Mercaptocalixarenes as Mercury(II) Extractors: Synthesis, Structural Analysis and Extraction Properties of Lipophilic Dimercaptocalix[4]arenes

Photon Rao,[a] Olivier Enger,[a] Ernest Graf,[a] Mir Wais Hosseini,*[a] André De Cian,[b] and Jean Fischer[b]

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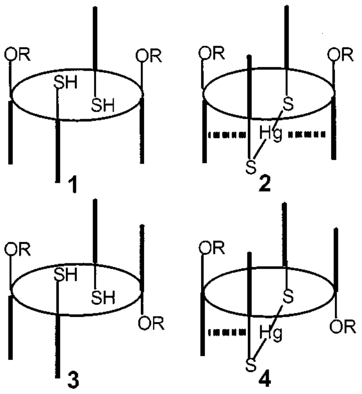
Lipophilic calix[4]arene derivatives that contain two O–C_{12} alkyl chains and two SH groups at the lower rim were synthesized and characterized in the 1,2- and partial-cone conformations. Both conformers were treated with Hg^{2+} and formed neutral mononuclear Hg^{2+} complexes, in which the cation was linearly coordinated to two sulfur atoms. The lipophilic dimercaptocalixarenes were shown to extract Hg^{2+} cations exclusively and efficiently from an aqueous phase into chloroform.

Introduction

The presence of toxic heavy metals in aqueous reservoirs is an important environmental issue.[1] In particular, the mercury(II) cation represents an environmental danger to a variety of living organisms, including mammals,[2] due to its toxicity. Because of the use of mercury derivatives in fungicides and insecticides, Hg^{2+} cations are present in our environment at a rather high level.[3] Since the extraction of heavy metal cations such as Hg^{2+} from aqueous solutions into organic phases may be a possible alternative for water purification, the design of selective extractors for heavy metals appeared to us to be an interesting challenge.

The affinity of mercury for sulfur-containing ligands has been well established.[4] Based on this observation, calixarene derivatives bearing pendent sulfur atoms,[5] and thiacrown ethers[6] have been used as extractors for Hg^{2+} cations. In this context, we and others have been working on sulfur-containing calixarene derivatives such as di-[7] and tetramercaptocalix[4]arenes,[8,9] in which two and four OH groups were replaced by two or four SH functions, respectively as well as mercaptoparacyclophane[10] and thiacalix[4]arenes.[11,12]

We have previously demonstrated that di-[7] and tetramercaptocalix[4]arenes[9] were able to form mono- and binuclear mercury complexes, respectively, in which the calix unit adopted the 1,3-alternate conformation. The cation was therefore strongly coordinated to two thiolate centres, and experienced other interactions with two aromatic rings, thus fulfilling its "2 + 4" coordination requirements. With this insight, the ligand **1**, composed of the *p-tert*-butylcalix[4]arene backbone bearing two SH and two OC_{12} groups, was designed. The two alkyl chains were introduced in order to increase the lipophilicity of the Hg^{2+} complex **2** (Scheme 1).



Scheme 1

In this contribution we report the synthesis of **1** and **3**, and their Hg^{2+} complexes **2** and **4**, respectively, as well as the extraction of mercury from water into chloroform by conformers **1** and **3**.

Results and Discussion

Synthesis

The synthetic strategy used to prepare **1** was based on dithiacarbamoylation of *p-tert*-butylcalix[4]arene **5**[13] at the 1- and 3-positions, followed by transformation of the remaining two OH groups into ether fragments by treatment with bromododecane. Thermal rearrangement of the $OCSNMe_2$ fragments into the $SCONMe_2$ groups was then accomplished by the Newman−Kwart method,[14] and finally, the reductive deprotection of the sulfur atoms using $LiAlH_4$ yielded the desired mercapto derivatives **1** and **3** (Scheme 2 and 3).

Thiacarbamoylation of *p-tert*-butylcalix[4]arene with $(Me)_2NCSCl$ in the presence of K_2CO_3 in refluxing acetone for 24 h yielded 5−10% of the trisubstituted derivative, as

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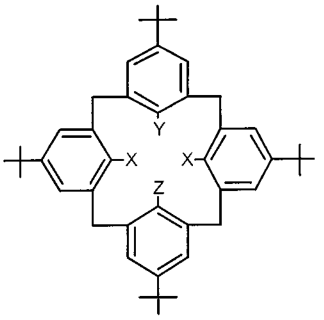
[a] Laboratoire de Chimie de Coordination Organique,
Université Louis Pasteur (UMR CNRS 7513),
67000 Strasbourg, France
E-mail: hosseini@chimie.u-strasbg.fr
[b] Laboratoire de Cristallochimie et Chimie Structurale,
Université Louis Pasteur (UMR CNRS 7513),
67000 Strasbourg, France



1 or **3** X = O-$(CH_2)_{11}$-CH_3, Y = Z = SH
5 X = Y = Z = OH
6 or **10** X = OH, Y = Z = $OCSNMe_2$
7 or **11** X = O-$(CH_2)_{11}$-CH_3, Y = Z = $OCSNMe_2$
8 or **12** X = O-$(CH_2)_{11}$-CH_3, Y =$OCSNMe_2$, Z = $SCONMe_2$
9 or **13** X = O-$(CH_2)_{11}$-CH_3, Y = Z = $SCONMe_2$

Scheme 2

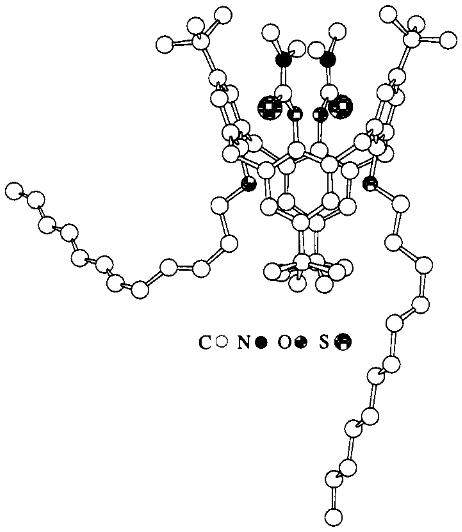
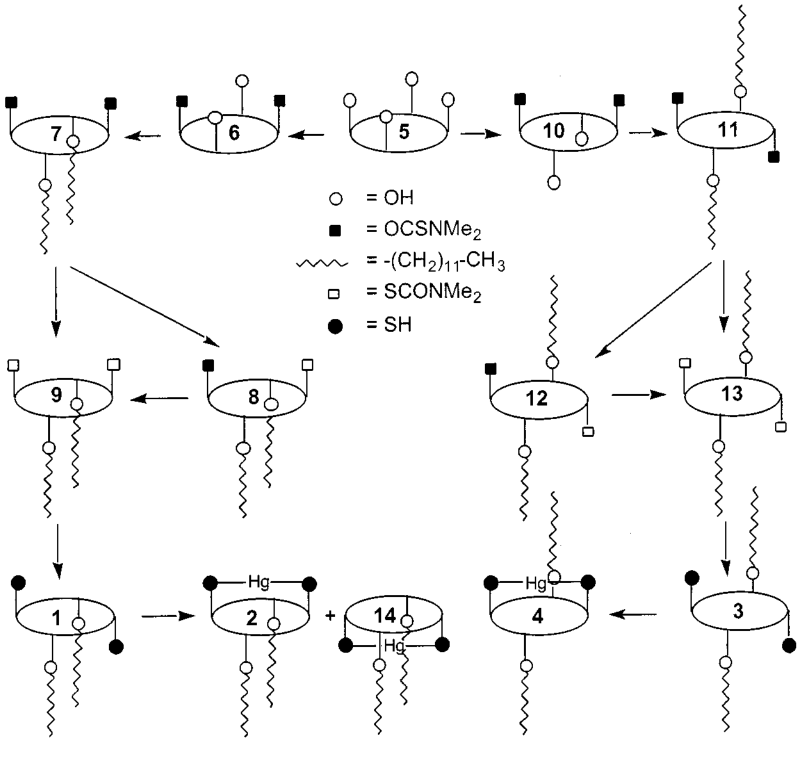


Figure 1. X-ray structure of the disubstituted compound **7** in the 1,3-alternate conformation; for the sake of clarity, H atoms are not represented; selected average bond lengths and angles: $d_{C=S}$ = 1.66 Å, d_{C-N} = 1.33 Å, d_{C-OPh} = 1.36 Å, d_{N-CH3} = 1.45 Å, OCS angle = 124.5°, NCS angle = 125.5°, NCO angle = 110.05°

well as the disubstituted conformers **6** (13%) and **10** (40%), non interconvertible at room temperature. While the treatment of **6** with bromododecane in the presence of NaH in refluxing THF afforded the tetrasubstituted compound **7** in the 1,3-alternate conformation in quantitative yield after 24 h, surprisingly, under the same conditions, the reaction of **10** afforded the compound **11** in the 1,2-alternate conformation. Both compounds **7** (Figure 1) and **11** (Figure 2) were characterized in the solid state by single-crystal X-ray diffraction methods.

The thermal rearrangement of **7** was performed in vacuum on the melt at 340 °C, and yielded the mono-rearranged compound **8** (50%), the bis-rearranged compound **9** (25%) and the unchanged starting material **7** (25%). Subsequently, compound **8** could be rearranged in 20% yield to **9** under similar conditions. Attempts to increase the yield



Scheme 3

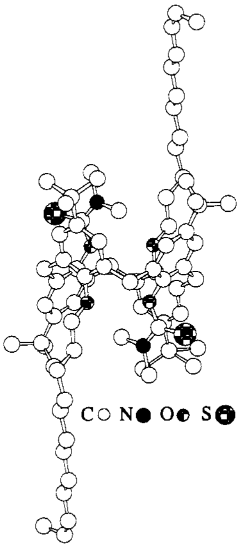


Figure 2. X-ray structure of compound **11** in the 1,2-alternate conformation; for the sake of clarity, H atoms are not represented; selected bond lengths and angles: $d_{C=S}$ = 1.66 Å, d_{C-N} = 1.32 Å, d_{C-OPh} = 1.36 Å, d_{N-CH_3} = 1.47 Å, OCS angle = 123.8°, NCS angle = 126.4°, NCO angle = 109.7°

by performing the reaction in refluxing ditolyl ether failed.[8] Reductive deprotection of **9** was performed using $LiAlH_4$ in refluxing THF, yielding the dimercapto compound **1** (80%) in the partial cone conformation. On the other hand, performing the same sequence of reactions on **11** afforded **12** (40%), the bis-rearranged derivative **13** (20%), and the starting compound **11** (40%). As before, **12** could be rearranged into **13** under the same conditions in 15% yield. Compound **13**, in the 1,2-alternate conformation, was transformed into the desired compound **3** in 74% yield by treatment with $LiAlH_4$ in refluxing THF. The final structural assignment of both **1** and **3** was based on 2D-ROESY NMR data.

Complexation

In order to isolate the mercury complexes **2** and **4**, compounds **1** and **3** were treated with mercuric acetate in refluxing THF for 30 min. For the Hg^{2+} complex **2** that formed with compound **1**, the calix unit was in the 1,3-alternate conformation, whereas in the case of the complex **4** formed with compound **3**, the calix unit was found to be in the partial cone conformation (Scheme 1). These two conformations for the calix backbone were established by 2D-ROESY as well as by ^{199}Hg-NMR experiments. Mercury resonances were observed at $\delta = -1375$ for **2** and at $\delta = -1294$ for **4**. These values are close to the one observed previously ($\delta = -1394$) for the bis(binuclear) mercury complex formed with tetramercaptocalix[4]arene,[9] in which the 1,3-alternate conformation was established by X-ray crystallography. The difference in the chemical shifts observed for **2** and **4** may be rationalized in terms of the Hg^{2+}−aromatic interactions. Indeed, based on previous observations, the rather negative chemical shift value observed may be attributed to the local environment of the metal centre in both **2** and **4** complexes, where the Hg^{2+} cation is completely and half-sandwiched between two aromatic rings, respectively. The observation of a ^{199}Hg-NMR signal at $\delta = -1054$ for the (*p*-*tert*-butyl−Ph−S)$_2$Hg complex supports the above explanation, because in that case, no Hg^{2+}−aromatic interactions would be present.

Extraction

In this contribution, we report only some preliminary investigations dealing with the extraction of heavy metal cations. The extraction ability of both compounds **1** and **3** was studied under the following conditions: A 5-mL $CHCl_3$ solution of **1** or **3** (mM concentration) was stirred for 30 min in the presence of a 5-mL 95% aqueous acetic acid solution containing $Hg(OAc)_2$ (mM concentration). Aliquots were taken from the aqueous phase, and the amount of mercury remaining was determined by colourimetric titration with dithizon (see Table 1).

Table 1. Extraction of M^{2+} by **1** and **3**

	(mM)[a]	M^{2+}	[M^{2+}] (mM)[b]	%[c]
1	2.8	Hg^{2+}	1.5	100
1	2.8	Hg^{2+}	3.0	87
1	2.8	Hg^{2+}	10.0	34
3	2.8	Hg^{2+}	10.0	34
1	2.8	Pb^{2+}	11.0	none[d]
1	2.8	Cd^{2+}	10.0	none[d]
3	3.0	Pb^{2+}	11.0	none[d]
3	3.0	Cd^{2+}	10.0	none[d]

[a] A solution of the ligand prepared in $CHCl_3$. − [b] A solution of $M(OAc)_2$ in 95% aqueous acetic acid. − [c] Determined (accuracy 0.05 mM) by titrating the aqueous layer after extraction with a solution of dithizon. − [d] Also confirmed by ^{1}H NMR which shows only the presence of the free ligand after the removal and evaporation of the $CHCl_3$ layer.

The nature of the complexes formed between ligands **1** or **3** and mercury cation under extraction conditions was investigated in the following manner: A biphasic mixture composed of a $CHCl_3$ solution containing either the ligand **1** or **3** in mM concentration, an aqueous phase containing 5% acetic acid, added in order to avoid the hydrolysis of the mercuric salt, and $Hg(OAc)_2$ in mM concentration, was stirred at room temperature. As expected, it was found that Hg^{2+} cations were extracted from the aqueous phase into the organic layer. After removal of the organic phase and evaporation of the $CHCl_3$, the nature of the extracted complexes was elucidated by ^{1}H NMR ($CDCl_3$, 25 °C), which showed that in both cases the extracted complexes were identical to the prepared and independently identified complexes **2** and **4**, respectively. However, in the case of ligand **1**, a small amount of another complex showing a rather high symmetry was detected by ^{1}H NMR. This compound was separated by preparative thin layer chromatography and was investigated by mass spectrometry in the FAB^+ mode, and showed a peak at 1216.8 (100%) identical to that observed for mercury complexes **2** and **4**. Furthermore, performing ^{1}H NMR ($CDCl_3$, 25 °C) on the isolated complex, demonstrated that it was the other possible complex **14** (Scheme 3), where the calix unit adopts the cone conformation. However, in marked contrast with complex **2**, where the calix unit, by adopting the 1,3-alternate conformation, allows both the coordination of the metal cation to two thiolate centres as well as metal−π interactions through the formation of the sandwich complex, in the case of **14** only the coordination of the metal cation to two thiolate groups is possible. This fact may explain the formation of **14** in rather low yield.

When compound **1** (2.8 mM) was present in excess with respect to Hg^{2+} (1.5 mM), 100% of the cation was extracted into chloroform, indicating the high affinity of **1** for mercury cations (see Table 1). On the other hand, in the case of a slight (3.0 mM) or a large (10.0 mM) excess of Hg^{2+} cations, 87% and 34% extraction was observed, respectively. Interestingly, under the same conditions, no extraction of Cd^{2+} or Pb^{2+} cations was observed using **1** or **3**, demonstrating the remarkable selectivity of both compounds **1** and **3** for the Hg^{2+} cations with respect to cadmium and lead cations. The latter observation demonstrates the validity of the design of selective extracting agents for mercury cations.

Conclusions

In conclusion, the synthesis of two new mercaptocalix[4]arene derivatives bearing long alkyl chains was achieved. Both compounds were shown to efficiently and selectively extract the Hg^{2+} cation from acidic aqueous solution into chloroform. Both compounds showed remarkable selectivity towards Hg^{2+} cation with respect to Cd^{2+} and Pb^{2+} cations. A systematic study of the extraction ability of the reported compounds is currently under investigation.

Experimental Section

General: ^{1}H-, ^{13}C- and ^{199}Hg-NMR spectra were recorded with Bruker WP 200SY and AM 400 instruments operating at 200.13, 50.32, and 71.66 MHz, respectively. ^{1}H-NMR peak positions are reported relative to $CHCl_3$ (δ = 7.26). ^{13}C-NMR peak positions are reported relative to $CDCl_3$ (δ = 77. 0). ^{199}Hg-NMR peak position are reported relative to $CH_3S-Hg-SCH_3$ as external reference. Mass spectra (FAB^+) were recorded in nitrobenzyl alcohol.

Procedure for the Preparation of Compounds 6 and 10: To a slurry of **5**[13] (16.00 g, 25 mmol) in acetone (600 mL), K_2CO_3 (13.8 g, 100 mmol) was added, and the mixture was heated under reflux for 30 min. Then, a solution of *N*,*N*-dimethylthiocarbamoyl chloride (12.5 g, 100 mmol) in acetone (20 mL) was added and refluxing was continued for a further 16 h. Volatile components were removed under vacuum, and the contents of the flask was diluted with water (50 mL) and acidified to pH = 2 by careful addition of dilute aqueous H_2SO_4. The solid thus obtained was extracted with CH_2Cl_2 (5×100 mL) and the removal of the solvent left a crude material which was purified by column chromatography (SiO_2, CH_2Cl_2), and yielded 13% (2.7 g) of **6** and 40% (8.1 g) of **10**.

Compound 6: M.p. > 350 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.00 (s, 18 H), 1.32 (s, 18 H), 3.13 (s, 12 H), 3.49 (s, 12 H), 3.48 (d, *J* = 15 Hz, 4 H), 3.82 (d, *J* = 15 Hz, 4 H), 4.79 (s, 2 H), 6.88 (s, 4 H), 7.07 (s, 4 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.1, 31.8, 33.7, 34.0, 34.1, 38.4, 43.6, 125.5, 126.1, 128.0, 132.2, 142.5, 146.6, 148.9, 150.6, 186.8. − MS (FAB^+); *m*/*z* (%): 823.3 (100) $[M^{\cdot+}]$, 734.2 (90) $[M^+ - OCSN(Me)_2]$. − $C_{50}H_{66}N_2O_4S_2{\cdot}H_2O$ (841.23): calcd. C 71.39, H 8.15; found C 71.53, H 7.95.

Compound 10: M.p. > 350 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.28 (s, 18 H), 1.32 (s, 18 H), 1.71 (s, 12 H), 3.21 (s, 12 H), 3.63 (d, *J* = 15 Hz, 4 H), 4.00 (d, *J* = 15 Hz, 4 H), 4.81 (s, 2 H), 7.06 (s, 4 H), 7.26 (s, 4 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.4, 31.8, 34.0, 34.4, 36.7, 43.4, 125.0, 126.4, 133.1, 142.8, 147.3, 149.1, 149.8, 184.7. − MS (FAB^+); *m*/*z* (%): 823.3 (100) $[M^+]$.

General Procedure for the Preparation of Compounds 7 and 11: To a slurry of either compound **6** or **10** (0.50 g, 0.6 mmol) in THF (50 mL) was added NaH (0.20 g, 8.3 mmol) followed by bromododecane (2.0 mL, 8.7 mmol), and the mixture heated under reflux for 8 h. Volatile components were removed under vacuum, and the reaction mixture quenched by dropwise addition of water (5 mL). After acidification with dilute aqueous H_2SO_4, the solid was extracted in CH_2Cl_2. Volatile components were again removed under vacuum, and the crude material was purified by column chromatography (SiO_2, CH_2Cl_2/hexane: 1:1) affording **7** or **11** in quantitative yields.

Compound 7: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.6 Hz, 6 H), 1.15−1.35 (m, 36 H), 1.50−1.65 (m, 4 H), 2.16 (s, 6 H), 3.39 (s, 6 H), 3.51 (t, *J* = 8 Hz, 4 H), 3.60 (d, *J* = 2.2 Hz, 2 H), 3.71 (d, *J* = 15 Hz, 4 H), 6.87 (s, 4 H), 7.09 (s, 4 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1, 22.6, 25.7, 26.1, 29.3, 29.5, 29.6, 29.7, 31.4, 31.6, 31.8, 33.9, 34.0, 38.2, 38.6, 43.4, 71.1, 126.0, 126.8, 132.5, 134.4, 143.3, 145.8, 148.6, 155.8, 185.9. − MS (FAB^+); *m*/*z* (%): 1159.7 (100) $[M^+]$. − $C_{74}H_{114}N_2O_4S_2$ (1159.86): calcd. C 76.63, H 9.91, N 2.42; found C 76.76, H 9.80, N 2.38.

Compound 11: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.6 Hz, 6 H), 1.11−1.37 (m, 40 H), 1.32 (s, 18 H), 1.34 (s, 18 H), 1.42 (s, 6 H), 3.13 (s, 6 H), 3.32 −3.52 (m, 6 H), 3.82−3.95 (m, 6 H), 6.91 (d, *J* = 2.2 Hz, 2 H), 7.09 (d, *J* = 2.2 Hz, 2 H), 7.28 (d, *J* = 2.2 Hz, 2 H), 7.35 (d, *J* = 2.2 Hz, 2 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1, 22.6, 25.5, 29.2, 29.5, 30.2, 31.5, 31.7, 31.8, 34.0, 34.2, 37.2, 39.3, 43.2, 74.2, 125.1, 125.3, 125.5, 125.8, 132.7, 133.3, 133.4, 134.8, 145.1, 147.0, 147.5, 154.0, 184.7. − MS (FAB^+); *m*/*z* (%): 1159.7 (100) $[M^+]$. − $C_{74}H_{114}N_2O_4S_2$ (1159.86): calcd. C 76.63, H 9.91, N 2.42; found C 76.57, H 9.76, N 2.36

Compounds 8 and 9: In a round-bottomed flask, compound **7** (0.21 g, 0.18 mmol) was heated under vacuum to 340 °C for 3 h. The reaction mixture was purified by column chromatography (SiO_2, CH_2Cl_2) affording 50% (0.10 g) of the mono-rearranged compound **8** and 25% (0.05 g) of the bis-rearranged compound **9**, along with 25% (0.06 g) of the starting material **7**.

Compound 8: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6.6 Hz, 6 H), 1.26 (s, 58 H), 1.32 (s, 18 H), 1.66 (s, 3 H), 2.70−3.00 (m, 6 H), 3.29 (s, 3 H), 3.35−3.50 (m, 4 H), 3.72 (d, *J* = 17 Hz, 2 H), 3.87 (d, *J* = 17 Hz, 2 H), 6.87 (d, *J* = 2.2 Hz, 2 H), 7.02 (s, 2 H), 7.02 (d, *J* = 2.2 Hz, 2 H), 7.19 (s, 2 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1, 14.2, 22.8, 25.9, 29.0, 29.4, 29.7, 30.1, 31.4, 31.7, 31.8, 32.0, 34.0, 34.2, 34.3, 36.6, 38.7, 39.7, 42.5, 43.5, 70.6, 77.4, 122.7, 125.5, 126.4, 128.0, 128.6, 133.0, 134.2, 134.8, 144.2, 146.4, 146.9, 148.9, 150.3, 155.0, 167.4, 184.4. − MS (FAB^+); *m*/*z* (%): 1160.0 (100) $[M^{\cdot+}]$.

Compound 9: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6 Hz, 6 H), 1.10−1.40 (m, 40 H), 1.26 (s, 18 H), 1.30 (s, 18 H), 2.60−2.80 (br. s, 6 H), 2.80−3.30 (br. s, 6 H), 3.35−3.45 (m, 4 H), 3.89 (s, 8

H), 7.00 (s, 4 H), 7.12 (s, 4 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.2, 21.0, 22.0, 25.9, 29.2, 29.4, 29.7, 30.0, 31.0, 31.4, 31.7, 34.0, 34.3, 36.7, 42.5, 71.1, 123.0, 126.1, 127.9, 134.5, 144.0, 146.3, 149.5, 150.0, 168.0. − MS (FAB$^+$); *m/z* (%): 1160.0 (100) [$M^{\cdot+}$].

Compounds 12 and 13: In a round-bottomed flask, compound **11** (0.1 g, 0.08 mmol) was heated under vacuum to 340 °C for 3 h. The reaction mixture was purified by column chromatography (SiO_2, CH_2Cl_2) affording 40% (0.04 g) of the mono-rearranged compound **12** and 20% (0.02 g) of the bis-rearranged compound **13**, along with 40% (0.04 g) of the starting material **11**.

Compound 12: ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.8−1.5 (m, 88 H), 2.74 (s, 6 H), 3.1−4.1 (m, 10 H), 4.54 (d, *J* = 12 Hz, 2 H), 6.88−7.43 (m, 8 H).

Compound 13: ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.8−0.9 (m, 6 H), 1.0−1.4 (m, 88 H) 2.6−4.0 (m, 10 H), 4.2−4.6 (m, 2 H), 6.84, − 7.38 (m, 8 H).

Compound 1: To a solution of **9** (0.08 g, 0.07 mmol) in dry THF (10 mL) was added $LiAlH_4$ (0.02 g, 0.5 mmol) and the solution was heated under reflux for 3 h. After cooling, the reaction mixture was quenched by dropwise addition of H_2O, and acidified to pH = 2 with aqueous 10% H_2SO_4. The crude product was extracted with CH_2Cl_2 (20 × 2 mL). After removal of the solvent, the crude material was purified by column chromatography (SiO_2; CH_2Cl_2/hexane, 75:25) affording the desired compound **1** in 80% yield (0.06 g). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6 Hz, 6 H), 1.04 (s, 18 H), 1.20−1.45 (m, 40 H), 1.32 (s, 9 H), 1.35 (s, 9 H), 2.15 (s, 1 H), 3.37 (s, 1 H), 3.48 (d, *J* = 3.2 Hz, 2 H), 3.63 (dd, *J* = 7.2 Hz, 4 H), 3.85−4.00 (m, 6 H), 6.60 (d, *J* = 2.5 Hz, 2 H), 7.11 (s, 2 H), 7.15 (d, *J* = 2.5 Hz, 2 H), 7.43 (s, 2 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.2, 22.8, 26.6, 29.4, 29.7, 30.9, 31.3, 31.5, 32.0, 33.8, 34.0, 34.3, 34.9, 40.6, 75.5, 125.0, 125.6, 128.5, 130.3, 130.7, 130.8, 140.0, 140.5, 141.7, 143.6, 145.7, 146.7, 154.1. − MS (FAB$^+$); *m/z* (%): 1016.8 (100) [$M^{\cdot+}$], 829.6 (60). − HRMS ($C_{68}H_{104}O_2S_2$): calcd. 1016.7478; found 1016.7474.

Compound 3: To a solution of **13** (0.05 g, 0.043 mmol) in dry THF (10 mL) was added $LiAlH_4$ (0.02 g, 0.5 mmol) and the solution was heated under reflux for 3 h. After cooling, the reaction mixture was quenched by dropwise addition of H_2O, and acidified to pH = 2 with aqueous 10% H_2SO_4. The crude product was extracted with CH_2Cl_2 (20×2 mL). After removal of the solvent, the crude material was purified by column chromatography (SiO_2; CH_2Cl_2/hexane, 75:25) affording the desired compound **3** in 74% yield (0.04 g). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.6 Hz, 6 H), 1.10−1.40 (m, 40 H), 1.24 (s, 18 H), 1.33 (s, 18 H), 2.84 (s, 2 H), 3.40 (t, *J* = 6.6 Hz, 4 H), 3.70 (d, *J* = 14 Hz, 4 H), 4.24 (d, *J* = 14 Hz, 4 H), 7.08 (s, 4 H), 7.19 (s, 4 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.0, 24.0, 27.2, 30.0, 30.2, 30.3, 30.8, 32.7, 32.8, 33.0, 35.5, 74.8, 125.3, 127.4, 128.0, 134.6, 143.2, 145.0, 155.0, 157.5.

General Procedure for the Preparation of Complexes 2 and 4: To a THF solution (1.0 mL) of the dithiol **1** or **3** (0.010 g, 0.01 mmol), excess $Hg(OAc)_2$ (0.10 g, 0.3 mmol) was added and the mixture stirred for 30 min. After evaporation of the solvent, the residue was extracted with CH_2Cl_2 (5×4 mL). After removal of the solvent, the crude mixture was purified by column chromatography (SiO_2) using as eluent 10−20% CH_2Cl_2/hexane in the case of the complex **2** and 20−40% CH_2Cl_2/hexane in the case of the complex **4**. Whereas complex **2** was obtained in quantitative yield (0.012 g), complex **4** was isolated in 74% yield (0.009 g).

Complex 2: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6 Hz, 6 H), 1.28 (s, 18 H), 1.31 (s, 58 H), 3.56 (t, *J* = 8 Hz, 4 H), 4.05 (d, *J* = 15 Hz, 4 H), 4. 17 (d, *J* = 15 Hz, 4 H), 7.11 (s, 4 H), 7.32 (s, 4 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0, 22.8, 26.1, 29.5, 29.6, 29.7, 29.8, 31.4, 31.7, 31.9, 34.2, 43.3, 72.0, 126.5, 132.0, 134.1, 145.0, 154.5. − ^{199}Hg NMR (72 MHz, $CDCl_3$): δ = −1375. − MS (FAB$^+$); *m/z* (%): 1216.8 (75) [M^+, $C_{68}H_{102}HgO_2S_2$], 1159.9 (25) [M^+ − isobutene], 1016.1 (25) [M − Hg]$^+$, 829.6 (55) [M^+ − Hg − $O(CH_2)_{11}CH_3$].

Complex 4: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 3 H), 0.89 (t, *J* = 6.6 Hz, 3 H), 1.20 (s, 18 H), 1.26 (s, 54 H), 1.95 (dd, *J* = 9.4 Hz, *J* = 7.2 Hz, 4 H), 3.13 (t, *J* = 8 Hz, 2 H), 3.54 (d, *J* = 12 Hz, 2 H), 3.95 (t, *J* = 7.0 Hz, 2 H), 4.07 (d, *J* = 16 Hz, 2 H), 4.33 (d, *J* = 16 Hz, 2 H), 5.29 (d, *J* = 12 Hz, 2 H), 6.92 (d, *J* = 2 Hz, 2 H), 7.23 (s, 2 H), 7.25 (d, *J* = 2 Hz, 2 H), 7.40 (s, 2 H). − ^{13}C NMR(50 MHz, $CDCl_3$): δ = 14.2, 22.7, 25.7, 26.4, 29.4, 29.7, 31.3, 31.6, 31.8, 32.0, 34.1, 34.3, 35.0, 44.6, 71.0, 124.8, 125.2, 125.6, 130.9, 134.2, 134.7, 144.7, 147.9. − ^{199}Hg NMR (72 MHz, $CDCl_3$): δ = −1294. − MS (FAB$^+$); *m/z* (%): 1216.8 (40) [M^+, $C_{68}H_{102}HgO_2S_2$], 829.6 (30) [M^+ − Hg − $O(CH_2)_{11}CH_3$].

Complex 14: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 2.5 Hz, 6 H), 0.89 (s, 18 H), 1.20 −1.40 (m, 40 H), 1.32 (s, 18 H), 3.45 (d, *J* = 13 Hz, 4 H), 3.92 (t, *J* = 8 Hz, 4 H), 5.40 (d, *J* = 13 Hz, 4 H), 6.73 (s, 4 H), 7.18 (s, 4 H). − MS (FAB$^+$); *m/z* (%): 1216.8 (100) [M^+], 829.5 (87) [M^+ − Hg − $O(CH_2)_{11}CH_3$].

Crystal Structures: X-ray structure determinations of single crystals were performed with an Enraf−Nonius Kappa CCD. For all computations the Nonius OpenMoleN package[15] was used. Absorption corrections were partially integrated in the data reduction procedure. Both structures were solved using direct methods and refined against |*F*|. Hydrogen atoms were introduced as fixed contributors when a residual electron density was observed near their expected positions. Crystallographic data (excluding structure factors) for structures reported have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138614 and -138615. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Crystallographic Data for 7: Colourless crystals, 173 K, $C_{74}H_{114}N_2O_4S_2$, *M* = 1159.87, triclinic, *a* = 14.2423(5), *b* = 15.5842(5), *c* = 19.1515(4) Å, α = 107.436(9), β = 91.359(9), γ = 118.149(9), *V* = 3506 (1) Å^3, space group *P*−1, *Z* = 2, $D_{calcd.}$ = 1.10 gcm^{-3}, Mo-K_α graphite kappa CCD, μ = 0.117 mm^{-1}, 6192 data with $I > 3\sigma(I)$, *R* = 0.078, *Rw* = 0.092.

Crystallographic Data for 11: Colourless crystals, 173 K, $C_{74}H_{114}N_2O_4S_2$, *M* = 1159.87, triclinic, *a* = 10.0750(4), *b* = 13.6749(6), *c* = 13.7344(6) Å, α = 107.099(9) Å, β = 90.294(9) Å, γ = 101.117(9) Å, *V* = 1749.8(4) Å^3, space group *P*−1, *Z* = 1, $D_{calcd.}$ = 1.10 gcm^{-3}, Mo-K_α graphite kappa CCD, μ = 0.117 mm^{-1}, 3575 data with $I > 3\sigma(I)$, *R* = 0.079, *Rw* = 0.102.

Extraction: In a 1.5-cm diameter tube, a $CHCl_3$ solution (5 mL, 2.8−3.0 mM) of the dithiol **1** or **3** was layered with a water/acetic acid (95:5) solution of $M(OAc)_2$ (5 mL, 1.5−11.0 mM, M = Hg, Cd, Pb), and the biphasic system was stirred vigorously at 26 °C for 45 min. Continued stirring beyond this period (up to 24 h) failed to show any additional extraction for any of the metals studied. An aliquot (25−100 μL, depending on the expected residual concentration of the metal ion) was taken from the top aqueous layer and added to a solution of dithizon[16] (300 mM) in $CHCl_3$, and the absorbance (*A*) measured at 480 nm. The metal concentration (*C*) was determined from the standard *A* versus *C* plot.

Determination of Standard (*A*/*C*) Plot for Metal Salts: Aliquots (10−60 μL) in 10-μL increments were withdrawn from a 95% aqueous acetic acid solution of the metal acetate [M(OAc)$_2$, 10 mM], and added to a solution of dithizon (300 mM, 10 mL) in CHCl$_3$ in a stoppered volumetric flask. After shaking the contents of the flask for 2 min, the absorption at 480 nm was measured and plotted against the concentration to yield a straight line. The unknown concentration of the metal salt was determined following the corresponding absorbance from the *A*/*C* plot with an accuracy of 0.05 mM.

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