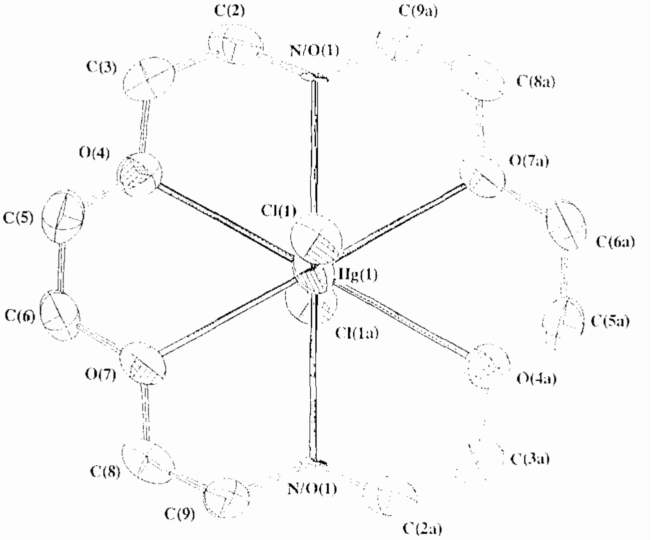

Fig. 1. A molecule of $[Hg(L^2)Cl_2]$ showing the numbering scheme (30% ellipsoids).

TABLE 1. Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for $[Hg(L^2)Cl_2]$

Atom	x	y	z	U_{eq}[a] (Å^2)
Hg(1)	0	1/2	1/2	0.0680(2)
Cl(1)	0.1916(3)	0.3448(3)	0.41721(17)	0.0794(10)
O(4)	0.2141(11)	0.4647(9)	0.6583(6)	0.076(3)
O(7)	−0.0206(10)	0.2024(8)	0.6023(5)	0.077(3)
N/O(1)	−0.2784(11)	0.2831(10)	0.4712(6)	0.018(3)
C(2)	0.3316(15)	0.7292(15)	0.6158(9)	0.088(5)
C(3)	0.3740(17)	0.5488(19)	0.6514(9)	0.089(5)
C(5)	0.2359(17)	0.2920(15)	0.6873(7)	0.085(5)
C(6)	0.0632(17)	0.2167(14)	0.6918(6)	0.080(4)
C(8)	−0.1950(16)	0.1339(14)	0.6003(8)	0.094(5)
C(9)	−0.2481(17)	0.1127(14)	0.5103(9)	0.094(5)

[a] $U_{eq} = 1/3$ of the trace of the orthogonalised U.

TABLE 2. Bond lengths (Å) and bond angles (°) for $[Hg(L^2)Cl_2]$

Hg(1)–Cl(1)	2.327(2)	O(7)–C(8)	1.437(14)
Hg(1)–O(4)	2.887(9)	N/O(1)–C(9)	1.482(14)
Hg(1)–O(7)	2.826(7)	N/O(1)–C(2a)	1.384(16)
Hg(1)–N/O(1)	2.748(8)	C(2)–C(3)	1.549(19)
O(4)–C(3)	1.398(16)	C(5)–C(6)	1.451(18)
O(4)–C(5)	1.437(14)	C(8)–C(9)	1.434(18)
O(7)–C(6)	1.496(13)		
Cl(1)–Hg(1)–O(4)	93.59(18)	Cl(1a)–Hg(1)–O(4a)	93.59(18)
Cl(1)–Hg(1)–O(7)	85.52(16)	Cl(1a)–Hg(1)–O(7a)	85.52(16)
Cl(1)–Hg(1)–N/O(1)	95.09(19)	Cl(1a)–Hg(1)–N/O(1a)	95.09(19)
Cl(1)–Hg(1)–Cl(1a)	180	O(4a)–Hg(1)–O(7a)	59.7(2)
Cl(1)–Hg(1)–O(4a)	86.41(18)	O(4a)–Hg(1)–N/O(1a)	118.9(2)
Cl(1)–Hg(1)–O(7a)	94.48(16)	O(7a)–Hg(1)–N/O(1a)	61.0(2)
Cl(1)–Hg(1)–N/O(1a)	84.91(19)	Hg(1)–O(4)–C(3)	110.9(7)
O(4)–Hg(1)–O(7)	59.7(2)	Hg(1)–O(4)–C(5)	114.0(6)
O(4)–Hg(1)–N/O(1)	118.9(2)	C(3)–O(4)–C(5)	112.3(10)
Cl(1a)–Hg(1)–O(4)	86.41(18)	Hg(1)–O(7)–C(6)	114.7(5)
O(4)–Hg(1)–O(4a)	180	Hg(1)–O(7)–C(8)	111.8(6)
O(4)–Hg(1)–O(7a)	120.3(2)	C(6)–O(7)–C(8)	114.1(8)
O(4)–Hg(1)–N/O(1a)	61.1(2)	Hg(1)–N/O(1)–(9)	112.9(7)
O(7)–Hg(1)–N/O(1)	61.0(2)	Hg(1)–N/O(1)–C(2a)	113.1(7)
Cl(1a)–Hg(1)–O(7)	94.48(16)	C(2a)–N/O(1)–C(9)	111.3(9)
O(4a)–Hg(1)–O(7)	120.3(2)	N/O(1a)–C(2)–C(3)	109.0(10)
O(7)–Hg(1)–O(7a)	180	O(4)–C(3)–C(2)	106.8(10)
O(7)–Hg(1)–N/O(1a)	119.0(2)	O(4)–C(5)–C(6)	107.8(10)
Cl(1a)–Hg(1)–N/O(1)	84.91(19)	O(7)–C(6)–C(5)	110.0(8)
O(4a)–Hg(1)–N/O(1)	61.1(2)	O(7)–C(8)–C(9)	106.7(10)
O(7a)–Hg(1)–N/O(1)	119.0(2)	N/O(1)–C(9)–C(8)	108.6(9)
N/O(1)–Hg(1)–N/O(1a)	180		

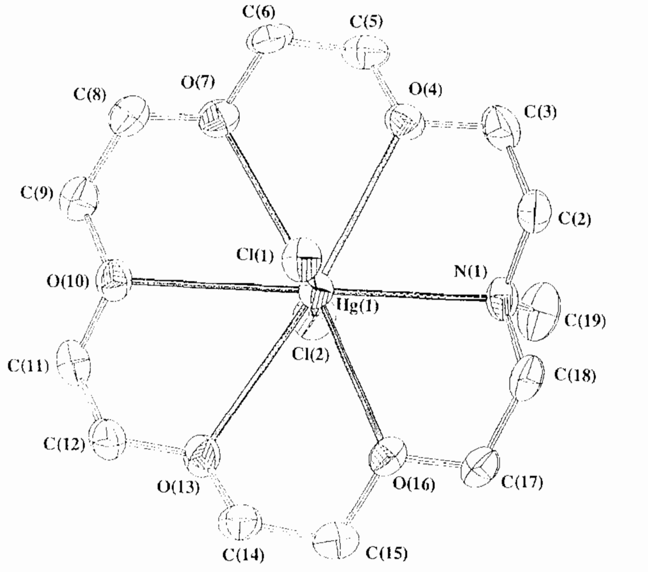

Fig. 2. A molecule of $[Hg(L^3)Cl_2]$ showing the numbering scheme (30% ellipsoids).

$-18 \leq l \leq 18$, 1894 measured, 1619 unique, 1155 observed ($I < 2.5\sigma(I)$) for 97 variables. Data were corrected for absorption (semi-empirically) and decomposition. The solution of this structure, which has an inversion centre at the Hg atom, was arrived at by calculating the N1 site as 50% N occupancy, 50% O occupancy.

TABLE 3. Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for $[Hg(L^3)Cl_2]$

Atom	x	y	z	U_{eq}[a] (Å^2)
Hg(1)	0.26110(2)	0.30557(3)	0.12461(1)	0.0452(1)
Cl(1)	0.26007(17)	0.4727(2)	0.07591(6)	0.0584(7)
Cl(2)	0.27285(19)	0.1266(2)	0.16824(7)	0.0649(8)
O(4)	0.4207(4)	0.4531(6)	0.16866(15)	0.0608(19)
O(7)	0.5082(5)	0.2637(5)	0.11523(18)	0.0586(19)
O(10)	0.3507(5)	0.1558(5)	0.05288(17)	0.0543(17)
O(13)	0.1127(5)	0.1475(6)	0.06995(16)	0.0564(17)
O(16)	0.0284(5)	0.3371(5)	0.12314(17)	0.0558(17)
N(1)	0.1811(6)	0.4405(5)	0.19205(18)	0.051(2)
C(2)	0.2578(7)	0.5505(8)	0.1974(3)	0.066(3)
C(3)	0.3799(8)	0.5131(10)	0.2059(3)	0.072(3)
C(5)	0.5297(7)	0.4008(10)	0.1745(3)	0.068(3)
C(6)	0.5738(6)	0.3675(9)	0.1316(3)	0.067(3)
C(8)	0.5360(8)	0.2338(9)	0.0725(3)	0.065(3)
C(9)	0.4676(7)	0.1219(9)	0.0589(3)	0.064(3)
C(11)	0.2787(7)	0.0529(7)	0.0420(3)	0.062(3)
C(12)	0.1630(7)	0.1035(9)	0.0316(2)	0.061(3)
C(14)	0.0075(7)	0.2070(9)	0.0620(3)	0.062(3)
C(15)	−0.0420(7)	0.2405(9)	0.1037(3)	0.065(3)
C(17)	−0.0128(7)	0.3787(9)	0.1626(3)	0.062(3)
C(18)	0.0656(7)	0.4821(9)	0.1783(3)	0.063(3)
C(19)	0.1769(10)	0.3656(11)	0.2317(3)	0.083(4)

[a] $U_{eq} = 1/3$ of the trace of the orthogonalised U.

The final difference Fourier map showed a maximum residual peak of 0.79 e Å^{-3} near the Hg atom. R 0.029, R_w 0.032 (weighting scheme $w = 1.00/$

TABLE 4. Bond lengths (Å) and bond angles (°) for $[Hg(L^3)Cl_2]$

Hg(1)–Cl(1)	2.327(2)	O(13)–C(12)	1.435(9)
Hg(1)–Cl(2)	2.327(2)	O(13)–C(14)	1.400(10)
Hg(1)–O(4)	2.767(5)	O(16)–C(15)	1.433(11)
Hg(1)–O(7)	2.961(6)	O(16)–C(17)	1.414(11)
Hg(1)–O(10)	2.968(6)	N(1)–C(2)	1.472(10)
Hg(1)–O(13)	2.922(6)	N(1)–C(18)	1.476(11)
Hg(1)–O(16)	2.753(6)	N(1)–C(19)	1.474(12)
Hg(1)–N(1)	2.739(6)	C(2)–C(3)	1.503(13)
O(4)–C(3)	1.425(11)	C(5)–C(6)	1.500(13)
O(4)–C(5)	1.400(10)	C(8)–C(9)	1.479(13)
O(7)–C(6)	1.421(10)	C(11)–C(12)	1.486(12)
O(7)–C(8)	1.426(11)	C(14)–C(15)	1.492(13)
O(10)–C(9)	1.426(10)	C(17)–C(18)	1.497(13)
O(10)–C(11)	1.408(10)		
Cl(1)–Hg(1)–Cl(2)	174.07(8)	C(3)–O(4)–C(5)	113.4(6)
Cl(1)–Hg(1)–O(4)	83.92(13)	Hg(1)–O(7)–C(6)	111.8(4)
Cl(1)–Hg(1)–O(7)	91.74(12)	Hg(1)–O(7)–C(8)	112.5(5)
Cl(1)–Hg(1)–O(10)	84.03(12)	C(6)–O(7)–C(8)	111.7(6)
Cl(1)–Hg(1)–O(13)	93.06(12)	Hg(1)–O(10)–C(9)	113.4(5)
Cl(1)–Hg(1)–O(16)	85.12(12)	Hg(1)–O(10)–C(11)	111.4(5)
Cl(1)–Hg(1)–N(1)	97.04(12)	C(9)–O(10)–C(11)	114.1(6)
Cl(2)–Hg(1)–O(4)	97.62(13)	Hg(1)–O(13)–C(12)	114.9(5)
Cl(2)–Hg(1)–O(7)	84.23(12)	Hg(1)–O(13)–C(14)	110.9(5)
Cl(2)–Hg(1)–O(10)	90.14(12)	C(12)–O(13)–C(14)	112.4(6)
Cl(2)–Hg(1)–O(13)	84.77(13)	Hg(1)–O(16)–C(15)	118.7(5)
Cl(2)–Hg(1)–O(16)	98.42(12)	Hg(1)–O(16)–C(17)	113.1(5)
Cl(2)–Hg(1)–N(1)	88.77(13)	C(15)–O(16)–C(17)	112.5(6)
O(4)–Hg(1)–O(7)	58.82(15)	Hg(1)–N(1)–C(2)	105.6(5)
O(4)–Hg(1)–O(10)	115.09(15)	Hg(1)–N(1)–C(18)	105.3(5)
O(4)–Hg(1)–O(13)	173.04(15)	Hg(1)–N(1)–C(19)	113.4(5)
O(4)–Hg(1)–O(16)	126.67(16)	C(2)–N(1)–C(18)	110.8(6)
O(4)–Hg(1)–N(1)	64.45(18)	C(2)–N(1)–C(19)	111.1(7)
O(7)–Hg(1)–O(10)	58.12(16)	C(18)–N(1)–C(19)	110.4(7)
O(7)–Hg(1)–O(13)	115.16(16)	N(1)–C(2)–C(3)	113.1(7)
O(7)–Hg(1)–O(16)	173.13(15)	O(4)–C(3)–C(2)	108.4(7)
O(7)–Hg(1)–N(1)	121.11(18)	O(4)–C(5)–C(6)	108.4(7)
O(10)–Hg(1)–O(13)	58.24(16)	O(7)–C(6)–C(5)	107.7(7)
O(10)–Hg(1)–O(16)	115.37(16)	O(7)–C(8)–C(9)	107.9(7)
O(10)–Hg(1)–N(1)	178.74(16)	O(10)–C(9)–C(8)	110.6(7)
O(13)–Hg(1)–O(16)	59.05(16)	O(10)–C(11)–C(12)	108.5(6)
O(13)–Hg(1)–N(1)	122.27(18)	O(13)–C(12)–C(11)	109.3(6)
O(16)–Hg(1)–N(1)	65.44(18)	O(13)–C(14)–C(15)	108.5(7)
Hg(1)–O(4)–C(3)	114.6(5)	O(16)–C(15)–C(14)	107.7(7)
Hg(1)–O(4)–C(5)	116.6(5)	O(16)–C(17)–C(18)	106.7(7)
N(1)–C(18)–C(17)	115.5(7)		

$(\sigma^2F_o+0.00024F_o^2)$), goodness of fit 1.87. The numbering of the atoms is defined in Fig. 1. Table 1 lists the non-hydrogen atom coordinates; Table 2 lists bond lengths and bond angles.

$[Hg(L^3)Cl_2]$. Unit cell dimensions were obtained by a least-squares fit to 23 reflections ($22<2\theta<26°$). Data were collected for 36.9 h, during which 9.1% decomposition occurred. Reflections $0\leqslant h\leqslant 14$, $0\leqslant k\leqslant 12$, $-32\leqslant l\leqslant 32$, 5349 measured, 3329 unique, 2508 observed ($I<2.5\sigma(I)$) for 226 variables. Data were corrected for absorption. The final difference Fourier map showed a maximum residual peak of 0.92 e Å^{-3} near the mercury atom. R 0.027, R_w 0.031 (weighting scheme $w=1.00/(\sigma^2F_o+0.00128F_o^2)$), goodness of fit 0.97. The numbering of the atoms is defined in Fig. 2. Table 3 lists the non-hydrogen atom coordinates; Table 4 lists bond lengths and bond angles.

$\{[HgCl(\mu\text{-}Cl)(L^1)][Hg(\mu\text{-}Cl)_2]\}_n$. Unit cell dimensions were obtained by a least-squares fit to 24 reflections ($16<2\theta<28°$). Data were collected for 35.6 h, during which 10.4% decomposition occurred. Reflections $0\leqslant h\leqslant 8$, $0\leqslant k\leqslant 18$, $0\leqslant l\leqslant 38$, 3735 measured, 3251 unique, 2020 observed ($I<2.5\sigma(I)$) for 191 variables. Data were corrected for absorption and decomposition. The final difference Fourier map showed a maximum residual peak of 1.13 e Å^{-3} near the atom Hg(1). R 0.039, R_w 0.040 [weighting scheme $w=1.00/(\sigma^2F_o+0.0031F_o^2)$), goodness of fit 0.80. The numbering

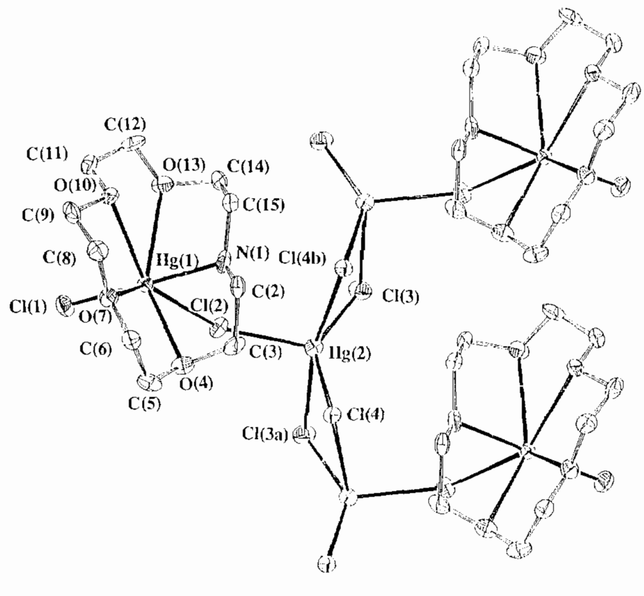

Fig. 3. A view of the {[HgCl(μ-Cl)(L^1)][Hg(μ-Cl)$_2$]}$_n$ chain.

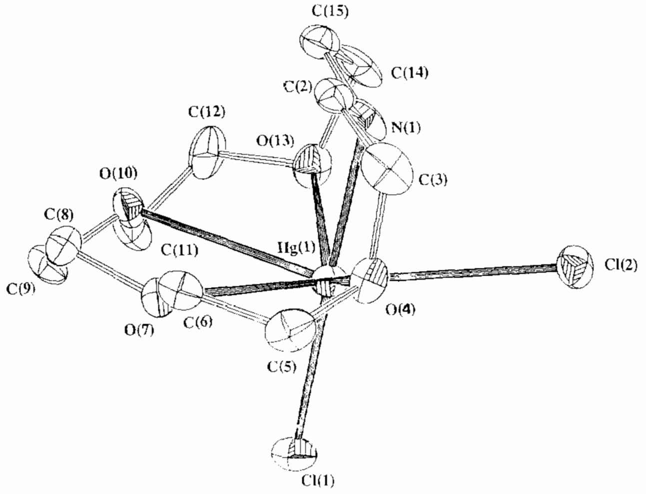

Fig. 4. A macrocyclic fragment [HgCl(μ-Cl)(L^1)] of the polymeric chain of {[HgCl(μ-Cl)(L^1)][Hg(μ-Cl)$_2$]}$_n$ showing the numbering scheme (30% ellipsoids).

of the atoms is defined in Figs. 3 and 4. Table 5 lists the non-hydrogen atom coordinates; Table 6 lists bond lengths and bond angles.

Results and discussion

TABLE 5. Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for {[HgCl(μ-Cl)(L^1)][Hg(μ-Cl)$_2$]}$_n$

Atom	x	y	z	U_{eq}[a] (Å^2)
Hg(1)	0.26971(7)	0.10487(4)	0.09638(2)	0.0334(2)
Hg(2)	0.04945(7)	−0.04049(5)	0.23282(2)	0.0451(2)
Cl(1)	0.1703(5)	0.0560(3)	0.03390(12)	0.0467(14)
Cl(2)	0.1009(5)	−0.0314(3)	0.15699(12)	0.0440(11)
Cl(3)	0.2242(5)	−0.1473(3)	0.26868(14)	0.0507(14)
Cl(4)	−0.1483(4)	0.0816(3)	0.24887(12)	0.0402(11)
O(4)	0.0320(13)	0.2170(6)	0.1274(4)	0.043(4)
O(7)	0.2595(12)	0.2746(7)	0.0649(3)	0.042(3)
O(10)	0.5809(11)	0.1779(7)	0.0628(3)	0.041(3)
O(13)	0.5892(12)	0.0178(7)	0.1063(3)	0.046(4)
N(1)	0.3680(15)	0.1445(8)	0.1555(3)	0.051(4)
C(2)	0.310(2)	0.2352(10)	0.1659(4)	0.038(5)
C(3)	0.112(2)	0.2437(13)	0.1657(6)	0.059(7)
C(5)	−0.016(2)	0.2865(11)	0.1009(6)	0.053(6)
C(6)	0.138(2)	0.3363(10)	0.0838(5)	0.040(5)
C(8)	0.4250(19)	0.3126(11)	0.0537(5)	0.049(6)
C(9)	0.534(2)	0.2421(12)	0.0326(5)	0.056(6)
C(11)	0.665(2)	0.1014(12)	0.0462(5)	0.049(5)
C(12)	0.7320(19)	0.0475(13)	0.0808(6)	0.056(6)
C(14)	0.617(2)	0.0383(13)	0.1497(5)	0.056(6)
C(15)	0.5667(19)	0.1313(11)	0.1584(5)	0.041(5)

[a] U_{eq} = 1/3 of the trace of the orthogonalised U.

Reaction of mercuric chloride with the 18-membered oxa-aza-coronand L^2 results in the isolation of colourless crystals of empirical formula Hg(L^2)Cl$_2$. The structure of the molecule is illustrated in Fig. 1; Table 2 gives the bond lengths and bond angles. The mercury atom sits directly in the plane of the one nitrogen and five oxygen donors from the macrocycle, and is eight-coordinate. The presence of the Hg atom at the inversion centre dictates that the two Hg–Cl distances be identical (2.327(2) Å) and that the Cl(1)–Hg–Cl(1a) angle be 180°. The Hg–N/O(1) bond length was assigned as 2.748(8) Å based on the observed Hg–N bond length assigned for the N-methylated analogue Hg(L^3)Cl$_2$, see below, and the Hg–N bond length (2.724(10) Å) observed for the mercury complex of the tetraoxa-diaza-coronand 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane [11]. The remaining average metal–donor (oxygen) distances were 2.826 and 2.887 Å, similar to those observed in the Hg(II) complex with 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) [12, 13]. The presence of the inversion centre and the associated ambiguity in the nitrogen and oxygen positions prevents a more definitive analysis of the structure.

In order to obtain more precise structural parameters of a mercury complex of an 18-membered oxa-aza-coronand, the N-methylated derivative of L^2 was prepared. In this complex the position of the Hg–N bond would be unambiguous. The secondary amine donor in the ligand L^2 was methylated by means of the Eschweiler–Clarke reaction [5–7] and the product, L^3, subsequently reacted with mercuric chloride in methanol resulting in the isolation of colourless crystals of empirical formula [Hg(L^3)Cl$_2$]. The structure of the cation is illustrated in Fig. 2; bond lengths and bond angles are given in Table 4. The metal ion is eight-coordinate, the coordination sphere comprising one nitrogen and five oxygen donors from the macrocycle and two chlorides. There are three long (2.968(6), 2.961(6) and

TABLE 6. Bond lengths (Å) and bond angles (°) for $\{[\mathrm{HgCl}(\mu\text{-Cl})(\mathrm{L}^1)][\mathrm{Hg}(\mu\text{-Cl})_2]\}_n$

Hg(1)–Cl(1)	2.291(4)	O(7)–C(6)	1.445(18)
Hg(1)–Cl(2)	3.129(4)	O(7)–C(8)	1.417(18)
Hg(1)–O(4)	2.664(10)	O(10)–C(9)	1.43(2)
Hg(1)–O(7)	2.777(11)	O(10)–C(11)	1.43(2)
Hg(1)–O(10)	2.806(9)	O(13)–C(12)	1.428(19)
Hg(1)–O(13)	2.756(9)	O(13)–C(14)	1.463(19)
Hg(1)–N(1)	2.145(10)	N(1)–C(2)	1.486(19)
Hg(2)–Cl(2)	2.504(4)	N(1)–C(15)	1.506(18)
Hg(2)–Cl(3)	2.391(4)	C(2)–C(3)	1.49(2)
Hg(2)–Cl(4)	2.432(4)	C(5)–C(6)	1.49(2)
Hg(2)–Cl(3a)	2.930(4)	C(8)–C(9)	1.51(2)
Hg(2)–Cl(4b)	2.989(4)	C(11)–C(12)	1.48(3)
O(4)–C(3)	1.45(2)	C(14)–C(15)	1.49(3)
O(4)–C(5)	1.41(2)		
Cl(1)–Hg(1)–Cl(2)	102.37(13)	Cl(3a)–Hg(2)–Cl(4b)	168.04(12)
Cl(1)–Hg(1)–O(4)	109.0(3)	Hg(1)–Cl(2)–Hg(2)	136.16(17)
Cl(1)–Hg(1)–O(7)	88.0(2)	Hg(2)–Cl(3)–Hg(2b)	94.11(15)
Cl(1)–Hg(1)–O(10)	93.0(2)	Hg(2)–Cl(4)–Hg(2a)	91.80(14)
Cl(1)–Hg(1)–O(13)	103.4(2)	Hg(1)–O(4)–C(3)	103.3(8)
Cl(1)–Hg(1)–N(1)	177.3(3)	Hg(1)–O(4)–C(5)	114.8(10)
Cl(2)–Hg(1)–O(4)	85.1(2)	C(3)–O(4)–C(5)	115.1(12)
Cl(2)–Hg(1)–O(7)	146.8(2)	Hg(1)–O(7)–C(6)	117.6(8)
Cl(2)–Hg(1)–O(10)	147.6(2)	Hg(1)–O(7)–C(8)	116.7(8)
Cl(2)–Hg(1)–O(13)	87.7(2)	C(6)–O(7)–C(8)	113.4(11)
Cl(2)–Hg(1)–N(1)	76.1(3)	Hg(1)–O(10)–C(9)	109.5(7)
O(4)–Hg(1)–O(7)	61.8(3)	Hg(1)–O(10)–C(11)	101.1(8)
O(4)–Hg(1)–O(10)	116.8(3)	C(9)–O(10)–C(11)	113.8(11)
O(4)–Hg(1)–O(13)	147.6(3)	Hg(1)–O(13)–C(12)	115.6(9)
O(4)–Hg(1)–N(1)	73.2(4)	Hg(1)–O(13)–C(14)	97.8(8)
O(7)–Hg(1)–O(10)	60.8(3)	C(12)–O(13)–C(14)	112.8(12)
O(7)–Hg(1)–O(13)	120.9(3)	Hg(1)–N(1)–C(2)	111.5(8)
O(7)–Hg(1)–N(1)	94.6(4)	Hg(1)–N(1)–C(15)	111.1(8)
O(10)–Hg(1)–O(13)	60.8(3)	C(2)–N(1)–C(15)	113.5(11)
O(10)–Hg(1)–N(1)	87.3(4)	N(1)–C(2)–C(3)	111.8(13)
O(13)–Hg(1)–N(1)	74.4(4)	O(4)–C(3)–C(2)	113.1(14)
Cl(2)–Hg(2)–Cl(3)	115.78(15)	O(4)–C(5)–C(6)	114.3(12)
Cl(2)–Hg(2)–Cl(4)	105.30(14)	O(7)–C(6)–C(5)	108.6(12)
Cl(2)–Hg(2)–Cl(3a)	98.18(13)	O(7)–C(8)–C(9)	107.5(13)
Cl(2)–Hg(2)–Cl(4b)	92.62(12)	O(10)–C(9)–C(8)	107.7(13)
Cl(3)–Hg(2)–Cl(4)	138.34(14)	O(10)–C(11)–C(12)	108.2(13)
Cl(3)–Hg(2)–Cl(3a)	95.05(13)	O(13)–C(12)–C(11)	111.3(12)
Cl(3)–Hg(2)–Cl(4b)	84.76(13)	O(13)–C(14)–C(15)	110.5(14)
Cl(3a)–Hg(2)–Cl(4)	85.36(12)	N(1)–C(15)–C(14)	111.4(12)
Cl(4)–Hg(2)–Cl(4b)	86.88(12)		

2.922(6) Å) and two shorter (2.767(5) and 2.753(6) Å) Hg–O bonds, both distances being shorter than the sum of the van der Waals radii of mercury(II) and oxygen (throughout this work the van der Waals radius of mercury was taken as 1.73 Å) [14]. The two shorter Hg–O distances are associated with the O(4)–N(1)–O(16) donor portion of the macrocycle and reflect the short Hg–N bond length of 2.739(6) Å which results in asymmetry in the location of the metal ion within the macrocyclic cavity. The Hg–Cl distance of 2.327(2) Å is longer than that observed in $\mathrm{HgCl_2}$ [15], a common observation in macrocyclic complexes of this type [13]. The Cl(1)–Hg(1)–Cl(2) angle was 174.07(8)°. The conformation of the macrocyclic ring is similar to that observed in the structure of the analogue [Hg(18-crown-6)$\mathrm{Cl_2}$] [13].

Reaction of the 15-membered coronand L^1 with mercuric chloride in methanol resulted in the isolation of a complex subsequently shown to be $\{[\mathrm{HgCl}(\mu\text{-Cl})(\mathrm{L}^1)][\mathrm{Hg}(\mu\text{-Cl})_2]\}_n$. The structure of a portion of the polymer is illustrated in Fig. 3, the macrocyclic moiety is illustrated in Fig. 4; bond lengths and angles are given in Table 6. The structure consists of two chloride bridged mercury atoms, Hg(1) associated with the macrocyclic ligand and one bridging chloride, and Hg(2) with five bridging chlorides. Hg(1) is seven-coordinate and located above the plane of the macrocyclic ring. The Hg–N distance (2.145(10) Å) is shorter than that observed in the structures with L^2 and L^3. The Hg–O distances span the range 2.664(10)–2.806(9) Å and are shorter than the sum of the van der Waals radii of mercury(II) and oxygen [13, 14]. The Hg–O bond distances associated with the portion of the macrocyclic ring containing the N donor tend toward the shorter end of the range of Hg–O bonds. The Hg(1)–Cl(1) and Hg(1)–Cl(2) distances are 2.291(4) and 3.129(4) Å, respectively, the non-bridging Hg–Cl bond length being shorter than the analogous bonds in the structures of L^2 and L^3. The two Cl ligands are located on the same side of the macrocyclic ring with Cl(1)–Hg(1)–Cl(2) 102.37(13)°. The region of the macrocyclic ring associated with the O(4)–N(1)–O(13) donors is distorted, the macrocycle folding to accommodate the close proximity of Hg(2) and the associated bridging halides in the polymeric unit. Hg(2) is five-coordinate with approximately square-pyramidal coordination and is involved in two short (2.432(4) and 2.391(4) Å) and two longer (2.930(4) and 2.989(4) Å) Hg–Cl bonds in the $[Hg(\mu\text{-}Cl)_2]$ chain, as well a chloro ligand (Cl(2)) bridging to Hg(1) in the macrocyclic appendage, (Hg(2)–Cl(2) 2.504(4) and Hg(1)–Cl(2) 3.129(4) Å, respectively, Hg(1)–Cl(2)–Hg(2) 136.16(17)°). The long Hg–Cl distances are shorter than the sum of the van der Waals radii of Hg(II) and Cl(3.25 Å) [16]. The overall structure of the molecule is dictated by the steric requirements of arranging the macrocyclic substituents $[HgCl(L^1)]$ along the polymeric chain of $[Hg(\mu\text{-}Cl)(\mu\text{-}Cl)_2]$. The effect is to produce a syndiotatic polymer of the form $[Hg(R)(\mu\text{-}Cl)(\mu\text{-}Cl)_2]$. The structure is similar to that observed in the extended structure of mercuric chloride with diphenylsulfoxide, a structure which exhibits two short (2.289(4), 2.291(4) Å) and two long (3.284(5), 3.230(6) Å) Hg–Cl bonds, with approximate square-pyramidal coordination at the Hg atom [17]. The structure of $HgCl_2$ itself shows a mean Hg–Cl distance of 2.291(9) Å, Cl(1)–Hg–Cl(2) 178.9(5)°; the approach of four halides from neighbouring molecules with four long Hg–Cl distances (average 3.34 and 3.63 Å) results in the description of the $HgCl_2$ lattice as molecular rather than polymeric [18].

Supplementary material

Positional parameters of all atoms, thermal parameters, listings of anisotropic thermal parameters, and observed and calculated structure factor amplitudes and tables of bond distances and angles are available from the authors.

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