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# Expanded Mercaptocalixarenes: A New Kind of Macrocyclic Ligands for Stabilization of Polynuclear Thiolate Clusters

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**Abstract:** The syntheses and properties of expanded 4-*tert*-butyl-mercaptocalix[4]arenes, in which the methylene linkers are replaced by $-CH_2NRCH_2-$ or $-CH_2NRCH_2-$ and $-CH_2NRCH_2CH_2CH_2NRCH_2-$ units, are described. The new macrocycles were obtained in a step-wise manner, utilizing fully protected, i.e. *S*-alkylated, derivatives of the oxidation-sensitive thiophenols in the cyclisation steps. Reductive cleavage of the macrobicyclic or macrotricyclic intermediates (**6**, **7**, **11**) afforded the free thiophenols ($H_4$**8**, $H_4$**9**, and $H_4$**12**) in preparative yields as their hydrochloride salts. The protected proligands can exist in two conformations, resembling the "cone" and "1,3-alternate" conformations found for the parent calix[4]arenes. The free macrocycles do not show conformational isomerism, but are readily oxidized forming intramolecular disulfide linkages. Preliminary complexation experiments show that these expanded mercaptocalixarenes can serve as supporting ligands for tetranuclear thiolato clusters.

## Introduction

Calixarenes represent a family of macrocycles in which phenol moieties are connected by methylene bridges via their positions 2 and 6.[1] Since the seminal report by Gutsche and coworkers on their definitive synthetic protocol and characterization,[2] calixarenes, in particular *p-tert*-butylcalix[4]arene and their derivatives, turned out to be very useful compounds in supramolecular chemistry[3] and coordination chemistry.[4] In addition, their easy functionalization made them ideal platforms for the development of chemical sensors, in particular for metal cations.[5]

Several derivatives of the *p-tert*-butylcalix[4]arenes[2] containing other donor atoms than the generic oxygen have been reported in the past three decades: Phosphorus (phosphine)-containing calixarenes have been used as ligands for supramolecular catalysis;[6] sulfur-containing calix[4]arenes, that is, mercaptocalix[4]arenes,[7,8] thiacalix[4]arenes,[9,10] and mercaptothiacalix[4]arenes.[11] These compounds, which incorporate respectively mercapto (SH) in place of hydroxo functions, sulfur in place of methylene linkers, and both, represent very prominent examples (Figure 1).[12] Besides, calix[4]arenes incorporating both phenol and thiophenol moieties are also known.

A common feature of these compounds is their affinity for soft metal ions, and the synthesis and structures of several complexes have been reported.[13] In particular, mercapto(thia)calix[4]arenes could be used as platforms for the stabilization of polynuclear metal complexes,[13a,14a] including those with lanthanides.[15] Giant core-shell and $M^{2+}/O^{2-}$ (M = Co and Ni) aggregates held by six *p-tert*-butyltetrathiacalix[4]arene ligand subunits were described.[16] In addition to the deprotonated thiophenol sulfur atoms, mercapto(thia)calix[4]arenes also often involve the thioether sulfur bridges in the metal coordination.[13b,14b,17a,b] Therefore, they can adapt to various coordination spheres: From low coordinate linear $Hg^{(II)}$,[8] tetrahedral $Cu^{(I)}$,[14a] and a rare flattened tetrahedral $Ni^{(II)}$,[14b] to hexacoordinate trigonal prismatic $Fe^{(II)}$,[18] heptacoordinate $Mo^{(IV)}$ hydrides,[14b,17a] and $Ln^{(III)}$ cations,[15] which exhibit even higher coordination numbers. Noticeably, these polytopic sulfur-containing ligands often form sandwich polynuclear complexes involving two calix[4]arene ligands,[13a,18,19a–c] or even more when they encapsulate spherical metal aggregates.[14a,19c] Tetrathia- and tetramercaptotetrathiacalix[4]arenes functionalized with nitrogen binding subunits have been also used as molecular tectons for the crystal engineering of $Ag^{(I)}$,[20] $Cd^{(II)}$, $Fe^{(II)}$, and $Co^{(II)}$,[21] and $Hg^{(II)}$ salts.[22]

In addition to these fundamental studies, mercapto(thia)-calix[4]arenes have been taylored for various applications. For example, lipophilic dithiamercaptocalixarenes bearing $C_{12}$ alkyl chains have been used for the extraction of mercury from aqueous solutions,[23] and the formation of well-defined mono-

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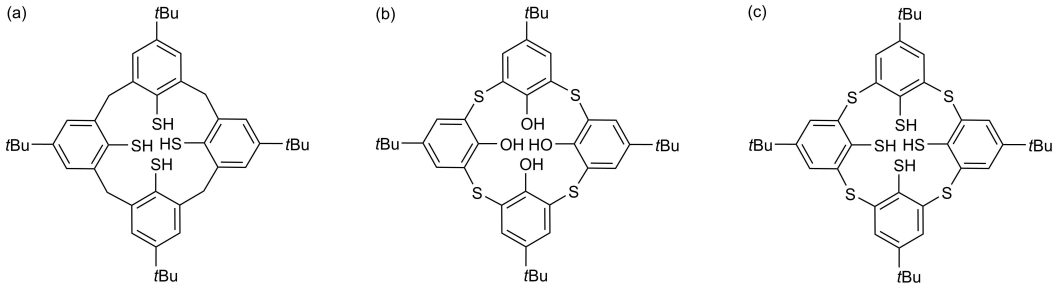



**Figure 1.** Chemical structures of (a), *p-tert*-butyltetramercaptocalix[4]arene (b) *p-tert*-butyltetrathiacalix[4]arene, and (c) *p-tert*-butyltetramercaptotetrathiacalix[4]arene.

layers of mercaptocalix[4]arenes on Au surface has also been described.[24] Finally, the detection of aromatics in aqueous solution by surface-enhanced Raman scattering using substrates chemically modified with *p-tert*-butyltetramercaptocalix[4]arene has also been investigated,[25] which further illustrates the interest of the calix[4]arene platform for the development of chemical sensors.

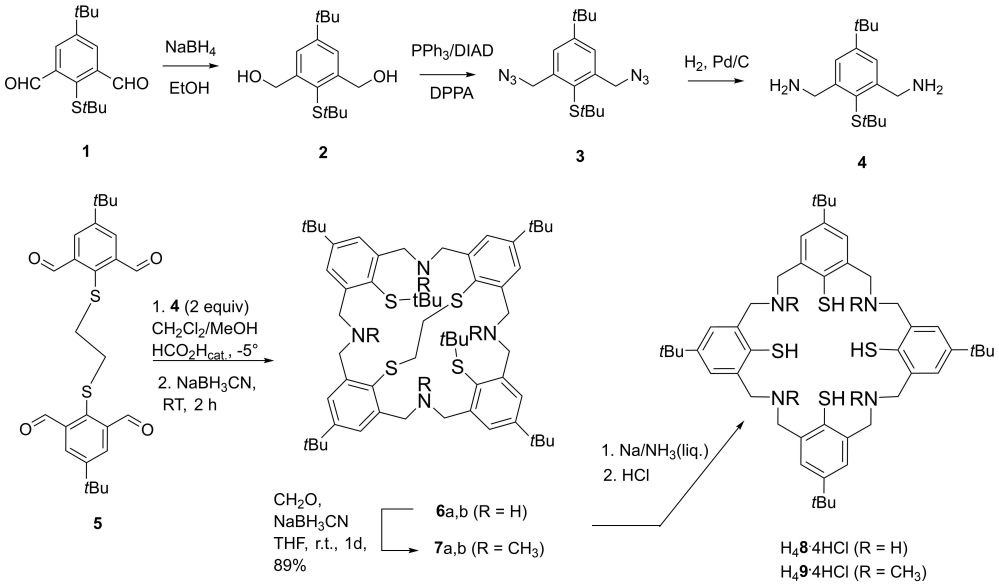
Our interest in this family of compounds comes from their ability to form multinuclear complexes with transition metals of biological interest (e.g., Ni, Fe, Mo) in an organic sulfur-rich coordination environment, which could mimic metal-sulfur aggregates that are commonly found in the active sites of various metalloenzymes, such as nitrogenases and hydrogenases. In seminal works, Holm[26] demonstrated that trithiolate ligands deriving from organic platforms exhibiting three-fold symmetry could be used for the efficient stabilization of $[Fe_4S_4]$ iron-sulfur clusters and the differentiation of one metal centre over the others.[26,27] Since then, diverse ligands incorporating thiophenol moieties were designed and used, in particular for the study of the coordination chemistry of iron in a sulfur-rich environment.[28] On our side, we have been interested for many years in the design and synthesis of ligands and receptors of various topologies including macro(poly)-cycles[29] and tripod ligands[30,31] incorporating nitrogen and sulfur donor atoms. In particular, macrocyclic polyamines incorporating two thiophenol moieties turned out to be key systems for making dinuclear 3d transition metal complexes with two bridging thiolate anions. These complexes are particularly relevant as long as modelling of the active sites of [FeFe] and [NiFe] hydrogenases is considered.[32]

We have synthesized a family of expanded mercaptocalix[4]arenes featuring $-CH_2NRCH_2-$ entities linking the thiophenolato head units. Such compounds have not been described previously. In this paper, we report on their preparation, their solution characterization, and their X-ray crystallographic study. We also illustrate the potential of these tetrathiolate precursors to stabilize metal/heteroatom aggregates in which the cations are bridged by organic sulfide ligand subunits.

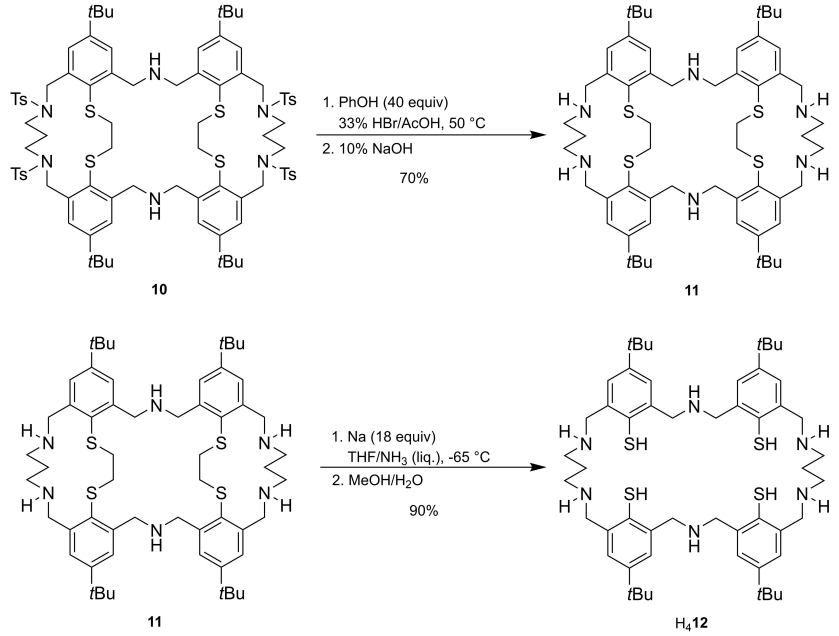
## Results and Discussion

### Synthesis and structural studies in solution and in the solid state

The synthetic procedures leading to tetrathiols $H_4$**8**, $H_4$**9** and $H_4$**12** are shown in Scheme 1 and Scheme 2, respectively. The synthesis of the 24-membered thiols $H_4$**8** and $H_4$**9** started by the reduction of dialdehyde **1** with $NaBH_4$ in EtOH, followed by Mitsunobu reaction and hydrogenation of the resulting azide **3**, which provided the diamine **4** as a colorless, hygroscopic solid in 84% overall yield. The Schiff base condensation reaction of tetraaldehyde **5** with two equiv. of diamine **4** at −5 °C under high-dilution conditions followed by reduction with $NaBH_3CN$ gave the protected mercaptocalixarene **6** as a ~50:50% mixture of two isomers (by NMR) in 46% yield after workup. Reductive methylation furnished the *N*-methylated derivative **7**. These macrocycles could be reproducibly obtained by the indicated methods. Under our conditions, compounds **6a**,**b** and **7a**,**b** were always obtained as a ca. 50:50% mixture of the *cone*- and *1,2-alternate conformers* (by NMR & X-ray crystallography). The pure, crystalline conformers produced the same NMR signal sets that were seen for the isomeric mixtures. Under the conditions adopted, there was no indication for the presence of more than two isomeric forms. However, it cannot be excluded that under other experimental conditions other low-energy energy conformers exist. In calix[4]arene chemistry, it is well known that conformations are both substituent- and guest-dependent.[33] Finally, reductive S–C bond cleavage with $Na/NH_3$ followed by acidic work-up provided the hydrochloride salts of the deprotected mercaptocalix[4]arene ligands $H_4$**8** and $H_4$**9** as air-sensitive yellow powders. Tetrathiol $H_4$**12** was obtained in two steps from the known macrotricycle **10**,[29d] in which the propanediamine bridges bear tosyl protecting groups and the thiophenol moieties are protected as ethylene-bridged bis-thioethers, as in compounds **6** and **7**. The tosyl substituents were removed by reaction of **10** with a large excess of phenol in 33% aqueous HBr in acetic acid at 50 °C, which, after 36 h reaction, afforded macrotricycle **11** in 70% yield after basification of the reaction mixture and extraction into dichloromethane. Higher temperatures used in order to decrease the reaction time led to the degradation of the starting material. Finally, the thioether functions of **11** were cleaved, as for **7**, by




**Scheme 1.** Synthesis of mercaptothiacalixarenes $H_4$**8** and $H_4$**9**.




**Scheme 2.** Synthesis of the mercaptothiacalix[4]arene $H_4$**12** from the known macrotricycle **10**[29d] via the intermediate macrotricycle **11**.

reaction with sodium in liquid ammonia, as reported earlier for related compounds,[29a,b,30] to provide the expanded mercaptocalix[4]arene $H_4$**12** as the free base in 90 % yield.

The products and all the intermediates were characterized by IR, $^1$H and $^{13}$C NMR spectroscopies and electrospray ionization (Supporting Information), or matrix assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrometry. 2D NMR experiments were used to correctly assign the chemical shifts of hydrogen and carbon atoms (Supporting Information). $^1$H NMR spectroscopic studies indicated that the protected mercaptocalix[4]arenes **6** and **7** existed as a mixture of two isomers (1,2-*alternate* or *cone* conformation) that do not interconvert rapidly on the NMR time scale, most likely due to restricted rotation of the aryl-*tert*-butylthioether units about the –$CH_2NRCH_2$– linkers. Such a phenomenon was not observed in the case of macrotricycle **11** and macrocycle $H_4$**12**, in which two of the dibenzylamine bridges of **6** and **7** were replaced by the more flexible –$CH_2NR(CH_2)_3NRCH_2$– linkers. The deprotected thiols were found to be very air-sensitive both in solution and in the solid state, most likely affording oxidation products with intramolecular disulfide linkages (see below). Some key com-

pounds **6a**, **7a**,**b**, and an oxidation product of $H_4$**9**·4HCl could also be characterized by X-ray crystallography.

### Structural characterization of key compounds by NMR and X-ray crystallography

Isomers **6a** and **6b** were found to exhibit different solubility properties. A separation by fractional crystallization from MeOH/$CH_2Cl_2$ was successful. Moreover, single crystals of **6a**·2MeOH suitable for X-ray crystallography could be grown by slow evaporation from MeOH/$CH_2Cl_2$. Figure 2 displays the molecular structure of the centrosymmetric molecule. The four arylthioether units are arranged in an *up*,*up*,*down*,*down* fashion with respect to the plane through the 4 *N* atoms of the macrobicyclic ring. According to the nomenclature utilized for the parent *p-tert*-butyl-calix[4]arenes, **6a** can be referred to the 1,2-*alternate* conformer (Figure 3). The inversion center in the ethylenic linkage (dihedral angle S–C–C–S = 180°) leads to the equivalence of the opposing groups in **6a**, and explains the small number of signals in the $^1$H and $^{13}$C NMR spectra. The central cavity in **6a** is occupied by the ethylene linker such that no guest inclusion occurs. The short N2···S1 distances at 3.313(3) Å suggest that the NH donors form intramolecular H bonds with the arylthioether groups. The other two NH moieties form hydrogen bonds with the MeOH solvent molecules (not shown in Figure 2).

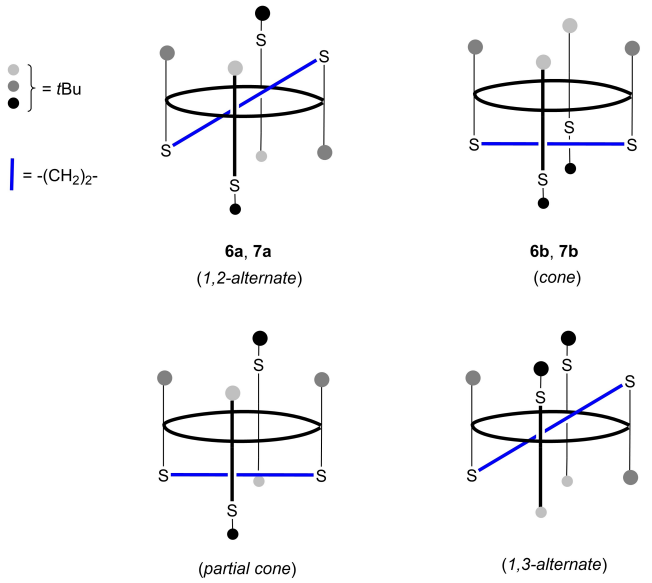



**Figure 3.** Schematic representation of the molecular structures of four potential isomers of the protected mercaptocalixarenes **6** and **7**. So far, only the 1,2-*alternate* and *cone* conformers have been isolated.

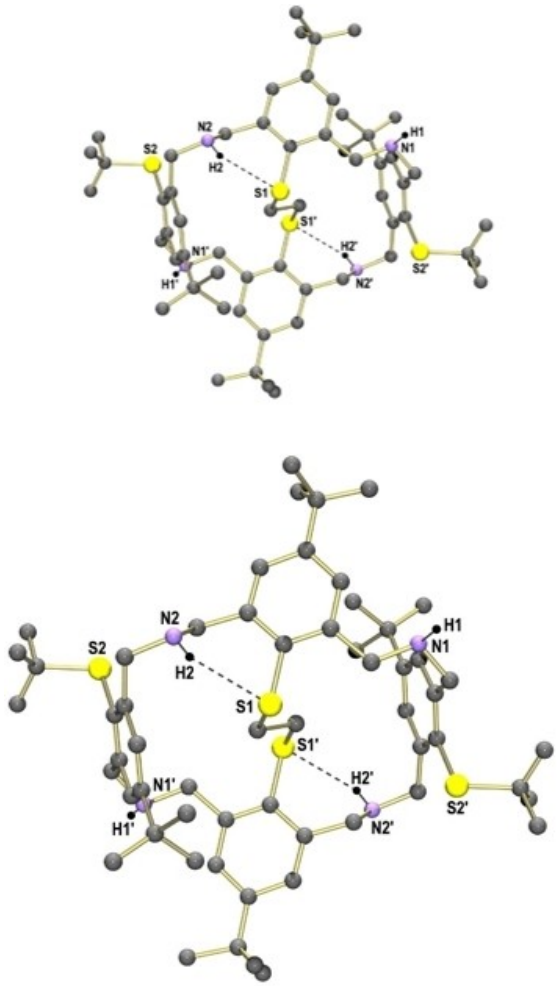



**Figure 2.** Molecular structure of **6a** in crystals of **6a**·2MeOH. H atoms and solvent molecules omitted for clarity. Dashed lines refer to intramolecular hydrogen bonding interactions (N2···S1 3.313(3) Å). Symmetry code used to generate equivalent atoms: -*x*, -*y*, -*z* (′).

The DFT calculated geometry for **6a** was found to be very similar to the experimental one (Supporting Information, Figure S16). So far, we have not been able to grow single crystals for conformer **6b**. We assume that all four arylthioether units are arranged in an *up*,*up*,*up*,*up* fashion (*cone* conformation, Figure 3) with respect to the plane through the 4 *N* atoms as found for isomer **7b** (see below). It is not yet clear, whether the *partial cone* or 1,3-*alternate* isomers exist.

Isomers **7a** and **7b** exhibit different solubility properties as observed for **6a** and **6b**. Isomer **7a** was found to be less soluble than **7b** in aprotic solvents such as $CH_2Cl_2$, $CHCl_3$, THF, and toluene. Single crystals of **7a**·4$CHCl_3$ suitable for X-ray crystallography could be grown by slow evaporation from a mixed MeOH/$CHCl_3$ solution. The *N*-methylated mercaptocalix[4]arene **7a** again exhibits the 1,2-*alternate* conformation shown by **6a** (Figure 4). The structure of **6a** is only slightly distorted upon *N*-methylation, as clearly manifested in similar intramolecular S2···S1, S2···S1′, and S2···S2′ distances (4.4549(9) Å, 6.053(1) Å, 10.957(1) Å in **6a** vs. 6.467(2) Å, 6.062(2) Å, 11.720(2) Å in **7a**, respectively).

Single crystals of **7b**·$CH_2Cl_2$ obtained by slow evaporation from a mixed MeOH/$CH_2Cl_2$ solution are monoclinic, space group *C*2/*c*. Figure 5 displays two views of the molecular structure of **7b**. All arylthioether units are situated below the plane through the 4 *N* atoms of the macrobicyclic ring, reminiscent of the "*flattened cone*" conformation of the parent

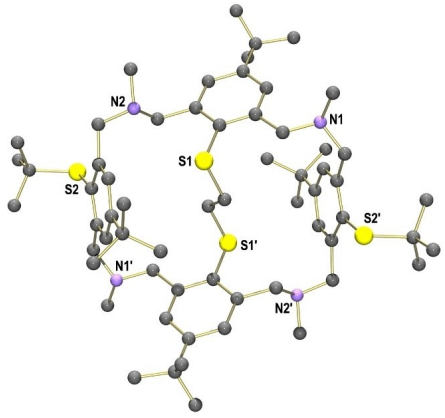



**Figure 4.** Molecular structure of **7a** in crystals of **7a**·4CHCl$_3$. Solvent molecules and H atoms omitted for clarity. Symmetry code used to generate equivalent atoms: *-x, -y, -z* (').

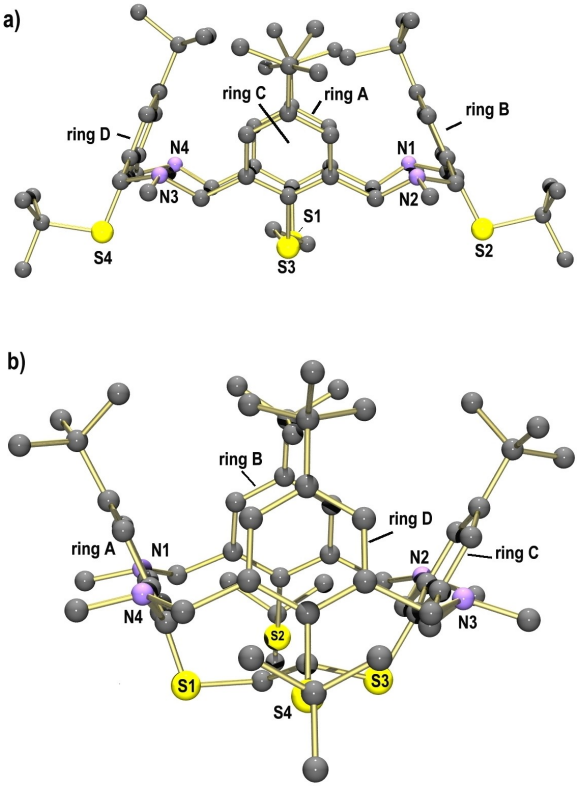


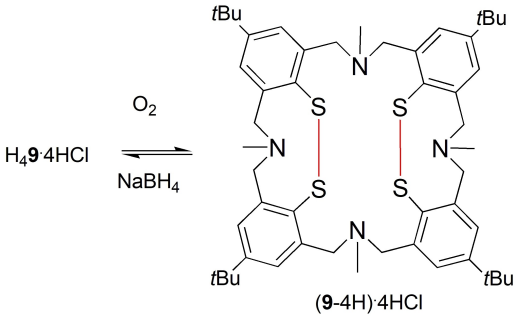

**Figure 5.** Two views of the molecular structure of **7b** in crystals of **7b**·$CH_2Cl_2$. Solvent molecules and H atoms omitted for clarity.

4-*tert*-butyl-calix[4]arenes. The molecule exhibits idealized $C_2$ symmetry. The best planes through the opposing aryl rings intersect at 55(1)° (A,C) and 47(2)° (B,D).

The dimensions of the cavity in **7b** can be estimated by the distance *d* between the centroids of the opposing aryl rings A and C (7.1611(2) Å) and B and D (8.8833(2) Å) or the distance between the hydrogen atoms of the upper rim *tert*-Bu groups and the hydrogen atoms of the ethylenic linkage at the lower rim H46a···H58b (4.9 Å). By taking into account the van der Waals radii of a benzene ring and a H atom,[34] these distances are calculated as (5.6211(2), 7.3433(2), and 2.5 Å). The presence of such a small cavity suggests that **7b** may be interesting to investigate as host compound for inclusion of small linear guest molecules.

According to the $^1$H and $^{13}$C NMR spectra, compounds $H_4$**8**·4HCl and $H_4$**9**·4HCl exhibit fourfold symmetry in solution. A solution of $H_4$**9**·4HCl in $CD_3OD$, for example, displays only four resonances at $\delta = 7.60$, 4.37, 2.85, and 1.37 ppm for the Ar*H*, Ar$CH_2$N, N$CH_3$, and C$(CH_3)_3$ protons, respectively. Due to fast H/D-exchange, the S*H* protons are not observed under these conditions. As already mentioned, the thiols are very air-sensitive, most likely due to the proximity of the thiol functions. The air oxidation of **9**·4HCl in MeOH is slow (5 days) but the product can be converted back to the starting material by $NaBH_4$ reduction as demonstrated by NMR spectroscopy (Scheme 3 and Supporting Information, Figure S9).

We have obtained preliminary X-ray crystallographic data for an oxidation product of the thiol $H_4$**9**, namely the hydrochloride salt of the disulfide (**9**-4H)·4HCl. The crystals were picked from a solution of $H_4$**9**·4HCl which was left to stand in air for 5 days. Although the structure determination is of low quality and not as good as desired for publication, it can serve to confirm the atom connectivity of (**9**-4H)·4HCl. There are two disulfide bridges that connect adjacent thiophenols to form a tricyclic structure (Figure 6), clearly demonstrating that the




**Scheme 3.** Reversible oxidation of $H_4$**9**·4HCl.

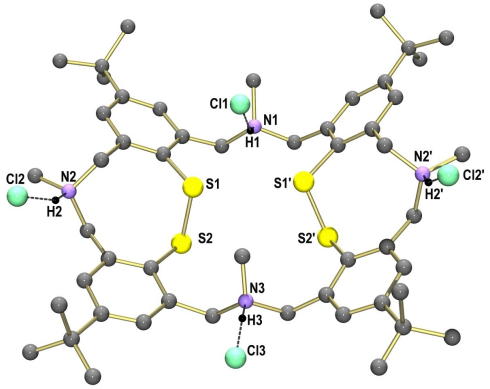



**Figure 6.** Molecular structure of (**9**-4H) in crystals of (**9**-4H)·4HCl. Hydrogen atoms omitted for clarity (except for NH groups). Dashed lines refer to NH···Cl bonds.

oxidation takes place within the macrocyclic structure. This behaviour contrasts the behaviour of the corresponding acyclic dithiols ($RN(CH_2–C_6H_4–o–SH)_2$)) which form 3 different kinds of oxidation products.[35] The different behaviour can be traced to the constraints imposed by the macrocyclic structure. It should be mentioned that based on the structure of (**9**-4H)·4HCl in the solid state, one would expect two signals for the two *t*Bu signals. The NMR spectrum (Figure S9), however, reveals four equally intense signals for *t*Bu groups (1.48, 1.45, 1.34, 1.31 ppm), suggesting that in solution (**9**-4H)·4HCl may exist in two different conformations.

The slow air oxidation of $H_4$**9**·4HCl into macrotricycle (**9**-4H)·4HCl incorporating two disulfide briges is not really a surprise. Oxidative coupling of thiols into disulfide by oxygen proceeds slowly, unless it is catalyzed by a base[36] or is performed in buffered aqueous solutions at pH above the p$K_a$ of the thiol. Most of the examples of disulfide-incorporating macro(poly)cycles have been prepared using these latter conditions,[37] but procedures avoiding a base have also been reported.[38] Noticeably, the use of iodine as oxidizing agent in high dilution conditions leads to fast reactions, even without a base.[39] Assuming the contribution of the conformational entropy can be neglected, the stability of cyclic disulfides in macrotricycles like $H_4$**9** will mainly depend on ring strain, an enthalpic contribution. The enthalpy of the disulfide bond depends on the CSSC dihedral angle $\theta$, being minimal for $\theta = 90°$ (fully relaxed disulfide), and maximal for $\theta = 0°$ (about 27 kJ mol$^{-1}$).[40] From the X-ray crystal structure data of $H_4$**9**·4HCl, we calculate $\theta = 103.06°$ for C1-S1-S4-C26, and 102.58° for C14-S2-S3-C18, values which are close to the $\theta = 90°$ value of the minimum of the potential energy curve. Therefore, we can conclude that the conversion of the tetramercapto-tetraazamacrocycle $H_4$**9** into the (**9**-4H) macrotricycle by double disulfide bridge formation is a favorable process, both from the entropy and enthalpy viewpoints.

It is noteworthy that compound (**9**-4H) and compound **11** have the same topology (both are macrotricycles), but for different reasons: The former, because of the establishment of disulfide bridges upon oxidation, the latter, because of the ethylene, protecting bridges. Interestingly, the tosylated precursor **10** of macrotricycle **11** had crystallized as a trifluoroacetic acid adduct, with protonation of both bridgehead nitrogen atoms. The X-ray molecular structure of **11**·2$CF_3CO_2H$ showed that the macrotricycle had a calix[4]arene-like 1,2-alternate conformation with an inversion center, and that each equivalent subunit of the molecule nested a trifluoroacetate anion, which was bound to both protonated bridgehead nitrogen atoms (Figure 7).[29d]

The $^1$H NMR spectra of the free base macrotricycle **11** and macrocycle $H_4$**12** show a number of signals corresponding to the $D_{2d}$ average symmetry at the $^1$H NMR timescale, attesting to the high flexibility of these compounds. As they have several common features, it is pertinent to compare the NMR spectra of **11** and **6a**, **6b** on the one hand, $H_4$**12** and $H_4$**8**·4HCl, on the other hand. The benzylic –$CH_2$NH– protons of **6a** and **6b** constitute diastereotopic pairs and give two AX systems, which show up, in the case of **6a** at 4.80 and 3.76 ppm for 8-H and 3.72 and 3.56 ppm for 7-H, and in the case of **6b**, at 4.77 and 3.69 ppm for 8-H, and 3.76 and 3.50 ppm for 7-H. The analogous benzylic C$H_2$ protons of **11** show up as two singlets, which attests to their enantiotopic nature, at 3.94 ppm for H-7 and 4.10 ppm for H-8. The latter value is close to the averaged chemical shifts of the diastereotopic H-8 protons of **6a** and **6b**. The protons of the ethylene bridges (H-13) appear as a singlet at 3.16 ppm, but they are considerably downfield shifted (+ 1.20 ppm) by comparison with their homologues (H-17) in the **6b** cone conformer, while there is no difference for the $^{13}$C NMR signals, which appear both at 36.2 ppm. The benzylic –$CH_2$NH– carbon atoms 7-C and 8-C resonate at 54.02 and 55.11 ppm, values that are close to those recorded for **6a** (53.45 for C-8 and 51.65 ppm for C-7) and for **6b** (53.04 for C-8, and 51.52 ppm for C-7). The $C_2$ symmetry of $H_4$**12** by comparison with the $C_4$ symmetry of $H_4$**8**·4HCl is revealed by the presence of two doublets vs. one singlet for the aromatic protons, the former at 6.78 and 7.09 ($CD_3OD/CDCl_3$, 1:1, v/v), the latter at 7.60 ppm ($CD_3OD$). In summary, while compounds **6** and **7** have retained conformational features that are characteristic of the classical calix[4]arenes, probably because of the ethylene bridges, this is not the case of **11**, which, in spite of the same protecting groups, seems to be flexible at the $^1$H NMR timescale. The absence of the thiophenol tethers makes $H_4$**8** flexible, as its $H_4$**12** analogue.

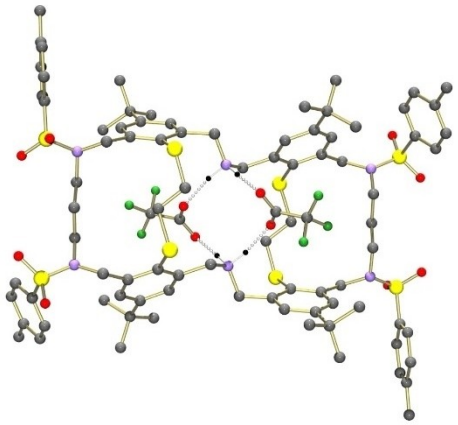
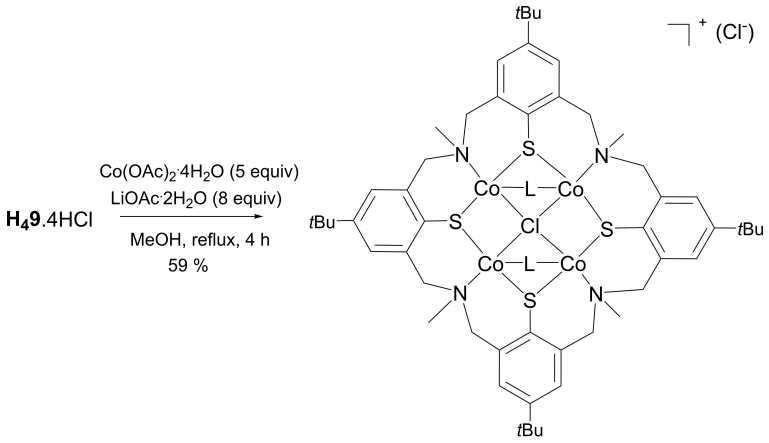


**Figure 7.** ORTEP view of the X-ray molecular structure of the 1:2 adduct **11**·2$CF_3CO_2H$ of macrotricycle **11** and trifluoroacetic acid. Dashed lines represent the bifurcated hydrogen bonds between the trifluoroacetate anions and the protonated bridgehead nitrogen atoms.[29d]

### Application of the expanded tetraazatetrathiacalix[4]arene $H_4$9·4HCl to the stabilization of a tetranuclear Co$^{II}$ thiolate complex

In orienting experiments, we examined the ability of these macrocycles to form discrete thiolate clusters with the divalent metal ions $Co^{2+}$ and $Ni^{2+}$. ESI MS, UV-vis and elemental analysis indicated that one to four metal ions could be accommodated by each of these compounds. This was finally confirmed by an X-ray crystal structure determination of the tetranuclear cobalt




[$Co_4$(**9**)(μ-Cl)(μ-$OAc)_2$]Cl

**13**

**Scheme 4.** Synthesis of the tetranuclear cobalt complex **13** (L = $Oac^-$).

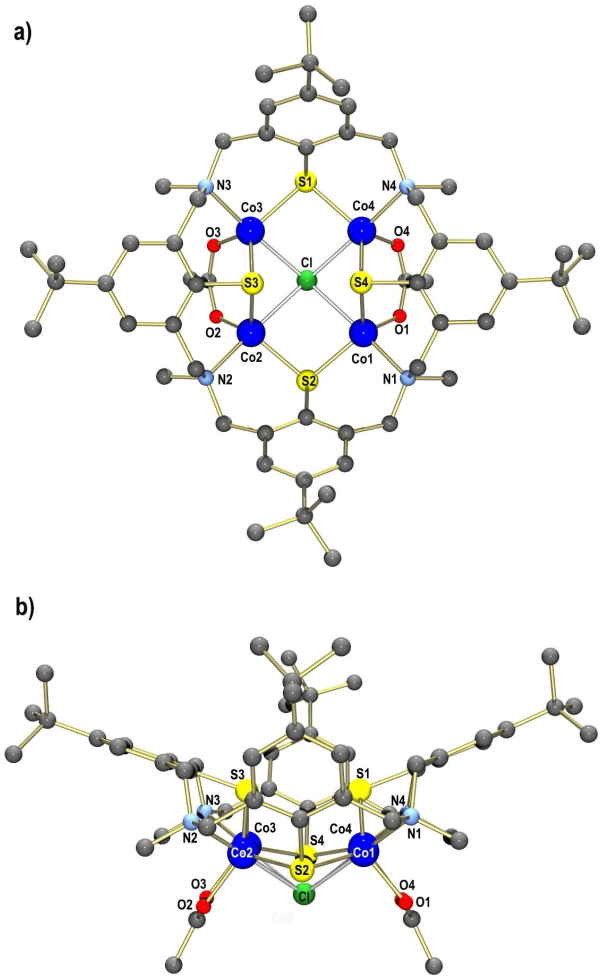



**Figure 8.** Two views of the molecular structure of the tetranuclear $Co_4$ complex **13**.

complex [$Co_4$(**9**)($\mu_4$-Cl)($\mu$-$OAc)_2$]Cl (**13**), which was obtained by treatment of $H_4$**9**·4HCl with $Co(OAc)_2$·$6H_2O$ and LiOAc as a base as illustrated in Scheme 4.

Dichroic (purple, blue-green) crystals of **13**·$3H_2O$·3.5*t*BuOH grown by slow evaporation from $CH_2Cl_2$/*t*BuOH are triclinic, space group *P*-1. The crystal structure determination clearly confirms the presence of a tetranuclear species. Figure 8 displays two views of the tetranuclear thiolate complex, which exhibits idealized $C_2$ symmetry. Interestingly, the $Co^{II}$ ions are pentacoordinated by two bridging S and one N atom from the mercaptocalixarene. One $\mu_4$-bridging $Cl^-$ and one O atom of a $\mu_{1,3}$-bridging acetate ion complete the coordination sphere. The structure thus clearly confirms that tetranuclear thiolate clusters can be accommodated by the mercaptocalixarenes. The finding that these mercaptocalixarenes support clusters through thiolate coordination completed by the binding of the bridgehead nitrogen atoms and external anions ($OAc^-$ and $Cl^-$) suggests that these compounds may also be interesting to investigate as catalysts in multielectron transfer reactions to the bound substrates.

## Conclusion

In this report we have shown that it was possible to synthesize polyazamacrocycles of various ring sizes incorporating four thiophenol subunits in several steps and preparative yields. Significantly, the synthetic strategy employed differs from the one used for making mercaptocalix[4]arenes, which relies on the Newman-Kwart rearrangement, as two to four of the aromatic thiols are protected in the form of ethylene-bridged dithioethers before the cyclisation reactions are carried out. Therefore, the compounds are obtained through macrobicyclic

or macrotricyclic intermediates, after release of the ethylene protections. These macropolycyclic intermediates are reminiscent of some calixarenes in which the small rim bears covalent intramolecular bridges. The smallest members of our family of expanded tetramercaptocalix[4]arenes have the same symmetry as the calix[4]arenes in general, but are slightly larger, as they are 24-membered rings whereas the latter are 16-membered rings. Unlike their macrobicyclic precursors, which are less flexible because of the ethylene bridge, and as the largest members of the series, which are 32-membered rings, they do not show the conformational isomerism typical of calix[4]arenes. In fact, their flexibility may be an advantage as far as their use in coordination chemistry is concerned: The arrangement of the donor sulfur atoms is likely to be dictated by the coordination demands of the metal aggregates to complex, not by the intrinsic structure of the expanded tetramercaptocalix[4]arene.

## Experimental Section

**Materials and General Methods**: Compounds **1**,[30] **5**[29a] and **10**[29d] were prepared as described in the literature. Tetrahydrofuran was dried and deoxygenated by distillation under argon over sodium/benzophenone. All other solvents and reagents were used as received. The synthesis of the metal complexes was carried out under a protective atmosphere of argon. Melting points were determined with an Electrothermal IA9000 series instrument using open glass capillaries and are uncorrected. $^{1}$H and $^{13}$C NMR spectra were recorded with a Bruker Avance 300 instrument. Mass spectra were obtained either using the positive ion electrospray ionization modus ((+)-ESI) on a FT-ICR-MS Bruker Daltronics APEX II instrument or by matrix assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrometry with a Bruker Daltonics Proflex III apparatus from a dispersion of the sample in a dithranol matrix. Infrared spectra (4000–400 $cm^{-1}$) were recorded at 4 $cm^{-1}$ resolution on a Bruker TENSOR 27 spectrometer. Solution absorption spectra were collected on a Jasco V-670 UV-vis-NIR spectrophotometer using 1 cm quartz cells (Hellma). Elemental analyses were carried out either on a VARIO EL elemental analyzer (Elementar Analysensysteme GmbH, Hanau) or an EA1108 CHNS Fisons Instrument analyzer.

**Synthesis and Characterization of Compounds**[41] **2,6-bis(hydroxymethyl)-4-(*tert*-butyl)phenyl)(*tert*-butyl)sulfane (2)**: To a solution of (2,6-di(formyl)-4-(*tert*-butyl)phenyl)(*tert*-butyl)sulfane (**1**) (2.79 g, 10.0 mmol) in $CH_2Cl_2$ (75 mL) was added a solution of $NaBH_4$ (0.95 g, 25.0 mmol) in EtOH (150 ml). The mixture was stirred for further 1 d at r.t. The pH of the solution was adjusted to 1 by addition of aqueous HCl (1 N). The solvent was evaporated under reduced pressure to give a colorless solid. Water was added and the product extracted with $CH_2Cl_2$ (3×50 mL). The combined organic phases were dried with $Na_2SO_4$. Evaporation of the solvent gave diol **2** as a colorless solid. Yield 2.82 g (>98%). M.p. 118–120 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ [ppm] = 7.48 (s, 2 H, Ar*H*), 4.94 (s, br, 4 H, ArC$H_2$OH), 2.29 (s, 2 H, O*H*), 1.34 (s, 9 H, C(C$H_3$)$_3$), 1.31 (s, 9 H, C(C$H_3$)$_3$). $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): $\delta$ [ppm] = 153.2 (ArCC(CH$_3$)$_3$), 147.0 (ArCCH$_2$OH), 125.7 (ArCSC (CH$_3$)$_3$), 125.7 (ArCH), 65.2 (ArCCH$_2$OH), 49.7 (SC(CH$_3$)$_3$), 35.0 (ArCC(CH$_3$)$_3$), 31.8 (C(CH$_3$)$_3$), 31.3 (C(CH$_3$)$_3$). IR (KBr): $\tilde{\nu}$/$cm^{-1}$ = 3241 (vs, br), 2963 (vs), 2902 (s), 2867 (s), 2712 (m), 2461 (w), 1773 (w), 1597 (m), 1558 (w), 1476 (s), 1460 (s), 1409 (s), 1394 (m), 1363 (s), 1295 (w), 1267 (w), 1217 (m), 1165 (s), 1148 (s), 1063 (vs), 1012 (s), 984 (m), 933 (w), 881 (s), 803 (w), 750 (m), 682 (m), 652 (m), 604 (w), 569 (w), 535 (w), 450 (w). (+)-ESI-MS ($CH_2Cl_2$/$CH_3OH$): *m/z* = 305.2 ($C_{16}H_{26}NaO_2S^+$, [M + $Na^+$]); calcd: 305.16; m/z = 321.1 ($C_{16}H_{26}KO_2S^+$, [M + $K^+$]$^+$); calcd: 321.13. Found: C 67.93, H 8.98, S 11.41; $C_{16}H_{26}O_2S$ (282.44) requires: C 68.04, H 9.28, S 11.35.

**(2,6-bis(azidomethyl)-4-(*tert*-butyl)phenyl)(*tert*-butyl)sulfane (3)**: *Method A:* To a solution of the diol **2** (0.71 g, 2.50 mmol) in THF (125 mL) was added triphenylphosphine (1.97 g, 7.5 mmol). After the reaction mixture was cooled to 0 °C, diisopropylazo dicarboxylate (DIAD, 1.52 g, 7.50 mmol) and diphenylphosphoryl azide (DPPA, 1.52 g, 7.5 mmol) were added dropwise. The mixture was stirred at r.t. for 12 h, and evaporated to dryness. The residue was loaded on a $SiO_2$ column and the product eluted with *n*-hexane/$CH_2Cl_2$ (4:1, v:v). Removal of the solvent provided the title compound as a pale-yellow oil. Yield: 0.72 g (2.17 mmol, 87%). *Method B:* To a solution of the diol **2** (2.82 g, 10.0 mmol) in $CH_2Cl_2$ (150 mL) was added methanesulfonyl chloride (2.82 g, 25.0 mmol) and $NEt_3$ (3.04 g, 30.0 mmol). The mixture was stirred for 60 min at 0 °C, washed with $H_2O$ (3×50 mL) and sat. aq. NaCl (150 mL). The organic phase was separated, dried with $Na_2SO_4$, and evaporated to dryness. The resulting oil was dissolved in DMF (150 mL). Solid $NaN_3$ (2.60 g, 40.0 mmol) was added and the mixture was allowed to stir for further 24 h at r.t. The mixture was quenched with ice/$H_2O$ (150 mL). The product was extracted with $CH_2Cl_2$ (3×50 mL). The combined organic phases were washed with $H_2O$ (2×50 mL) and sat. aq. NaCl (150 mL). The organic phase was separated, dried with $Na_2SO_4$, and evaporated to dryness. Yield: 2.96 g (8.90 mmol, 89%), pale yellow oil. This compound was used in the next step without further purification. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ [ppm] = 1.27 (s, 9 H, SC(C$H_3$)$_3$), 1.36 (s, 9 H, ArC(C$H_3$)$_3$), 4.81 (br, 4 H, ArC$H_2$N$_3$), 7.48 (s, 2 H, Ar*H*). $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): $\delta$ [ppm] = 31.2, 31.5 (C(CH$_3$)$_3$), 35.0 (*C*(CH$_3$)$_3$), 49.4 (SC(CH$_3$)$_3$), 54.1 (CH$_2$), 126.5 (ArCH), 128.0 ArCSC(CH$_3$)$_3$, 142.2 (ArCCH$_2$), 153.3 (ArCC(CH$_3$)$_3$). IR (KBr): $\tilde{\nu}$/$cm^{-1}$ = 3441 (m, br), 3056 (w), 2965 (vs), 2933 (sh), 2903 (m), 2867 (m), 2478 (w, br), 2097 (vs), 1682 (m), 1598 (m), 1558 (w), 1476 (m), 1460 (m), 1410 (m), 1394 (m), 1364 (s), 1334 (m), 1275 (s), 1223 (m), 1165 (s), 1152 (s), 1089 (w), 1049 (w), 1024 (w), 996 (w), 955 (w), 926 (w), 867 (m), 805 (w), 764 (w), 750 (w), 634 (w), 556 (w), 509 (w), 441 (w).

**(2,6-bis(aminomethyl)-4-(*tert*-butyl)phenyl)(*tert*-butyl)sulfane (4)**: The diazide **3** (2.96 g, 8.90 mmol) was dissolved in $CH_2Cl_2$ (75 mL) and MeOH (150 mL). Pd/C (10 wt%, 2.96 g) was added, and the mixture stirred for 12 h under a $H_2$ atmosphere (1 bar). The mixture was filtered and evaporated under reduced pressure to give a colorless solid, which was dried in vacuum. The product was used without further purification in the next step. Yield: 2.46 g (8.77 mmol, >98%), colorless, hygroscopic solid. M.p. 63–64 °C. $^{1}$H NMR (400 MHz, $CD_3OD$): $\delta$ [ppm] = 1.27 (s, 9 H, SC(C$H_3$)$_3$), 1.37 (s, 9 H, ArC(C$H_3$)$_3$), 4.70-3.73 (br, 4 H, ArC$H_2$NH$_2$), 7.59 (s, 2 H, ArH). $^{1}$H NMR (300 MHz, DMSO-$d_6$, 80 °C): $\delta$ [ppm] = 1.21 (s, 9 H, SC(C$H_3$)$_3$), 1.32 (s, 9 H, ArC(C$H_3$)$_3$), 3.51 (br, 4 H, ArC$H_2$NH$_2$), 7.57 (s, 2 H, ArH). $^{13}$C{$^{1}$H} NMR (100 MHz, $CD_3OD$): $\delta$ [ppm] = 31.5, 31.7 (C(*C*H$_3$)$_3$), 35.8 (*C*(CH$_3$)$_3$), 45.8 (CH$_2$), 50.1 (SC(CH$_3$)$_3$), 127.2 (Ar*C*H), 128.8 Ar*C*SC(CH$_3$)$_3$, 147.5 (Ar*C*CH$_2$), 154.8 (Ar*C*C(CH$_3$)$_3$). IR (KBr): $\tilde{\nu}$/$cm^{-1}$ = 3425 (s), 2962 (vs), 2902 (vs), 2870 (vs), 2867 (vs), 2624 (m), 2091 (w), 1599 (s), 1477 (s), 1460 (s), 1411 (m), 1393 (m), 1363 (vs), 1313 (w), 1225 (m), 1205 (w), 1163 (s), 1044 (w), 977 (m), 926 (m), 886 (m), 762 (w), 666 (w), 567 (w), 492 (w), 441 (w). (+)-ESI-MS (MeOH): *m/z* = 281.21 ($C_{16}H_{29}N_2S^+$, [M + $H^+$]$^+$) calcd: 281.21.

**Protected mercaptocalix[4]arenes 6a and 6b**: A solution of tetraldehyde **5** (1.88 g, 4.0 mmol) in $CH_2Cl_2$ (60 mL) and a solution of the diamine **4** (2.36 g, 8.4 mmol) in $CH_3OH$ (60 mL) were simultaneously added dropwise with vigorous stirring at 0–5 °C over a period of 2 h to a mixture of MeOH, $CH_2Cl_2$ (100 mL each) and formic acid (0.2 mL) and the resulting mixture was stirred for further 6 h at room temperature. Sodium cyanoborohydride (2.01 g,

32.0 mmol) was carefully added in small portions at 0 °C. The reaction mixture was stirred for further 12 h, 2 M aq. NaOH (50 mL) was added at 0 °C to destroy excess reducing agent. The mixture was allowed to stir for further 3 h and the solvent was evaporated under reduced pressure to give a pale-yellow solid. Water (100 mL) was added, and the product extracted with $CH_2Cl_2$ (1×75 mL, 3× 50 mL). The combined organic phases were washed with brine (100 mL) and dried with $K_2CO_3$. The solvent was concentrated to 100 mL under reduced pressure, methanol (100 mL) was added and again concentrated under reduced pressure until a precipitate (i.e. macrobicyclic thioether **6a**) formed. To complete precipitation, the solution was stored at 4 °C overnight. The colorless solid was collected by filtration and dried in air. The mother liquor was concentrated to dryness under reduced pressure. The colorless residue was dissolved in dichloromethane (50 mL), 2 N hydrochloric acid (5 mL) was added and the mixture was stirred overnight at room temperature to give a colorless precipitate which was filtered off and dried in air. The solid was reprecipitated once from methanol/acetonitrile to give the tetrahydrochloride salt of the macrobicyclic thioether (**6b**·4HCl). The solid was dissolved in methanol (50 mL), and the pH of the solution was adjusted to 7 by addition of 2 M aqueous $K_2CO_3$. The solution was concentrated to about 30 mL under reduced pressure and stored overnight at 4 °C to give analytically pure conformer **6b** as a microcrystalline solid, which was filtered off and dried in air. Yield **6a**: 981 mg (1.01 mmol), **6b**: 809 mg (0.84 mmol), total yield: 1.79 g, (1.85 mmol, 46 %).

Analytical data for **6a** (*1,2-alternate conformer*): colorless solid, MW 967.59 g/mol, m.p. 267–269 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ [ppm] = 7.43 (s, 4 H, H-4), 7.37 (s, 4 H, H-10), 4.80 (d, $^2J_{HH}$ = 13 Hz, 4 H, H$^a$-8), 3.76 (d, $^2J_{HH}$ = 13 Hz, 4 H, H$^b$-8), 3.72 (d, $^2J_{HH}$ = 13 Hz, 4 H, H$^a$-7), 3.56 (d, $^2J_{HH}$ = 13 Hz, 4 H, H$^b$-7), 1.98 (d, $^2J_{HH}$ = 10 Hz, 2 H, H$^a$-17), 1.94 (d, $^2J_{HH}$ = 10 Hz, 2 H, H$^b$-17), 1.34 (s, 18 H, H-1), 1.27 (s, 18 H, H-13), 1.22 (s, 18 H, H-16). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ [ppm] = 152.2 (C-3), 152.0 (C-11), 145.9 (C-9), 144.5 (C-5), 129.1 (C-14), 128.0 (C-6), 126.9 (C-10), 126.1 (C-4), 53.5 (C-8), 51.7 (C-7), 49.0 (C-15), 35.9 (C-17), 34.9 (C-2), 34.7 (C-12), 31.4 (C-1), 31.4 (C-13), 31.4 (C-16). IR (KBr): $\tilde{\nu}$/cm$^{-1}$ = 3425 (m), 3049 (w), 2963 (vs), 2926 (s), 2905 (s), 2866 (s), 2711 (w), 1636 (w), 1596 (m), 1559 (w), 1477 (s), 1457 (s), 1407 (m), 1393 (m), 1362 (s), 1288 (w), 1259 (w), 1220 (m), 1202 (m), 1165 (m), 1150 (m), 1118 (m), 1095 (sh), 1043 (w), 981 (w), 926 (w), 881 (m), 810 (m), 781 (m), 751 (m), 680 (w), 649 (w), 571 (w), 498 (w). (+)-ESI-MS ($CH_2Cl_2$/$CH_3CN$): *m/z* = 967.6 ($C_{58}H_{87}N_4S_4^+$, $[M+H^+]^+$) calcd: 967.58. Found: C 69.45, H 8.53, N 5.46 S 12.93; $C_{58}H_{86}N_4S_4 \cdot 2CH_3OH$: requires C 69.85, H 9.18, N 5.43, S 12.43.

Analytical data for **6b** *(cone conformer)*: colorless solid, MW 967.59 g/mol, m.p. 169 – 173 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ [ppm] = 7.36 (s, 8 H, H-4/H-10), 4.77 (d, $^2J_{HH}$ = 1.3 Hz, 4 H, H$^a$-8), 3.76 (d, $^2J_{HH}$ = 13 Hz, 4 H, H$^a$-7), 3.69 (d, $^2J_{HH}$ = 13 Hz, 4 H, H$^b$-8), 3.50 (d, $^2J_{HH}$ = 13 Hz, 4 H, H$^b$-7), 1.87 (s, 4 H, H-17), 1.31 (s, 18 H, ArC($CH_3$)$_3$), 1.31 (s, 18 H, ArC($CH_3$)$_3$), 1.15 (s, 18 H, H-16). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ [ppm] = 151.5 (ArCC($CH_3$)$_3$), 151.7 (ArCC($CH_3$)$_3$), 146.0 (C-9), 144.2 (C-5), 128.9 (C-14), 128.5 (C-6), 126.9 (C-10), 125.9 (C-4), 53.0 (C-8), 51.5 (C-7), 48.8 (C-15), 36.2 (C-17), 34.7 (ArCC($CH_3$)$_3$), 34.6 (ArCC($CH_3$)$_3$), 31.3 (C-1/C-13), 31.1 (C-16). (+)-ESI-MS ($CH_2Cl_2$/$CH_3OH$): *m/z* = 967.6 ($C_{58}H_{87}N_4S_4^+$, $[M+H^+]^+$) calcd: 967.58. The identity of this compound was further confirmed by an X-ray crystallographic analysis of its tetra-*N*-methylated derivative **7b**.

**Bicyclic macrocycles 7a and 7b**: To a solution of the macrobicyclic thioether **6** (isomeric mixture or pure **6a**,**b**, 1.38 g, 1.43 mmol) in THF (150 mL) was added 37 % aqueous formaldehyde solution (6.40 mL, 86.0 mmol) and a few drops of formic acid. The mixture was cooled with an ice bath, and $NaBH_3CN$ was added (1.08 g, 17.2 mmol, 12 equiv.) in small portions. After stirring for 2 days NaOH (2 M, 40 mL) was added and stirring was continued for further 3 h to destroy excess reducing agent. The reaction mixture was evaporated in vacuo to remove the volatiles. The resulting colorless residue was taken up in $CHCl_3$ (100 mL) and $H_2O$ (75 mL). The organic phase was separated, and the aqueous phase was extracted for another four times with $CHCl_3$ (50 mL). The combined organic phases were washed with saturated NaCl solution (150 mL), dried with $K_2CO_3$, and filtered. Evaporation of the solvent under vacuum gave a colorless solid (mixture of **7a** and **7b** or pure **7a**, pure **7b** depending on the starting compound) which was purified by crystallization from $CHCl_3$/MeOH. Colorless solids, yield: 1.30 g (mixture of **7a** and **b**, 1.27 mmol, 89 %). M = 1023.70 g/mol. (+)-ESI-MS ($CH_2Cl_2$/$CH_3OH$): *m/z* = 1023.6 ($C_{62}H_{95}N_4S_4^+$, $[M+H^+]^+$); calcd: 1023.64. Found: C 65.80, H 8.62, N 4.81 S 11.04; $C_{62}H_{94}N_4S_4 \cdot CHCl_3$: requires C 66.20, H 8.38, N 4.90, S 11.22.

Analytical data for **7a** (*1,2-alternate conformer*): colorless solid, MW 1023.60 g/mol, m.p. > 280 °C (decomp.). $^1$H NMR (400 MHz, toluene-d$_8$, 90 °C): $\delta$ [ppm] = 7.79 (s, 4 H, ArH), 7.62 (s, 4 H, ArH), 4.78 (d, $^2J_{HH}$ = 13 Hz, 4 H, ArC$H_2$N), 3.72 (d, $^2J_{HH}$ = 13 Hz, 4 H, ArC$H_2$N), 3.67 (d, $^2J_{HH}$ = 16 Hz, 4 H, ArC$H_2$N), 3.39 (d, $^2J_{HH}$ = 16 Hz, 4 H, ArC$H_2$N), 2.35 (s, 12 H, NC$H_3$), 1.82 (d, $^2J_{HH}$ = 10 Hz, 2 H, SC$H_2$), 1.75 (d, $^2J_{HH}$ = 10 Hz, 2 H, SC$H_2$), 1.44 (s, 18 H, C($CH_3$)$_3$), 1.14 (s, 18 H, C($CH_3$)$_3$), 1.14 (s, 18 H, C($CH_3$)$_3$). $^{13}$C{$^1$H} NMR (100 MHz, toluene-d$_8$, 90 °C): $\delta$ [ppm] = 151.5 (ArCC($CH_3$)$_3$), 151.2 (ArCC($CH_3$)$_3$), 145.1 (ArCCH$_2$), 145.0 (ArCCH$_2$), 131.6 (ArCS), 62.6 (ArCCH$_2$N), 59.5 (ArCCH$_2$N), 48.6 (SC-($CH_3$)$_3$), 44.3-43.9 (NC$H_3$), 35.2, 35.1, 32.3-31.3 (C($CH_3$)$_3$). IR (KBr): $\tilde{\nu}$/cm$^{-1}$ = 3442 (w, br), 3054 (w), 2964 (vs), 2904 (s), 2866 (s), 2835 (s), 2779 (s), 2714 (sh), 1790 (w), 1596 (s), 1588 (w), 1478 (sh), 1457 (s), 1417 (m), 1405 (m), 1393 (m), 1362 (vs), 1282 (m), 1252 (m), 1219 (s), 1201 (m), 1166 (s), 1136 (s), 1041 (m), 1018 (m), 992 (m), 972 (w), 927 (w), 907 (w), 884 (s), 869 (sh), 846 (m), 805 (w), 755 (vs), 708 (w), 687 (m), 665 (w), 644 (w), 624 (w), 574 (w), 527 (w), 431 (w). This compound was additionally identified by X-ray crystallography.

Analytical data for **7b** (*cone conformer*): colorless solid, MW 1023.60 g/mol, m.p. > 265 °C (decomp.). $^1$H NMR (400 MHz, toluene-d$_8$, 90 °C): $\delta$ [ppm] = 7.85 (s, 4 H, ArH), 7.67 (s, 4 H, ArH), 4.84 (d, $^2J_{HH}$ = 13 Hz, 4 H, ArC$H_2$N), 3.76 (d, $^2J_{HH}$ = 13 Hz, 4 H, ArC$H_2$N), 3.66 (d, $^2J_{HH}$ = 16 Hz, 4 H, ArC$H_2$N), 3.37 (d, $^2J_{HH}$ = 16 Hz, 4 H, ArC$H_2$N), 2.39 (s, 12 H, NC$H_3$), 1.98 (s, 4 H, SC$H_2$), 1.43 (s, 18 H, C($CH_3$)$_3$), 1.19 (s, 18 H, C($CH_3$)$_3$), 1.16 (s, 18 H, C($CH_3$)$_3$). $^{13}$C{$^1$H} NMR (100 MHz, toluene-d$_8$, 90 °C): $\delta$ [ppm] = 152.1 (ArCC($CH_3$)$_3$), 151.6 (ArCC($CH_3$)$_3$), 145.7 (ArCCH$_2$), 144.5 (ArCCH$_2$), 131.4 (ArCS), 127.4 (ArCH), 62.1 (ArCCH$_2$N), 58.2 (ArCCH$_2$N), 48.7 (SC($CH_3$)$_3$), 44.1 (NC$H_3$), 43.9 (NC$H_3$), 36.1 (SC$H_2$), 35.4 (ArCC($CH_3$)$_3$), 35.2 (ArCC($CH_3$)$_3$), 32.1 (C($CH_3$)$_3$), 32.0 (C($CH_3$)$_3$), 32.0 (C($CH_3$)$_3$), 31.7 (C($CH_3$)$_3$), 31.6 (C($CH_3$)$_3$). IR (KBr): $\tilde{\nu}$/cm$^{-1}$ = 3442 (w, br), 3056 (w), 2964 (vs), 2905 (s), 2866 (s), 2835 (s), 2779 (s), 2712 (sh), 1790 (w), 1596 (s), 1560 (w), 1478 (sh), 1458 (s), 1417 (m), 1404 (m), 1393 (m), 1362 (vs), 1280 (m), 1261 (m), 1219 (s), 1198 (m), 1166 (s), 1132 (s), 1039 (s), 993 (m), 972 (m), 927 (w), 886 (s), 864 (w), 845 (w), 807 (m), 709 (w), 684 (m), 645 (w), 628 (w), 573 (w), 542 (w), 434 (w).

**Macrocycle $H_4$8·4HCl**: A solution of compound **6** (1.84 g, 1.90 mmol, mixture of conformers **6a**,**b**) in THF (70 mL) was added dropwise to a solution of sodium (900 mg, 39.15 mmol, 20 equiv.) in liquid $NH_3$ (400 mL) at −78 °C. The dark blue reaction mixture was stirred for further 5 h at −60 °C to ensure complete deprotection of the thioether linkages. Excess reducing equivalents was destroyed by careful addition of small portions of $NH_4Cl$ (total amount ~1.8 g) at −78 °C. After the ammonia was allowed to evaporate overnight by removal of the *i*PrOH/dry-ice cooling bath, the remaining volatiles were removed at room temperature under a vacuum. The resulting pale-yellow residue was taken up in a mixture of conc. HCl (25 mL), water (80 mL) and MeOH (350 ml) and stirred for 2 h to give a pale-yellow solution. The mixture was evaporated until incipient precipitation and kept at 4 °C for 12 h in a fridgerator. The resulting colourless solid was filtered under an

inert atmosphere, washed with HCl (1 M, 35 mL), dried in a vacuum and stored under $N_2$ atmosphere. Yield: 1.54 g (1.57 mmol, 83 %). Colorless, air-sensitive solid, MW 975.18 g/mol, m.p. >260 °C (decomp.). $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ [ppm] = 7.76 (s, 8 H, ArH), 4.61 (s, 16 H, $ArCH_2N$), 1.37 (s, 36 H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CD_3OD$): $\delta$ [ppm] = 152.9 ($ArCC(CH_3)_3$), 151.6 ($ArCC(CH_3)_3$), 136.3 ($ArCCH_2$), 132.3 (ArCS), 131.9 (ArCH), 52.1 ($ArCCH_2N$), 35.7 ($ArC(CH_3)_3$), 31.5 ($C(CH_3)_3$). IR (KBr): $\tilde{\nu}$/cm$^{-1}$ = 3424 (s, br), 2962 (vs), 2931 (sh), 2910 (sh), 2868 (sh), 2760 (s, br), 2692 (sh), 2597 (m, br), 2398 (m, br), 1627 (m), 1603 (m), 1586 (m), 1568 (m), 1478 (sh), 1448 (s), 1408 (m), 1366 (m), 1312 (w), 1270 (w), 1232 (m), 1203 (w), 1160 (m), 1056 (m), 1015 (w), 926 (w), 895 (m), 830 (w), 742 (w), 665 (w), 581 (w, br), 533 (w, br). (+)-ESI-MS ($CH_3OH$): *m/z* = 829.4 ($C_{48}H_{69}N_4S_4^+$ $[M+H^+]^+$); calcd: 829.44. Found: C 58.23, H 7.62, N 5.41, 11.99; $C_{48}H_{72}Cl_4N_4S_4{\cdot}H_2O$: requires C 58.05, H 7.51, N 5.64, S 12.91.

**Macrocycle $H_4$9·4HCl**: This compound was synthesized as detailed above for $H_4$**8**·4HCl. Analytical data for $H_4$**9**·4HCl: yield, 1.66 g, (1.61 mmol, 82 %). Colorless, air-sensitive solid, MW 1031.28 g/mol, m.p. >250-253 °C (decomp.). $^1$H NMR (300 MHz, $CD_3OD$): $\delta$ [ppm] = 7.60 (s, 8 H, ArH), 4.76-3.98 (m, 16 H, $ArCH_2N$), 2.85 (s, 12 H, $NCH_3$), 1.37 (s, 36 H, $C(CH_3)_3$). IR (KBr): $\tilde{\nu}$/cm$^{-1}$ = 3424 (vs, br), 3022 (sh), 2957 (vs), 2907 (sh), 2870 (s), 2806 (m), 2689 (m, br), 2359 (m, br), 1880 (w), 1626 (m), 1603 (sh), 1465 (vs), 1409 (s), 1397 (s), 1366 (s), 1320 (w), 1299 (w), 1233 (s), 1205 (sh), 1150 (m), 1112 (m), 1053 (m), 1011 (w), 972 (sh), 954 (sh), 928 (m), 885 (s), 841 (w), 743 (w), 691 (sh), 593(m, br), 539 (m, br). (+)-ESI-MS ($CH_3OH$): Found *m/z* = 885.5 ($C_{52}H_{77}N_4S_4^+$ $[M+H^+]^+$); calcd: 885.50. Found: C 55.72, H 8.02, N 4.92, S 11.01; $C_{52}H_{80}Cl_4N_4S_4{\cdot}5H_2O$: requires C 55.70, H 8.09, N 5.00, S 11.44.

**Macrotricycle 11**: **10** (0.127 g, 0.078 mmol) and phenol (0.295 g, 3.13 mmol) were mixed in 33 % aqueous HBr in acetic acid (3 mL) under nitrogen and heated at 50 °C. The progress of the reaction was monitored by examining aliquots (0.1 mL) of the mixture by MALDI-TOF MS. After 36 h, the reaction was quenched by addition of 48 % aqueous HBr (7 mL), which produced the precipitation of a colorless material. The reaction mixture was basified by slow addition of a 10 % aqueous NaOH solution (30 mL) at 0 °C, and stirred vigorously for 2 h after addition of dichloromethane (30 mL). Two clear phases were obtained and separated. The aqueous phase was extracted with dichloromethane (20 mL), and the combined organic extracts were washed with a 10 % aqueous NaOH solution (2×20 mL), separated, and dried over $MgSO_4$. Filtration and evaporation of the solvent afforded **11** (0.055 g, 70 %) as a colorless solid of acceptable purity. $^1$H NMR ($CDCl_3$, 300 MHz, 300 K): $\delta$ [ppm] = 1.31 (s, 36 H; H-1), 1.86 (m, 4 H; H-12), 2.84 (t, $^3J_{HH}$ = 5.2 Hz, 8 H, H-11), 3.16 (s, 8 H; H-13), 3.94 (s, 8 H; H-7), 4.10 (s, 8 H, H-8), 7.23 (d, $^4J_{HH}$ = 2.2 Hz, 4 H; H-10), 7.52 (d, $^4J_{HH}$ = 2.2 Hz, 4 H; H-4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 300 K): $\delta$ [ppm] = 30.3 (C-12), 31.4 (C-1), 34.8 (C-2), 36.2 (C-13), 50.4 (C-11), 54.0 (C-8), 55.1 (C-7), 125.5 (C-4), 127.2 (C-10), 129.2 (C-6), 144.2 (C-5, C-9), 152.1 (C-3). MALDI-TOF MS: Found, *m/z* = 995 ($C_{58}H_{86}N_6S_4^+$ $[M^+]$); calcd: 995.61. Found: C 67.55, H 8.94, N 7.99, S 12.21; $C_{58}H_{86}N_6S_4{\cdot}1/2CH_2Cl_2$: requires C 67.69, H 8.45, N 8.10, S 12.36.

**Macrocycle $H_4$12**: A solution of **11** (0.520 g, 0.52 mmol) containing sodium pieces (0.215 g, 9.34 mmol) in THF (20 mL) under nitrogen was cooled down to −65 °C. Liquid ammonia (50 mL) was then transferred into the reaction mixture via canula, which produced a deep blue color change. The temperature of the cooling bath was kept between −50 and −79 °C for 3 h. It was then raised to −30 °C for 1 h. The vessel was opened and the reaction was quenched by addition of solid ammonium chloride (0.310 g). Ammonia was allowed to evaporate and the remaining THF was removed under reduced pressure. The colorless residue was dissolved in a mixture of dichloromethane and ethyl acetate (7:3, v/v). The resulting solution was diluted with methanol (2 mL) and water (30 mL). After stirring the mixture, the organic phase was separated, washed with water (2 × 40 mL), dried over $MgSO_4$, filtered, and the solvent removed in vacuo. $H_4$**12** (0.445 g) was isolated as a pink solid in 90 % yield. $^1$H NMR ($CDCl_3/CD_3OD$ 1:1 v/v, 300 MHz, 300 K): $\delta$ [ppm] = 1.22 (s, 36 H; H-1), 1.58 (m, 4 H; H-12), 2.68 (br t, 8 H; H-11), 3.66 (br s, 8 H; H-7), 4.23 (br s, 8 H; H-8), 6.78 (br s, 4 H; H-10), 7.99 (s, 4 H; H-4). MALDI-TOF MS: *m/z* = 942.72 ($C_{54}H_{83}N_6S_4$ $[M]^+$); calcd: 943.55. Found: C 63.67, H 8.52, N 8.01, S 12.03; $C_{54}H_{82}N_6S_4{\cdot}CH_2Cl_2$: requires C 64.23, H 8.23, N 8.17, S 12.47.

**Cobalt complex 13**: $[Co^{II}_4$(**9**)($\mu$-Cl)($\mu$-OAc)$_2$]Cl (**13**). To a hot solution of $H_4$**9**·4HCl (155 mg, 0.15 mmol) in MeOH (20 mL), was added a solution of $CoCl_2{\cdot}6H_2O$ (178 mg, 0.75 mmol) in EtOH (5 mL) and $LiOAc{\cdot}2H_2O$ (122 mg, 1.20 mmol). The resulting dark green solution was refluxed for 8 h to give a blue-green solution. The mixture was evaporated to 1/3 in volume until incipient crystallization, and kept in a freezer at 4 °C to complete precipitation of the product. The solid was collected by filtration, washed with little cold MeOH (2 mL) and dried in vacuum. Yield: 116 mg (0.09 mmol, 58 %), blue-green solid. (+)-ESI-MS ($CH_3OH$): *m/z* = 1251.2 ($C_{56}H_{78}Co_4N_4O_5S_4^+$) $[M–Cl^- + OH^-]^+$; calcd: 1251.23; m/z = 1269.2, ($C_{56}H_{78}ClCo_4N_4O_4S_4^+$ $[M–Cl]^+$); calcd: 1269.16. IR (KBr): $\tilde{\nu}$/cm$^{-1}$ = 3425 (s, br), 2955 (s), 2905 (m), 2867 (m), 1623 (m), 1553 (s), 1455 (sh), 1441 (vs), 1395 (sh), 1369 (m), 1298 (w), 1229 (m), 1202 (w), 1181 (w), 1157 (m), 1082 (m), 1056 (m), 1023 (m), 986 (m), 955 (w), 885 (m), 840 (m), 666 (m), 627 (m), 536 (w), 489 (w), 471 (w). UV/Vis ($CHCl_3$, 295 K): $\lambda_{max}$ [nm] ($\varepsilon$ [M$^{-1}$cm$^{-1}$]) = 248 (30210), 326 sh (7736), 378 (5971), 585 (804), 630 sh (565), 856 (291), 943 sh (264). Found: C 50.00, H 6.09, N 4.16, S 9.64; $C_{56}H_{78}Cl_2Co_4N_4O_4S_4{\cdot}2H_2O$: requires C 50.11, H 6.16, N 4.17, S 9.56.

**X-ray crystallography**: Suitable single crystals of **6a**·2MeOH, **7a**·4$CHCl_3$, **7b**·$CH_2Cl_2$ and **13**·3$H_2O$·3.5*t*BuOH were selected and mounted on the tip of a glass fibre using perfluoropolyether oil. The data sets were collected at 180(2) K using a STOE IPDS 2T diffractometer equipped with graphite monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). Reflection data were processed using the X-area package.[42] Empirical absorption corrections were performed with STOE X-Red 32. The structures were solved by direct methods and refined by full-matrix least-squares techniques on the basis of all data against $F^2$ using SHELXL-2018/3[43] and Olex2.[44] PLATON was used to search for higher symmetry.[45] All non-hydrogen atoms were refined anisotropically. Graphics were produced with Ortep3 for Windows[46] and PovRAY.[47]

**Crystallographic data for 6a·2MeOH**: $C_{60}H_{94}N_4O_2S_4$, $M_r$ = 1031.63 g/mol, triclinic space group *P*-1, *a* = 14.3561(8) Å, *b* = 14.7687(9) Å, *c* = 15.0754(8) Å, $\alpha$ = 93.790(5)°, $\beta$ = 101.860(4)°, $\gamma$ = 102.007(4)°, *V* = 3039.8(3) Å$^3$, *Z* = 2, $\rho_{calcd}$ = 1.127 g/cm$^3$, *T* = 180(2) K, $\mu$(Mo K$_\alpha$) = 0.199 mm$^{-1}$ ($\lambda$ = 0.71073 Å), 25404 reflections measured, 12661 unique, 7962 with $I > 2\sigma(I)$. Final $R_1$ = 0.059, $wR_2$ = 0.179 ($I > 2\sigma(I)$), 719 parameters/113 restraints, min./max. residual electron density = 0.472/-0.292 e/Å$^3$. One *tert*-butyl group was found to be disordered over two positions, modeled with a split atom model yielding site occupancy factors of 0.63/0.37 (refined). One MeOH solvent molecule was found to be highly disordered. A reasonable model was constructed by splitting the molecule into three parts. Site occupancy factors of 0.67/0.13/0.20 were refined using the free variables and the SUMP instruction. The H atoms bonded to the N atoms were located from final Fourier maps and were refined with a riding model.

**Crystallographic data for 7a·4$CHCl_3$**: $C_{66}H_{98}Cl_{12}N_4S_4$, $M_r$ = 1501.12 g/mol, triclinic space group *P*-1, *a* = 10.674(1) Å, *b* = 14.645(2) Å, *c* = 14.702(2) Å, $\alpha$ = 114.542(9)°, $\beta$ = 96.36(1)°, $\gamma$ = 102.78(1)°, *V* = 1984.8(4) Å$^3$, *Z* = 1, $\rho_{calcd}$ = 1.256 g/cm$^3$, *T* = 180(2) K, $\mu$(Mo K$_\alpha$) = 0.562 mm$^{-1}$ ($\lambda$ = 0.71073 Å), 12378 reflections measured, 6798

unique, 4574 with $I > 2\sigma(I)$. Final $R_1 = 0.0826$, $wR_2 = 0.2637$ ($I > 2\sigma(I)$), 373 parameters/18 restraints, min./max. residual electron density = 0.485/−0.460 e/Å$^3$. The ethylene group was found to be disordered over two positions, modeled with a split atom model yielding site occupancy factors of 0.75/0.25. Two $CHCl_3$ molecules occupy interstitial spaces between molecules of **7a** and were found to be highly disordered. SQUEEZE implemented in Platon was applied to remove diffuse electron density. The total potential solvent accessible void volume per unit cell was determined to be 403 Å$^3$ (electron count = 116 electrons), corresponding to two $CHCl_3$ molecules per formula unit.

**Crystallographic data for 7b·$CH_2Cl_2$**: $C_{63}H_{96}Cl_2N_4S_4$, $M_r = 1108.57$ g/mol, monoclinic space group *C*2/*c*, $a = 40.4338(11)$ Å, $b = 13.3006(5)$ Å, $c = 25.8550(7)$ Å, $\gamma = 109.803(2)°$, $V = 13082.4(7)$ Å$^3$, $Z = 8$, $\rho_{calcd} = 1.126$ g/cm$^3$, $T = 180(2)$ K, $\mu$(Mo $K_\alpha$) = 0.181 mm$^{-1}$ ($\lambda = 0.71073$ Å), 33300 reflections measured, 13800 unique, 9573 with $I > 2\sigma(I)$. Final $R_1 = 0.0852$, $wR_2 = 0.2546$ ($I > 2\sigma(I)$), 759 parameters/138 restraints, min./max. residual electron density = 0.731/−0.526 e/Å$^3$. The ethylene group and the *tert*-butyl groups were found to be disordered over two positions. This disorder was modeled with a split atom model yielding site occupancy factors of 0.53/0.47 (C34-C36), 0.72/0.28 (C38-C40), 0.80/0.20 (C42-C44), 0.55/0.45 (C46-C48) and 0.59/0.41 (C57,C58). The $CH_2Cl_2$ molecules occupy interstitial spaces between molecules of **7b** and were found to be highly disordered. SQUEEZE implemented in Platon was applied to remove diffuse electron density. The total potential solvent accessible void volume per unit cell was determined to be 1020 Å$^3$ (electron count = 320 electrons), corresponding to one $CH_2Cl_2$ molecule per formula unit.

**Crystallographic data for 13·3$H_2O$·3.5*t*BuOH**: $C_{70}H_{119}Cl_2Co_4N_4O_{10.5}S_4$, $M_r = 1619.54$ g/mol, triclinic space group *P*-1, $a = 13.8026(7)$ Å, $b = 17.8216(11)$ Å, $c = 19.3859(12)$ Å, $\alpha = 68.110(4)°$, $\beta = 89.430(5)°$, $\gamma = 68.259(4)°$, $V = 4065.6(4)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.323$ g/cm$^3$, $T = 180(2)$ K, $\mu$(Mo $K_\alpha$) = 1.024 mm$^{-1}$ ($\lambda = 0.71073$ Å), 26806 reflections measured, 15033 unique, 10178 with $I > 2\sigma(I)$. Final $R_1 = 0.0583$, $wR_2 = 0.1796$ ($I > 2\sigma(I)$), 840 parameters/91 restraints, min./max. residual electron density = 1.054/−0.861 e/Å$^3$. The chloride counter ion was found to be heavily disordered. A reasonable model was constructed by splitting the atom into three parts. Site occupancy factors of 0.23/0.10/0.67 were refined using the free variables, the SUMP instruction and the EADP constraint. The water molecules and 0.5 *t*BuOH were found to be highly disordered. SQUEEZE implemented in Platon was applied to remove diffuse electron density. The total potential solvent accessible void volume per unit cell was determined to be 437 Å$^3$ (electron count = 97 electrons), corresponding to 0.5 *t*BuOH and 3 $H_2O$ molecules per formula unit.

**Computational Details**: Geometry optimizations were carried out using version 4.2.0 of the ORCA package.[48] All DFT calculations utilized the PBE0[49,50] functionals using the def2-TZVP basis set for all atoms.[51] Dispersion effects were accounted by Grimme's D3 correction with Becke-Johnson (BJ) damping.[52,53] The RIJCOSX approximation[54] with the related basis set def2/J was used to speed up the calculations.[55] The VeryTightSCF criteria implemented on ORCA was used employing the Grid5/NoFinalGrid option. The structural parameters were first optimized starting from the X-ray structures followed by frequency calculations to rule out the presence of any imaginary frequencies.

## Supporting Information

Supporting Information available: $^1$H NMR spectra for all new compounds. $^{13}$C NMR spectra for compounds **8**·4HCl and **11**. MALDI-TOF mass spectra for compounds **11** and **12**. Plots of DFT calculated geometries and coordinates for **6a**, **6b**, **7a** and **7b**.

Deposition Number(s) 2123379 (for **6a**·2MeOH), 2123378 (for **7a**·4$CHCl_3$), 2123377 (for **7b**·$CH_2Cl_2$), 2123376 (for **13**·3$H_2O$·3.5*t*BuOH) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** coordination chemistry · expanded mercaptocalix[4]arenes · synthesis · X-ray crystallography

[1] a) C. D. Gutsche, *Calixarenes*, Royal Society of Chemistry, Cambridge, **1989**; b) *Calixarenes: A Versatile Class of Macrocyclic Compounds* (Eds: J. Vincens, V. Böhmer), Kluwer, Dordrecht, The Netherlands, **1991**; c) V. Böhmer, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 713—745; Angew. Chem. 1995, 107, 785–818.
[2] C. D. Gutsche, R. Muthukrishnan, *J. Org. Chem.* **1978**, *43*, 4905–4906.
[3] a) A. Pochini, R. Ungaro, in *Comprehensive Supramolecular Chemistry*, Vol. 2 *Molecular Recognition: Receptors for Molecular Guests* (Eds: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, J. M. Lehn), Elsevier Science Ltd, Oxford, **1996**, pp. 103; b) C. Talotta, C. Gaeta, M. De Rosa, A. Soriente, P. Neri, in *Comprehensive Supramolecular Chemistry II*, Vol. 3 *Supramolecular Receptors* (Eds: J. L. Atwood, G. W. Gokel, L; J. Barbour, K. Rissanen) Elsevier Ltd, Amsterdam, **2017**, pp. 49.
[4] Y. K. Agrawal, V. S. Mishra, *Rev. Inorg. Chem.* **2004**, *24*, 1–29.
[5] R. Kumar, A. Sharma, H. Singh, P. Suating, H. S. Kim, K. Sunwoo, I. Shim, B. C. Gibb, J. S. Kim, *Chem. Rev.* **2019**, *119*, 9657–9721.
[6] C. Wieser, C. B. Dieleman, D. Matt, *Coord. Chem. Rev.* **1997**, *165*, 93–161.
[7] a) C. G. Gibbs, C. D. Gutsche, *J. Am. Chem. Soc.* **1993**, *115*, 5338–5339. b) C. G. Gibbs, P. K. Sujeeth, J. S. Rogers, G. G. Stanley, M. Krawiec, W. H. Watson, C. D. Gutsche, *J. Org. Chem.* **1995**, *60*, 8394–8402.
[8] a) X. Delaigue, M. W. Hosseini, *Tetrahedron Lett.* **1993**, *34*, 8111–8112; b) X. Delaigue, J. M. Harrowfield, M. W. Hosseini, A. de Cian, J. Fischer, N. Kyritsakas, *J. Chem. Soc. Chem. Commun.* **1994**, 1579–1580.

[9] T. Sone, Y. Ohba, K. Moriya, H. Kumada, K. Ito, *Tetrahedron* **1997**, *53*, 10689–10698.
[10] N. Morohashi, F. Narumi, N. Iki, T. Hattori, S. Miyano, *Chem. Rev.* **2006**, *106*, 5291–5316.
[11] a) H. Akdas, E. Graf, M. W. Hosseini, P. Rao, A. De Cian, *J. Supramol. Chem.* **2002**, *2*, 21–28; b) H. Akdas, L. Bringel, V. Bulach, E. Graf, M. W. Hosseini, A. De Cian, *Tetrahedron Lett.* **2002**, *43*, 8975–8979.
[12] M. W. Hosseini, in *Calixarenes 2001* (Eds: Z. Asfari, V. Böhmer, J. M. Harrowfield, J. Vicens, M. Saadioui), Springer, Dordrecht, **2001**, p. 110.
[13] a) H. Akdas, E. Graf, M. W. Hosseini, A. De Cian, A. Bilyk, B. W. Skelton, G. A. Koutsantonis, I. Murray, J. M. Harrowfield, A. H. White, *Chem. Commun.* **2002**, 1042–1043; b) K. Hirata, T. Suzuki, A. Noya, I. Takei, M. Hidai, *Chem. Commun.* **2005**, 3718–3720.
[14] a) N. Frank, A. Dallmann, B. Braun-Cula, C. Herwig, C. Limberg, *Angew. Chem. Int. Ed.* **2020**, *59*, 6735–6739; *Angew. Chem.* **2020**, *132*, 6801–6805; b) D. Bucella, G. Parkin, *Chem. Commun.* **2009**, 289–291.
[15] A. Bilyk, J. W. Dunlop, R. O. Fuller, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, G. A. Koutsantonis, I. W. Murray, B. W. Skelton, A. N. Sobolev, R. L. Stamps, A. H. White, *Eur. J. Inorg. Chem.* **2010**, 2127–2152.
[16] A. Gehin, S. Ferlay, J. M. Harrowfield, D. Fenske, N. Kyritsakas, M. W. Hosseini, *Inorg. Chem.* **2012**, *51*, 5481–5486.
[17] a) S. Takemoto, S. Tanaka, Y. Mizobe, M. Hidai, *Chem. Commun.* **2004**, 838–839; b) E. Hoppe, C. Limberg, *Chem. Eur. J.* **2007**, *13*, 7006–7016.
[18] C. Desroches, G. Pilet, P. A. Szilágyi, C. Molnár, S. A. Borshch, A. Bousseksou, S. Parola, D. Luneau, *Eur. J. Inorg. Chem.* **2006**, 357–365.
[19] a) A. Bilyk, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, B. W. Skelton, A. H. White, *Inorg. Chem.* **2001**, *40*, 672–686; b) A. Bilyk, J. W. Dunlop, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, G. A. Koutsantonis, B. W. Skelton, A. H. White, *Eur. J. Inorg. Chem.* **2010**, 2089–2105; c) A. Bilyk, J. W. Dunlop, R. O. Fuller, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, G. A. Koutsantonis, I. W. Murray, B. W. Skelton, R. L. Stamps, A. H. White, *Eur. J. Inorg. Chem.* **2010**, 2106–2126.
[20] A. S. Ovsyannikov, M. H. Noamane, R. Abidi, S. Ferlay, S. E. Solovieva, I. S. Antipin, A. I. Konovalov, N. Kyritsakas, M. W. Hosseini, *CrystEngComm* **2016**, *18*, 691-703.
[21] A. Ovsyannikov, S. Ferlay, S. E. Solovieva, I. S. Antipin, A. I. Konovalov, N. Kyritsakas, M. W. Hosseini, *CrystEngComm* **2014**, *16*, 3765–3772.
[22] A. Ovsyannikov, S. Ferlay, S. E. Solovieva, I. S. Antipin, A. I. Konovalov, N. Kyritsakas, M. W. Hosseini, *Inorg. Chem.* **2013**, *52*, 6776–6778.
[23] P. Rao, O. Enger, E. Graf, M. W. Hosseini, A. De Cian, J. Fischer, *Eur. J. Inorg. Chem.* **2000**, 1503–1508.
[24] S. Yoshimoto, M. Abe, K. Itaya, F. Narumi, K. Sashikata, K. Nishiyama, I. Taniguchi, *Langmuir* **2003**, *19*, 8130–8133.
[25] W. Hill, B. Wehling, C. G. Gibbs, C. D. Gutsche, D. Klockow, *Anal. Chem.* **1995**, *67*, 3187–3192.
[26] a) T. D. P. Stack, R. H. Holm, *J. Am. Chem. Soc.* **1987**, *109*, 2546–2547; b) S. Ciurli, R. H. Holm, *Inorg. Chem.* **1989**, *28*, 1685–1690; c) J. A. Weigel, R. H. Holm, *J. Am. Chem. Soc.* **1991**, *113*, 4184–4191.
[27] a) G. P. F. Van Strijdonck, J. A. E. H. Van Haare, J. G. M. Van der Linden, J. J. Steggerda, R. J. M. Nolte, *Inorg. Chem.* **1994**, *33*, 999–1000; b) G. P. F. Van Strijdonck, J. A. E. H. Van Haare, P. J. M. Hönen, R. C. G. M. Van den Schoor, M. C. Feiters, J. G. M. Van der Linden, J. J. Steggerda, R. J. M. Nolte, *J. Chem. Soc. Dalton Trans.* **1997**, 449–461.
[28] a) N. Govindaswamy, D. A. Quarless, Jr., S. A. Koch, *J. Am. Chem. Soc.* **1994**, *117*, 8468–8469; b) F. M. MacDonnell, K. Ruhlandt-Senge, J. J. Ellison, R. H. Holm, P. P. Power, *Inorg. Chem.* **1995**, *34*, 1815–1822; c) T. Beissel, T. Glaser, F. Kesting, K. Wieghardt, B. Nuber, *Inorg. Chem.* **1996**, *35*, 3936–3947; d) D. Sellmann, A. Hille, A. Rösler, F. W. Heinemann, M. Moll, G. Brehm, S. Schneider, M. Reiher, B. A. Hess, W. Bauer, *Chem. Eur. J.* **2004**, 10, 819–830; e) M. Yuki, T. Matsuo, H. Kawaguchi, *Angew. Chem. Int. Ed.* **2004**, *43*, 1404–1407; *Angew. Chem.* **2004**, *116*, 1428–1431; f) A. Takaoka, N. P. Mankad, J. C. Peters, *J. Am. Chem. Soc.* **2011**, *133*, 8440–8443.
[29] a) B. Kersting, G. Steinfeld, T. Fritz, J. Hausmann, *Eur. J. Inorg. Chem.* **1999**, 2167–2172; b) M. H. Klingele, G. Steinfeld, B. Kersting, *Z. Naturforsch.* **2001**, *56b*, 901–907; c) B. Kersting, *Angew. Chem. Int. Ed.* **2001**, *40*, 3988–3990; *Angew. Chem.* **2001**, *113*, 4109–4112; d) C. Bonnot, J.-C. Chambron, E. Espinosa, R. Graff, *J. Org. Chem.* **2008**, *73*, 868–881; e) L. Wang, C. Michelin, J.-C. Chambron, *Synthesis* **2009**, 3419–3426; f) L. Wang, J.-C. Chambron, E. Espinosa, *New J. Chem.* **2009**, *33*, 327–336.
[30] B. Kersting, G. Steinfeld, J. Hausmann, *Eur. J. Inorg. Chem.* **1999**, 179–187.
[31] a) B. Kersting, D. Siebert, D. Volkmer, M. J. Kolm, C. Janiak, *Inorg. Chem.* **1999**, *38*, 3871–3882; b) G. Steinfeld, B. Kersting, *Chem. Commun.* **2000**, 205–206.
[32] a) T. R. Simmons, G. Berggren, M. Bacchi, M. Fontecave, V. Artero, *Coord. Chem.* Rev. **2014**, *270–271*, 127–150; b) R. D. Bethel, M. Y. Darensbourg, in *Bioorganometallic Chemistry* (Eds: G. Jaouen, M. Salmain), Wiley-VCH, Weinheim, **2015**, p. 241–272; c) C. Elleouet, F. Y. Pétillon, P. Schollhammer, in *Advances in Bioinorganic Chemistry*, (Eds. T. Hirao, T. Moriuchi), Elsevier B. V., Amsterdam, **2019**, 347–364.
[33] R. Kumar, A. Sharma, H. Singh, P. Suating, H. S. Kim, K. Sunwoo, I. Shim, B. C. Gibb, J. S. Kim, *Chem. Rev.* **2019**, *119*, 9657–9721.
[34] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.
[35] K. Kanakarajan, H. Meier, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 244; *Angew. Chem.* **1984**, *96*, 220.
[36] a) T. J. Wallace, A. Schriesheim, *J. Org. Chem.* **1962**, *27*, 1514–1516; b) T. J. Wallace, A. Schriesheim, W. Bartok, *J. Org. Chem.* **1963**, *28*, 1311–1314.
[37] a) J. Houk, G. M. Whitesides, *Tetrahedron* **1989**, *45*, 91–102; b) S.-W. Tam-Chang, J. S. Stehouwer, J. Hao, *J. Org. Chem.* **1999**, *64*, 334–335; c) F. Ulatowski, A. Sadowska-Kuzioła, J. Jurczak, *J. Org. Chem.* **2014**, *79*, 9762–9770.
[38] For selected early examples: a) S. Otto, R. L. E. Furlan, J. K. M. Sanders, *J. Am. Chem. Soc.* **2000**, *122*, 12063–12064; b) C. Naumann, S. Place, J. C. Sherman, *J. Am. Chem. Soc.* **2002**, *124*, 16–17; c) A. L. Kieran, A. D. Bond, A. M. Belenguer, J. K. M. Sanders, *Chem. Commun.* **2003**, 2674–2675; d) K. R. West, K. D. Bake, S. Otto, *Org. Lett.* **2005**, *7*, 2615–2618; e) S. Hamieh, R. F. Ludlow, O. Perraud, K. R. West, E. Mattia, S. Otto, *Org. Lett.* **2012**, *14*, 5404–5407.
[39] Y.-C. Horng, T.-L. Lin, C.-Y. Tu, T.-J. Sung, C.-C. Hsieh, C.-H. Hu, H. M. Lee, T.-S. Kuo, *Eur. J. Org. Chem.* **2009**, 1511–1514.
[40] J. A. Burns, G. M. Whitesides, *J. Am. Chem. Soc.* **1990**, *112*, 6296–6303.
[41] Atom numbering of compounds **6a**, **6b**, **11**, and $H_4$**12** is given in the Supporting Information.
[42] Stoe & Cie, *X-AREA and X-RED 32*; V1.35, Stoe & Cie: Darmstadt, Germany, **2006**.
[43] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8.
[44] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard, K. H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
[45] A. L. Spek, *PLATON - A Multipurpose Crystallographic Tool*; Utrecht University, Utrecht, The Netherlands, **2000**.
[46] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.
[47] C. Cason, T. Froehlich, N. Kopp, R. Parker, POV-Ray for Windows, version 3.6.2msvc9.win64.
[48] F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2012**, *2*, 73–78.
[49] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 3865–3868.
[50] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158–6169.
[51] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
[52] S. Grimme, L. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.
[53] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
[54] F. Neese, F. Wennmohs, A. Hansen, U. Becker, *Chem. Phys.* **2008**, *356*, 98–109.
[55] F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.

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