A preliminary observation of additive thermodynamic contribution of pendant arms to the complexation of calixarene derivatives with mercury(II)

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An additive thermodynamic contribution of pendant arms to the complexation of calixarene derivatives with mercury(II) in acetonitrile is for the first time demonstrated.

This communication concerns *experimental* thermodynamics involving the complexation of Hg(II) with the hydrophilic cavity of calix[4]arenes formed from either four identical pendant arms, *a*, (I); two identical pendant arms *b* and two OH groups on the lower rim, the latter groups taking no (thermodynamic) part in the complexation process to Hg(II) however, (II); or, pairs of mixed pendant arms *a* and *b*, (III).

An important *additivity principle* emerges from these results (shown in Table 1). The thermodynamics of Hg(II) complexation with *p-tert*-butylcalix[4]arenes in acetonitrile such that, $\Delta_c P$, for the cases where $P = G, H$ or S shows that:

$$\Delta_c P_{abab} = 2[\tfrac{1}{4}\Delta_c P_{aaaa}] + 2[\tfrac{1}{2}\Delta_c P_{bOHbOH}] = \tfrac{1}{2}\Delta_c P_{aaaa} + \Delta_c P_{bOHbOH} \quad (1)$$

where the notation $\Delta_c P_{aaaa}$ relates to the parameter P for the calix[4]arene having four pendant arms, *a*, $\Delta_c P_{bOHbOH}$ to the calix[4]arene having two pendant arms *b* and two OH groups attached to the lower rim. We are able to confirm also that the OH group plays no part in the thermodynamics of complexation. It is also anticipated that:

$$\Delta_c P_{abab} = 2[\tfrac{1}{4}\Delta_c P_{aaaa}] + 2[\tfrac{1}{4}\Delta_c P_{bbbb}] = \tfrac{1}{2}[\Delta_c P_{aaaa} + \Delta_c P_{bbbb}] \quad (2)$$

although, the corresponding experiment involving the calix[4] arene having four *b* pendant groups (in the case where b = $OCH_2CH_2SCH_2CH_3$) cannot be performed because the solubility of the latter material is (unfortunately) too low.

The result reported is important for several reasons. Firstly, preliminary indications suggest if this can be applicable to complexation of tetra-*tert*-butyl calix[4]arenes or calix[4]arenes where R = groups other than t-Bu, both *with other pendant arms*

and with *other metal centres* this additivity principle will drastically reduce the number of experiments necessary to quantify the thermodynamics underpinning complexation between metal and hosts.[1–3] Such an achievement would be of environmental topicality[4–6] and could lead the way to development of important new methods for the purging of heavy metals from polluted waters, especially since these calix[4]arene materials are often easily regenerated by pH change or other means. Secondly, once the thermodynamics are quantified for *one metal system*, say Hg(II),

Table 1 Thermodynamic parameters of complexation, pendant arms and additive contributions for mercury(II) complexes with **I**, **II** and **III** in acetonitrile at 298.15 K

Complex	$\Delta_c H^\circ$/ kJ mol^{-1}	Pendant arm contribution/ kJ mol^{-1}	Additive contribution/ kJ mol^{-1}
Hg^{2+}–I	-21.1^a	-5.3	
Hg^{2+}–II	-74^a	-37	
Hg^{2+}–III	-84 ± 1^b	—	-84.6^c
	-83 ± 2^a		

Complex	$T\Delta_c S^\circ$/ kJ mol^{-1}	Pendant arm contribution/ kJ mol^{-1}	Additive contribution/ kJ mol^{-1}
Hg^{2+}–I	-0.1^a	0	
Hg^{2+}–II	-38.2^a	-19.1	
Hg^{2+}–III	-33.2^b	—	-38.2^d

Complex	$\Delta_c G^\circ$/ kJ mol^{-1}	Pendant arm contribution/ kJ mol^{-1}	Additive contribution/ kJ mol^{-1}
Hg^{2+}–I	-21.1^a	-5.3	
Hg^{2+}–II	-37.2^a	-18.6	
Hg^{2+}–III	-50^a	—	-47.8^d

[a] Values determined using 'direct macrocalorimetric titration'. [b] Values determined using 'competitive macrocalorimetric titration'. [c] Sum of two ester + two thioethyl pendant arms (kJ mol^{-1}) = $(2 \times -5.3) + (2 \times -37) = -84.6$ kJ mol^{-1}. [d] $(2 \times -5.3) + (2 \times -18.6) = -47.8$ kJ mol^{-1} and $(2 \times 0) + (2 \times -19.1) = -38.2$ kJ mol^{-1}. [e] Macro-calorimetric titrations were performed as detailed elsewhere[7,8] to determine the thermodynamic parameters of complexation for the systems investigated. A solution of the mercury perchlorate ($2.0–5.0 \times 10^{-2}$ mol dm^{-3}) was prepared in acetonitrile, placed in the burette, and titrated into the vessel containing a solution of **II**, (50 cm^3, $6.0 \times 10^{-4}–1.0 \times 10^{-3}$ mol dm^{-3}) prepared in the same solvent. Thermodynamic parameters for a single system were determined at different concentrations of the metal-ion salt, to ensure that no ion-pair formation occurred within the working concentration range. All measurements were conducted in triplicate and the average value is reported in Table 1.

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measurement of $\Delta_c P_{aaaa}$ and either $\Delta_c P_{bbbb}$ (or $\Delta_c P_{bOHbOH}$) for a *second* metal will then enable the prediction of the remaining thermodynamics involving other pendant arms *etc.* to be made quickly and easily. This in turn will enable us to circumvent practical problems which can arise from either low solubility of materials or where interaction of complexing arene and metal ion (*e.g.* Ag$^+$ with (**I**) when a = the (ethylethanoate)oxy pendant in the solvent acetonitrile) is so relatively weak (log $K_s \approx 1$; $\Delta_c G$/kJ mol$^{-1} \approx -6$) as to prevent accurate measurement by any of the techniques available (*i.e.* titration calorimetry, potentiometry and UV spectrophotometry).

Thirdly, the thermodynamic feasibility of employing metal calix[4]arene extractants which would be time consuming and possibly difficult to synthesize could be gauged initially by analogy. For example, $\Delta_c P_{abcd}$ for a calixarene having *four different* pendant arms (*a, b, c, d*) could be estimated from:

$$\Delta_c P_{abcd} = \frac{1}{4}[\Delta_c P_{aaaa} + \Delta_c P_{bbbb} + \Delta_c P_{cccc} + \Delta_c P_{dddd}] \quad (3)$$

This communication presents for the first time in the field of calixarene chemistry, a thermodynamic model involving the complexation of Hg^{2+} with three calix[4]arene derivatives (in acetonitrile at 298.15 K) listed in Table 1, demonstrating the additive contribution of pendant arms. The three calixarenes[7,8] investigated experimentally are the fully substituted 5,11,17,23-tetra-*tert*-butyl-[25,26,27,28-(ethylethanoate)oxy]-calix[4]arene, (**I** having a = O·CH$_2$·(C=O)·O·CH$_2$·CH$_3$ and 5,11,17, 23-tetra-*tert*-butyl[25,27-bis(ethylethanoate)oxy-26,28-bis(ethylthioethoxy)]-calix[4]arene, (**III** having two pairs of pendants: a and the ethyl-thioethoxy pendant, b = O·CH$_2$·CH$_2$·S·CH$_2$·CH$_3$) and the partially substituted 5,11,17,23,tetra-*tert*-butyl-[25,27-bis(hydroxy)-26,28-bis(ethylthioethoxy)]-calix[4]arene, (**II** having a pair of pendants b = O·CH$_2$·CH$_2$·S·CH$_2$·CH$_3$ (see Fig. 1).

As far as the complexation of Hg^{2+} and these ligands in acetonitrile is concerned, the additive cooperative effect of the ester and the thioethyl pendant arms of **I** and **II** respectively (through the O in **I** and sulfur donor atoms in **II**) to the complexation of **III** is demonstrated through thermodynamics. Indeed the data fits into a model in which the hydrophilic cavity of **III** is built from the contribution of two of the four-ester pendant arms of **I** and two thioethyl arms of **II** as detailed in Table 1. This table shows the thermodynamic parameters of complexation for these ligands and Hg^{2+} in acetonitrile (second column in Table 1). Then data for **I** and **II** are split into four and two respectively (eqn. 1) to calculate the impact of each arm (third column in Table 1). The sum of the contributions of two ester and two thioethyl pendant arms from **I** and **II** yields $\Delta_c G°$, $\Delta_c H°$ and $T\Delta_c S°$ values for the complexation of **III** and Hg^{2+} in acetonitrile (last column in Table 1). For this system excellent agreement is found between the data obtained directly (column 2, Table 1) and indirectly (last column in Table 1).
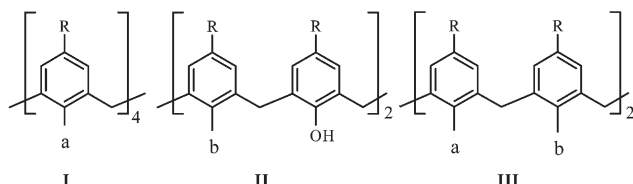
From the above discussion it follows that in the complexation of this cation and **III** in acetonitrile, although the strongest interaction occurs with the pendant arms containing sulfur donor atoms, the ester pendant arms are also participating in the binding process.

$$\Delta_c P_{bOHbOH} = \frac{1}{2}\Delta_c P_{bbbb} \quad (4)$$

The above findings are concomitant with the X-ray structure of the mercury(II) complex with **II** (see the ORTEP[9] plot of Fig. 2) which shows that in the solid state mercury(II) ion binds to the two sulfur atoms of the calix pendant arms and to two perchlorate ions (counter ions of the mercury salt) to form a tetra-coordinated complex. The calix[4]arene ligand adopts the conformation of a cone squashed onto a plane defined by the largest cone aperture and the calix axis. The sulfur-containing pendant arms are approximately mirror related to each other through this plane. This is quantitatively indicated by the close absolute values and opposite signs of the corresponding torsion angles of both Ph–O–CH$_2$–CH$_2$–S–CH$_2$–CH$_3$ pendant arms (absolute differences less than 7.8°). The mercury(II) ion, laying onto the mirror plane and shifted in about 2 Å from the calix axis, is *trans* coordinated to the sulfur atoms of the opposite pendant arms, conforming a nearly linear S–Hg–S bonding with Hg–S distances of 2.381(2) and 2.388(2) Å. A pair of oxygen atoms from two neighbouring perchlorate anions complete the remaining *trans* positions of a distorted square coordination S$_2$O$_2$ around mercury [Hg–O(perch) contacts of 2.655(7) and 2.70(2) Å]. *Trans* S–Hg–S and O–Hg–O angles are 170.12(8) and 161.7(5)°, respectively, and *cis* S–Hg–O angles vary in the range from 74.4(5) to 95.8(5)°. The S$_2$O$_2$ group departs slightly from a planar arrangement (rms deviation of 0.168 Å) with the metal at 0.181(5) Å from the least-squares plane. The short O1···O4 and O3···O2 distances of 2.758 and 2.818 Å observed in the calix[4]arene lower bore suggest that the complex is further stabilized by a pair of O–H···O bonds.†
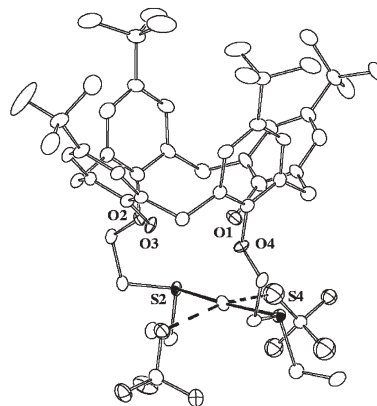
Fig. 2 Side view of the mercury(II) complex with **II** in the **II**Hg(ClO$_4$)$_2$·2MeCN crystal. Only one of the two positions exhibited by the rotationally disordered perchlorate ion is included in the plot. For clarity, only a few representative atomic labels are shown. Mercury–sulfur bonds are emphasized by full lines and Hg···O(perch) and O–H···O(pend) contacts by dashed lines. Selected bond distances (Å): Hg–S(2) = 2.381(2), Hg–S(4) = 2.388(2), Hg–O(perch) contacts of 2.655(7) and 2.70(2).

Fig. 1 Structures of ligands **I**, **II** and **III**.

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