Synthesis, Characterization and Crystal Structures of 1,7-dioxa-4-thia-10-azacyclododecane ([12]aneNO$_2$S) and [Hg([12]aneNO$_2$S)(NO$_3$)$_2$]†

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Reaction of 6-(4-methylphenylsulfonyl)-1,11-bis(4-methylphenylsulfonyloxy)-3,9-dioxa-6-azaundecane and ethane-1,2-dithiol in the presence of NaH, results, after removal of the protecting group, in the unexpected isolation of the twelve-membered macrocycle 1,7-dioxa-4-thia-10-azacyclododecane, [12]aneNO$_2$S. The product, suggested to arise from the intramolecular displacement of a tosyl group by a thioether instead of the terminal thiol as in the expected ring closing procedure, was characterised by ^{13}C NMR spectroscopy, mass spectrometry, microanalysis and a single-crystal X-ray structure determination. The macrocycle crystallizes in the monoclinic space group $P2_1$, with a = 7.448(5), b = 5.1740(10), c = 12.769(9) Å, β = 93.28(2)°, Z = 2 with R = 0.046. All the donors in the macrocyclic ring are in the endodentate conformation with close contacts between the N–H and atoms O(1) and O(7). Reaction of mercury nitrate with 1 molar equivalent of [12]aneNO$_2$S in methanol, and subsequent crystallization of the product, resulted in colourless prisms of [Hg([12]aneNO$_2$S)(NO$_3$)$_2$] which crystallize in the monoclinic space group $P2_1/c$, with a = 9.165(17), b = 10.657(15), c = 14.80(2) Å, β = 92.57(8)°, Z = 4 with R = 0.055. In this molecule the mercury(II) cation is co-ordinated by the macrocyclic donors and the nitrate anions, one in a bidentate manner, the other in a monodentate mode.

The structures of twelve-membered macrocyclic ligands containing four donor atoms have been extensively investigated.[1] Ligands such as 1,4,7,10-tetraazacyclododecane, [12]aneN$_4$,[2–4] 1,4,7,10-tetraoxacyclododecane, [12]aneO$_4$,[5] and 1,4,7,10-tetrathiacyclododecane, [12]aneS$_4$,[6] and their metal complexes have been reported. In addition a number of mixed-donor ligands such as 1,4,7-trioxa-10-azacyclododecane, [12]aneNO$_3$,[7] 1,4-dithia-7,10-diazacyclododecane, [12]aneN$_2$S$_2$,[8] and 1-oxa-4,7-dithia-10-azacyclododecane, [12]aneNOS$_2$,[9] have been prepared. Herein we report the preparation of the new mixed-donor macrocycle 1,7-dioxa-4-thia-10-azacyclododecane, [12]aneNO$_2$S, and a mercury(II) complex of this ligand.

Experimental

Dry dimethylformamide (dmf) was distilled from CaH$_2$ before use. Pyridine was dried by standing over KOH pellets overnight before distillation. 1,2-Dimethoxyethane (dme) was distilled from sodium immediately before use. Fourier-transform ^{13}C-{^{1}H} NMR spectra were recorded with a JEOL GX-400 spectrometer, 1,4-dioxane and sodium 3-trimethylsilylpropane-1-sulfonate (D$_2$O) or SiMe$_4$ (CDCl$_3$) being the internal reference. Chemical shifts (δ) for the ^{13}C and ^{1}H NMR spectra recorded in CDCl$_3$ are reported in ppm as positive downfield from the internal reference SiMe$_4$.

3,9-Dioxa-6-azaundecane-1,11-diol was prepared as described previously.[10]

Syntheses.—6-(4-*Methylphenylsulfonyl*)-1,11-*bis*(4-*methylphenylsulfonyloxy*)-3,9-*dioxa*-6-*azaundecane*. To a well stirred solution of 3,9-dioxa-6-azaundecane-1,11-diol (38.6 g, 200 mmol) at −5 °C in dry pyridine (200 cm^3) solid toluene-*p*-sulfonyl (ts) chloride (125.7 g, 660 mmol) was added over approximately 1 h, maintaining the temperature to within a few degrees of −5 °C. Initial addition of the toluene-*p*-sulfonyl chloride induced a bright orange colouration and a thick precipitate of pyridinium hydrochloride formed towards the end of the addition. After completion of the addition and stirring for a further 2.5 h at −5 °C, the mixture was poured on to a well stirred acidic ice–water slurry (200 cm^3 concentrated HCl + 400 g ice). A heavy oil separated upon standing. The aqueous and organic layers were separated by decantation and the organic layer taken up in CHCl$_3$ (200 cm^3). This solution was washed with 1 mol dm^{-3} HCl (4 × 200 cm^3) and dried over Na$_2$SO$_4$. The solution was filtered, treated with activated charcoal (10 g) and filtered over Celite. Removal of the solvent under reduced pressure resulted in an orange oil which was subsequently purified by column chromatography (silica gel, 400 g, ethyl acetate–hexane 2:3, TLC; R_f = 0.37). This produced a pale yellow oil that solidified upon standing to give a clear crystalline *product* (87.9 g, 67%); δ_C(CDCl$_3$) 21.4 (p-CH$_3$C$_6$H$_4$SO$_2$NR$_2$), 21.5 (p-CH$_3$C$_6$H$_4$SO$_2$OR), 48.6 (NCH$_2$CH$_2$), 68.3, 69.2, 70.0 (CH$_2$$CH_2OCH_2$$CH_2$Ots), 127.1, 127.8, 129.7, 129.9 (aromatic CH) and 132.7, 136.9, 143.3, 144.9 (aromatic quaternary C); δ_H(CDCl$_3$) 2.40 (3 H, s, p-CH_3C$_6$H$_4$SO$_2$NR$_2$), 2.41 (6 H, s, p-CH_3C$_6$H$_4$SO$_2$OR), 3.29 (4 H, t, J 5.7, NCH_2CH$_2$), 3.52 (4 H, t, J 5.7, NCH$_2$CH_2O), 3.56 (4 H, t, J 4.5, CH_2CH$_2$Ots), 4.08 (4 H, t, J 4.5 Hz, CH$_2$CH_2Ots) and 7.29–7.77 (12 H, m, aromatic CH).

10-(4-*Methylphenylsulfonyl*)-1,7-*dioxa*-4-*thia*-10-*azacyclododecane*. Ethane-1,2-dithiol (10.2 cm^3, 122 mmol) was stirred with NaH (250 mmol) in dmf (700 cm^3) at 50 °C for 50 min. The mixture was heated to 90 °C over 0.25 h and 6-(4-methylphenylsulfonyl)-1,11-bis(4-methylphenylsulfonyloxy)-3,9-dioxa-6-azaundecane (80 g, 122 mmol) dissolved in dry dmf (300 cm^3) was added dropwise over 2.5–3 h, resulting in a yellow solution. After stirring for a further 5 h the solvent was removed *in vacuo* resulting in a thick brown oil. This oil was dissolved in an equal volume of chloroform and washed with water (8 × 100 cm^3). After drying the organic layer with Na$_2$SO$_4$ and removing the solvent, the oil was chromatographed (neutral alumina II, 100 g,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

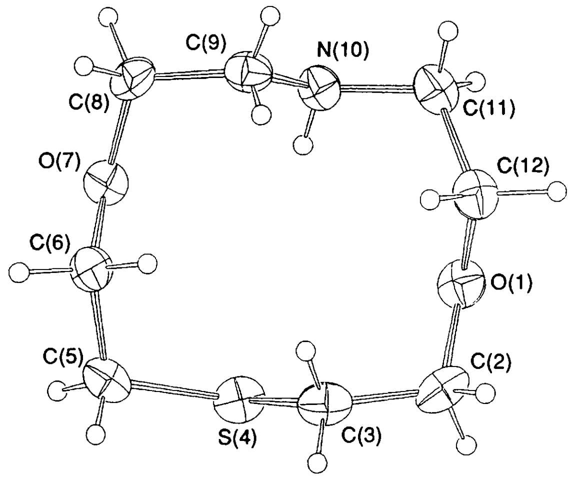


Fig. 1 Structure of [12]aneNO_2S with relevant atoms labelled. 30% Probability ellipsoids are shown

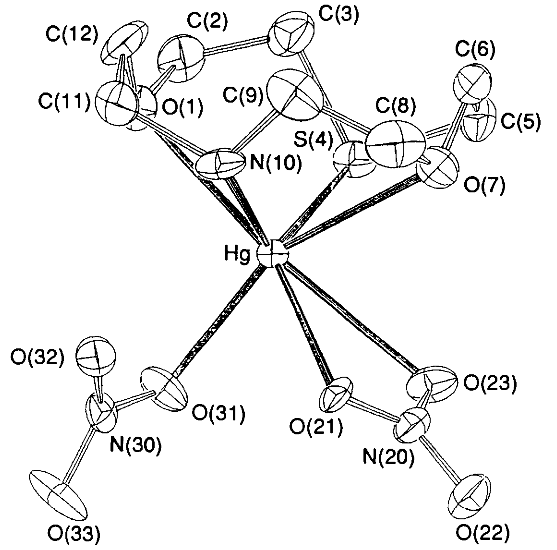


Fig. 2 Structure of [Hg([12]aneNO_2S)$(NO_3)_2$] with relevant atoms labelled. 30% Probability ellipsoids are shown

chloroform–hexane 2:3). The *product* was obtained as a fine white solid which was recrystallized from dichloromethane–ethanol to give white crystals (31.5 g, 75%) (Found: C, 52.2; H, 6.7; N, 4.0. $C_{15}H_{23}NO_4S_2$ requires C, 52.1; H, 6.7; N, 4.1%); $\delta_C(CDCl_3)$ 21.5 (p-$\mathit{C}H_3C_6H_4SO_2NR_2$), 31.5 ($OCH_2\mathit{C}H_2S$), 51.0 ($N\mathit{C}H_2CH_2$), 69.4, 71.3 ($CH_2\mathit{C}H_2O\mathit{C}H_2CH_2$), 127.5, 129.7 (aromatic CH) and 135.4, 143.5 (aromatic quaternary C); $\delta_H(CDCl_3)$ 2.43 (3 H, s, p-$C\mathit{H}_3C_6H_4SO_2NR_2$), 2.77 (4 H, t, *J* 5.7, $OCH_2C\mathit{H}_2S$), 3.28 (4 H, t, *J* 4.6 Hz, $NC\mathit{H}_2CH_2O$), 3.75–3.80 (8 H, m, $NCH_2C\mathit{H}_2OC\mathit{H}_2CH_2S$) and 7.31–7.73 (4 H, m, aromatic CH).

1,7-*Dioxa*-4-*thia*-10-*azacyclododecane*, [12]aneNO_2S. A solution of sodium anthracenide was prepared in dry dme (300 cm^3) by the addition of finely cut sodium (7.7 g) and anthracene (60 g) in a conical flask closed with a septum. After stirring overnight a thick blue solution was obtained. The solution was cooled to between −20 and −15 °C and a solution of *N*-tosylated [12]aneNO_2S (30 g, 86.8 mmol) in dry dme (300 cm^3) was added dropwise with a syringe. The temperature of the reaction was maintained below −15 °C during, and for 5 min after completion of the addition. The reaction was quenched with a few drops of water, the flask was opened to the atmosphere and the yellow mixture was poured on to a stirred acidic ice–water slurry (60 cm^3 concentrated HCl + 300 g ice–water). The precipitate was filtered over Celite and washed with 1 mol dm^{-3} HCl (20 cm^3). The filtrate was washed with $CHCl_3$ (3 × 50 cm^3), made basic (pH 13–14) with LiOH, then extracted with diethyl ether (8 × 50 cm^3). After drying the ether extracts over $MgSO_4$ the solvent was removed resulting in a yellow oil (8 g). The product was purified by chromatography (neutral alumina II, 100 g, CH_2Cl_2–hexane, 1:4) and sublimation [100 °C, 0.1 mmHg ($\approx$13.3 Pa)]. Upon recrystallization from ether a crystalline *solid* was obtained (3.1 g, 19%) (Found: C, 50.0; H, 9.20; N, 7.25. $C_8H_{17}NO_2S$ requires C, 50.2; H, 8.95; N, 7.30%); $\delta_C(CDCl_3)$ 34.0 ($OCH_2\mathit{C}H_2S$), 46.6 ($N\mathit{C}H_2CH_2$), 67.8 ($NCH_2\mathit{C}H_2O$) and 69.1 ($O\mathit{C}H_2CH_2S$); $\delta_H(CDCl_3)$: 2.37 (1 H, s, NH), 2.79 (t, *J* 5.5, $OCH_2C\mathit{H}_2S$), 2.85 (t, *J* 4.9, $NC\mathit{H}_2CH_2O$), 3.63–3.67 (8 H, m, $NCH_2C\mathit{H}_2OC\mathit{H}_2CH_2S$), *m*/*z* 191.0980 ($M^+$).

[Hg([12]aneNO_2S)$(NO_3)_2$]. Reaction between [12]aneNO_2S (1 mmol) and $Hg(NO_3)_2$ (1 mmol) in methanol (50 cm^3) resulted in a white precipitate which was subsequently recrystallized from acetonitrile–diethyl ether to give colourless prisms (38%), suitable for X-ray crystallographic analysis (Found: C, 18.6; H, 3.65; N, 8.05. $C_8H_{17}HgN_3O_8S$ requires C, 18.6; H, 3.30; N, 8.15%).

Crystal-structure Analyses.—Crystal data. [12]aneNO_2S: $C_8H_{17}NO_2S$, $M = 191.29$, monoclinic, space group $P2_1$, $a = 7.448(5)$, $b = 5.1740(10)$, $c = 12.769(9)$ Å, $\beta = 93.28(2)°$, $U = 491.3(5)$ Å^3, $Z = 2$, $D_c = 1.293$ g cm^{-3}, Mo-Kα radiation, $\lambda = 0.710\,73$ Å, μ(Mo-Kα) = 2.8 cm^{-1}, $T = 298$ K, $F(000) = 208$, specimen 0.70 × 0.25 × 0.23 mm.

[Hg([12]aneNO_2S)$(NO_3)_2$]: $C_8H_{17}HgN_3O_8S$, $M = 515.89$, monoclinic, space group $P2_1/c$, $a = 9.165(17)$, $b = 10.657(15)$, $c = 14.80(2)$ Å, $\beta = 92.57(8)°$, $U = 1444(4)$ Å^3, $Z = 4$, $D_c = 2.373$ g cm^{-3}, Mo-Kα radiation, $\lambda = 0.710\,73$ Å, μ(Mo-Kα) = 108.3 cm^{-1}, $T = 298$ K, $F(000) = 984$, specimen 0.50 × 0.40 × 0.36 mm.

Data were collected with an Enraf-Nonius CAD4 diffractometer. Structures were solved using the direct methods and Patterson approaches in SHELXS-86,[11] respectively, for the two compounds. Neutral complex scattering factors were used.[12] Positional and anisotropic thermal parameters for non-hydrogen atoms were refined by full-matrix least squares using SHELX 76.[13] For [12]aneNO_2S the hydrogen atoms were located by Fourier difference synthesis and refined fully. For [Hg([12]aneNO_2S)$(NO_3)_2$] the hydrogen atoms were calculated and constrained at 1.08 Å. Figures were drawn with PLATON.[14] The chirality of the ligand [12]aneNO_2S was checked using SHELXL-92[15] which indicated the correct conformation had been used [Flack parameter 0.07(17)]. For [12]aneNO_2S, final $R = 0.046$, $R' = 0.049$, number of reflections 1680, number used 982 [$I > 2.5\sigma(I)$], goodness of fit 1.33, final difference density residues, minimum −0.36, maximum 0.46. For [Hg([12]aneNO_2S)$(NO_3)_2$], final $R = 0.055$, $R' = 0.055$, number of reflections 2874, number used 1838 [$I > 3.0\sigma(I)$], goodness of fit 0.92, final difference density residues, minimum −2.10, maximum 3.94. For the mercury complex the data were corrected and refined using the ψ-scan empirical method and the approximate spherical absorption correction (radius 0.040 cm). Neither removed the two background peaks of magnitude 3.7 e Å^{-3} which were close to the Hg atom in the final Fourier difference synthesis. The next background peak at 1.7 Å away from the heavy atom had a peak height of 1.07 e Å^{-3}. These peaks were probably ripples from the Hg atom. The geometries of the molecules are shown in Figs. 1 and 2, together with the atomic numbering schemes. Positional parameters for [12]aneNO_2S and [Hg([12]aneNO_2S)$(NO_3)_2$], are given in Tables 1 and 2, respectively. Selected bond lengths and angles for [12]aneNO_2S and [Hg([12]aneNO_2S)$(NO_3)_2$] are reported in Tables 3 and 4, respectively. Torsion angles are reported in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 1 Non-hydrogen positional parameters for [12]aneNO_2S

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
S(4)	0.056 21(15)	0.434 1(7)	0.625 38(9)
O(1)	0.030 7(4)	0.502 21 *	0.864 7(2)
O(7)	0.439 1(4)	0.192 0(10)	0.645 4(3)
N(10)	0.361 3(5)	0.192 5(11)	0.863 0(3)
C(2)	−0.022 8(6)	0.713 7(14)	0.797 4(4)
C(3)	0.086 7(7)	0.725 9(12)	0.701 5(4)
C(5)	0.239 9(7)	0.454 9(18)	0.539 5(3)
C(6)	0.423 4(5)	0.431 2(16)	0.593 7(3)
C(8)	0.575 9(5)	0.188 9(14)	0.729 1(4)
C(9)	0.519 5(6)	0.318 9(15)	0.825 9(4)
C(11)	0.287 2(7)	0.314 3(14)	0.955 3(4)
C(12)	0.187 0(7)	0.565 8(13)	0.933 0(4)

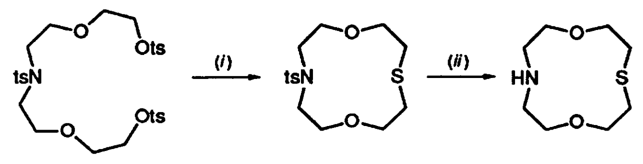
* Not refined.

Table 2 Non-hydrogen positional parameters for [Hg([12]aneNO_2S)-$(NO_3)_2$]

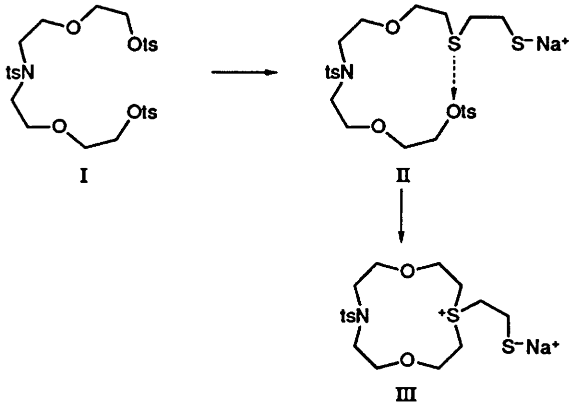
Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Hg	−0.201 54(6)	0.555 90(5)	0.405 91(3)
S(4)	0.015 3(4)	0.693 6(4)	0.380 0(3)
O(1)	−0.160 7(15)	0.555 0(10)	0.224 9(8)
O(7)	−0.279 7(13)	0.781 9(11)	0.461 4(7)
O(21)	−0.342 7(11)	0.506 6(10)	0.546 5(6)
O(22)	−0.278 6(13)	0.536 1(11)	0.689 3(7)
O(23)	−0.129 6(11)	0.584 8(11)	0.583 2(7)
O(31)	−0.160 7(10)	0.343 0(10)	0.419 5(8)
O(32)	−0.388 6(12)	0.325 4(10)	0.374 0(7)
O(33)	−0.271 7(14)	0.166 7(10)	0.428 6(10)
N(10)	−0.419 6(12)	0.602 0(13)	0.333 7(8)
N(20)	−0.251 5(14)	0.542 4(11)	0.606 3(8)
N(30)	−0.277 7(13)	0.275 9(11)	0.403 8(8)
C(2)	−0.030 2(19)	0.625 0(18)	0.210 3(11)
C(3)	−0.014(2)	0.742 1(19)	0.262 7(12)
C(5)	−0.044(2)	0.840 8(18)	0.436 6(11)
C(6)	−0.193(3)	0.876 0(18)	0.423 4(11)
C(8)	−0.443(2)	0.777(2)	0.433 4(14)
C(9)	−0.466 8(18)	0.729 5(18)	0.341 1(15)
C(11)	−0.415 7(18)	0.559 3(14)	0.229 9(13)
C(12)	−0.294(2)	0.607(2)	0.186 3(10)

Table 3 Selected bond lengths (Å) and angles (°) in [12]aneNO_2S

S(4)–C(3)	1.803(7)	N(10)–C(9)	1.451(7)
S(4)–C(5)	1.805(5)	N(10)–C(11)	1.471(7)
O(1)–C(2)	1.434(7)	C(2)–C(3)	1.511(7)
O(1)–C(12)	1.452(6)	C(5)–C(6)	1.501(6)
O(7)–C(6)	1.404(9)	C(8)–C(9)	1.489(8)
O(7)–C(8)	1.434(6)	C(11)–C(12)	1.519(9)
C(3)–S(4)–C(5)	101.6(3)	S(4)–C(5)–C(6))	114.6(3)
C(2)–O(1)–C(12)	111.9(4)	O(7)–C(6)–C(5)	109.7(5)
C(6)–O(7)–C(8)	113.4(5)	O(7)–C(8)–C(9)	113.1(4)
C(9)–N(10)–C(11)	114.7(5)	N(10)–C(9)–C(8)	109.9(5)
O(1)–C(2)–C(3)	111.9(4)	N(10)–C(11)–C(12)	114.8(4)
S(4)–C(3)–C(2)	110.2(4)	O(1)–C(12)–C(11)	106.7(5)



Scheme 1 ts = *p*-$MeC_6H_4SO_2$–; (*i*) $NaSCH_2CH_2SNa$–dmf; (*ii*) $Na^+C_{14}H_9^-$ –dme



Scheme 2

Results and Discussion

Syntheses.—The *N*-tosylated twelve-membered macrocycle 10-(4-methylphenylsulfonyl)-1,7-dioxa-4-thia-10-azacyclododecane has been isolated from reaction between 6-(4-methylphenylsulfonyl)-1,11-bis(4-methylphenylsulfonyloxy)-3,9-dioxa-6-azaundecane and the product of the reaction between ethane-1,2-dithiol and sodium hydride, in dimethylformamide (Scheme 1). The product was not as anticipated in that instead of the expected incorporation of the –SCH_2CH_2-S– fragment in the macrocyclic product, a single sulfur donor had been inserted. The product cannot be accounted for by a prior decomposition of the dithiol in the reaction mixture as the sodium salt of ethane-1,2-dithiol appears to be stable under the reaction conditions, and can readily be isolated in high yield from a mixture of the dithiol and NaH in dmf heated to the reaction temperature for 12 h.

A possible explanation for the observed product is that the sulfur comes from the intramolecular displacement of a tosyl group by a thioether instead of the terminal thiol as in the expected ring closing procedure. The terminal thiolate anion of the initial condensation product (**II**, Scheme 2) is of course expected to be much more nucleophilic than the thioether of this compound. The failure of an expected reaction to dominate the product distribution in cyclization reactions of this kind is occasionally observed.[16,17] Generally this is attributed to poor template directive effects and/or difficulties associated with closing the macrocyclic system of the desired size. In this case the 'side reaction' is a synthetically useful process. The reaction course proposed involves the formation of a sulfonium species (**III**, Scheme 2) which undergoes *in situ* thermolysis, or later hydrolysis to liberate the isolated product.

The product 1,7-dioxa-4-thia-10-azacyclododecane, [12]ane-NO_2S, results after removal of the protecting group. Whilst the use of refluxing acid (HBr–CH_3CO_2H) appears to be a common procedure for aza-, oxaaza- and thiaaza-macrocycles, there are reports of a lack of success with this method.[18] In our hands, the most consistent procedure for the removal of the protecting group proved to be sodium anthracenide, at low temperature.[19]

The ^{13}C NMR spectrum of [12]aneNO_2S displays four peaks indicative of carbon atoms adjacent to a thioether (δ 34.0), a secondary amine (δ 46.6) and ether oxygen (δ 67.8, 69.1). The higher field resonance associated with a carbon adjacent to an ether oxygen (δ 67.8) would appear to be that β to the amine[20] by its greater movement to higher field upon protonation of the secondary nitrogen by HCl(g).

Reaction between the macrocycle and $Hg(NO_3)_2$, in methanol, and subsequent recrystallization of the product from acetonitrile–diethyl ether, resulted in the formation of colourless crystals of [Hg([12]aneNO_2S)$(NO_3)_2$].

Crystal Structures.—The solid-state conformation of [12]-aneNO_2S is based on a distinct quadrangular structure, the ring conformation being [3333].[1,21] The C–C bond lengths are in the range 1.489(9)–1.519(9) Å with the C–O [1.404(9)–1.452(6)

Table 4 Selected bond lengths (Å) and angles (°) in [Hg([12]aneNO_2S)$(NO_3)_2$]

Hg–S(4)	2.5146(6)	S(4)–C(3)	1.820(19)	O(21)–N(20)	1.249(16)	N(10)–C(9)	1.43(2)
Hg–O(1)	2.722(13)	S(4)–C(5)	1.870(19)	O(22)–N(20)	1.266(16)	N(10)–C(11)	1.60(2)
Hg–O(7)	2.654(13)	O(1)–C(2)	1.43(2)	O(23)–N(20)	1.266(16)	C(2)–C(3)	1.47(3)
Hg–O(21)	2.554(10)	O(1)–C(12)	1.44(2)	O(31)–N(30)	1.301(16)	C(5)–C(6)	1.42(3)
Hg–O(23)	2.694(12)	O(7)–C(6)	1.41(2)	O(32)–N(30)	1.211(16)	C(8)–C(9)	1.46(3)
Hg–O(31)	2.307(11)	O(7)–C(8)	1.54(2)	O(33)–N(30)	1.221(16)	C(11)–C(12)	1.42(2)
Hg–N(10)	2.277(12)						

S(4)–Hg–O(1)	73.0(3)	O(7)–Hg–O(31)	155.6(4)	Hg–O(1)–C(12)	103.8(9)	O(22)–N(20)–O(23)	119.7(12)
S(4)–Hg(O(7)	75.1(3)	O(7)–Hg–N(10)	72.9(4)	C(2)–O(1)–C(12)	116.1(13)	O(31)–N(30)–O(32)	119.8(12)
S(4)–Hg–O(21)	132.6(3)	O(21)–Hg–O(23)	48.8(3)	Hg–O(7)–C(6)	110.9(11)	O(31)–N(30)–O(33)	116.4(12)
S(4)–Hg–O(23)	85.5(3)	O(21)–Hg–O(31)	79.2(4)	Hg–O(7)–C(8)	99.1(10)	O(32)–N(30)–O(33)	123.4(13)
S(4)–Hg–O(31)	117.5(3)	O(21)–Hg–N(10)	87.8(4)	C(6)–O(7)–C(8)	118.4(15)	O(1)–C(2)–C(3)	115.2(14)
S(4)–Hg–N(10)	119.1(3)	O(23)–Hg–O(31)	89.8(4)	Hg–O(21)–N(20)	99.6(8)	S(4)–C(3)–C(2)	105.6(13)
O(1)–Hg–O(7)	111.0(3)	O(23)–Hg–N(10)	127.1(4)	Hg–O(23)–N(20)	92.4(8)	S(4)–C(5)–C(6)	117.2(13)
O(1)–Hg–O(21)	154.0(4)	O(31)–Hg–N(10)	112.9(4)	Hg–O(31)–N(30)	113.3(8)	O(7)–C(6)–C(6)	108.2(16)
O(1)–Hg–O(23)	157.0(4)	Hg–S(4)–C(3)	103.2(6)	Hg–N(10)–C(9)	115.5(10)	O(7)–C(8)–C(9)	111.5(14)
O(1)–Hg–O(31)	93.1(4)	Hg–S(4)–C(5)	100.0(6)	Hg–N(10)–C(11)	109.4(8)	N(10)–C(9)–C(8)	111.5(17)
O(1)–Hg–N(10)	72.3(4)	C(3)–S(4)–C(5)	99.0(8)	C(9)–N(10)–C(11)	111.2(13)	N(10)–C(11)–C(12)	112.9(13)
O(7)–Hg–O(21)	77.3(3)	Hg–O(1)–C(2)	107.4(9)	O(21)–N(20)–O(22)	121.1(22)	O(1)–C(12)–C(11)	110.7(15)
O(7)–Hg–O(23)	69.7(3)			O(21)–N(20)–O(23)	119.2(11)		

Table 5 Torsion angles (°) for [12]aneNO_2S and [Hg([12]aneNO_2S)-$(NO_3)_2$]

	[12]aneNO_2S	[Hg[12]aneN_2S) $(NO_3)_2$]
O(1)–C(2)–C(3)–S(4)	61.0(1.5)	68.9(1.6)
C(2)–C(3)–S(4)–C(5)	−165.1(1.3)	−157.9(1.3)
C(3)–S(4)–C(5)–C(6)	67.0(1.4)	64.6(1.5)
S(4)–C(5)–C(6)–O(7)	59.6(1.4)	63.2(1.7)
C(5)–C(6)–O(7)–C(8)	−157.8(1.3)	−162.7(1.6)
C(6)–O(7)–C(8)–C(9)	77.4(1.5)	72.9(1.9)
O(7)–C(8)–C(9)–N(10)	59.4(1.6)	64.5(1.8)
C(8)–C(9)–N(10)–C(11)	−176.7(1.4)	−168.6(1.5)
C(9)–N(10)–C(11)–C(12)	74.3(1.7)	76.5(1.7)
N(10)–C(11)–C(12)–O(1)	64.5(1.5)	65.8(1.7)
C(11)–C(12)–O(1)–C(2)	−150.8(1.3)	−159.0(1.5)
C(12)–O(1)–C(2)–C(3)	82.4(1.6)	72.3(1.8)

Å], C–S [1.803(7), 1.805(5) Å] and C–N [1.451(7), 1.471(7) Å] bond lengths generally as expected.[22–27] Of interest is the intramolecular contact of the hydrogen on the amine with the oxygen heteroatoms of the ring. The proton on N(10) has close contacts of 2.6 and 2.5 Å to the oxygen atoms O(1) and O(7), respectively, with associated N(10)···O(1) and N(10)···O(7) distances of 2.94 and 2.87 Å, respectively. The endodentate conformation of the N–H and close contacts with oxygen donors have been observed previously for the cryptate 4,7,13,-18-tetraoxa-1,10-diazabicyclo[8.5.5]icosane (L) in L·2HCl·$2H_2O$ where the contacts were reported as 2.43(4) and 2.39(3) Å.[28]

A distinctive feature of the structure of the macrocycle is that the heteroatoms are at the 'sides' of the structure. In [12]aneNO_2S the thioether does not appear to exert sufficient demands on the system for it to adopt its typically preferred 'all *gauche*' interactions about the C–C–S–C bonds.[27] The torsion angles around the ring clearly indicate that two of the four C–O bonds are *gauche* and that one of each pair of C–N and C–S interactions are *gauche*. The importance of *gauche* or *anti* placements of C–C–E–C and E–C–C–E (E is a heteroatom) has been widely recognised.[6,22,27] In general it has been observed that the O–C–C–O unit prefers a *gauche* placement due to 1,4-stabilization between the oxygens, whilst S–C–C–S and C–C–O–C prefer *anti* orientations to avoid unfavourable steric interactions.[27] If in this macrocycle the heteroatoms were to take up 'corner' positions as in [12]aneS_4, there would then be four *anti* C–C bonds, four *gauche* C–O bonds and two pairs of *gauche* C–N and C–S interactions. Only the single extra *gauche* C–S placement would definitely improve the 1,4-interactions. A consequence of the positioning of the heteroatoms in the quadrilateral structure is that all of the heteroatoms are found in an endodentate conformation. Typically, with thioether donors the endodentate conformation is regarded as being the most favourable to the formation of metal complexes, a consequence of the lower co-ordination reorganisation energies.[22] For [12]aneNO_2S the endodentate arrangement of the S and O donors will enhance metal binding; however, reorganisation of the NH from *endo* to *exo* is required prior to complexation.

The structure of the mercury complex consists of the metal cation, the macrocycle and two associated anions which are co-ordinated to the cation, one in a bidentate manner, the other as a monodentate ligand. The metal ion is situated asymmetrically above the plane of the macrocyclic ring with the shortest metal–donor interaction being Hg–N 2.28(1) Å, with Hg–S 2.514(6) Å, both distances typical of those found previously for these types of interactions.[29–32] The Hg–O bond distances were found to be 2.722(13) and 2.654(13) Å, shorter than the Hg–O interactions reported in the 18-crown-6 (1,4,7,10,13,16-hexaoxacyclohexadecane) complexes with this metal (2.83 Å),[33] and shorter than the sum of the van der Waals radii of mercury(II) and oxygen.[34]

The Hg–O (nitrate) interactions indicate that one nitrate is co-ordinated in a typically asymmetrically bidentate configuration, with Hg–O(21) 2.554(10) Å and Hg–O(23) 2.694(12)Å.[35,36] The second nitrate is co-ordinated in a monodentate manner with Hg–O(31) 2.307(11) Å, the bond distance being longer than previously observed for similar monodentate nitrate co-ordination to Hg^{II}.[37,38] The unco-ordinated nitrate oxygen O(32) is, however, within hydrogen-bonding distance of the proton of the secondary amine on the macrocyclic ring, at 3.02 Å. Formally the mercury atom is seven-co-ordinate.

The macrocycle itself has undergone little structural change from the free ligand. The rearrangement of the previously endodentate NH to exodentate in the metal complex, with the consequent removal of the stabilization of the hydrogen-bond interactions and complexation of the Hg^{II} results in minor changes in the torsion angles.

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