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Site specific Co(III) sarcophagine binding in multi-component phosphonium and \(p\)-sulfonatocalix[4]arene systems†

Irene Ling,*a Yatimah Alias,a Alexandre N. Sobolev,b Brian W. Skeltonb and Colin L. Rastonc,a

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Co(III) sarcophagine-type cage molecules, [Co(diCLsar)]\textsuperscript{3+} or [Co(HONOsr)\textsuperscript{3+}], form either 1 : 1 or 1 : 2 host–guest inclusion complexes with mono-phosphonium cations and sodium \(p\)-sulfonatocalix[4]arene in the solid state yielding complex I \([p\text{-sulfonatocalix}[4]\text{arene-Co(diCLsar)}]2\{benzyltriphenylphosphonium\} \], complex II \([p\text{-sulfonatocalix}[4]\text{arene-Co(diCLsar)}]3\{tetraphenylphosphonium\} \] and complex III \([p\text{-sulfonatocalix}[4]\text{arene-Co(HONOsr)}]\text{-tetraphenylphosphonium\} \]. The diversity of the structural types of these multi-component systems, including the orientation of the Co(III) molecules in the cavities of the calixarenes, depends on the nature of their terminal functional groups. The secondary coordination interactions binding between the Co(III) molecules and \(p\)-sulfonatocalix[4]arene have also been investigated in water using NMR techniques.

Introduction

A class of saturated nitrogen atom donor macrobicyclic ligands known as ‘cage amines’ was first developed by Sargeson and co-workers, and are known as ‘sepulchrates’. They contain eight nitrogen atoms with two of them in 1,8-apical positions as tertiary amines. Replacing these capping nitrogen atoms with quaternary carbons gives the more versatile cage amine ligand, known as ‘sarcophagine’ (a derivative of 3,6,10,13,16,19-hexaaazabicyclo[6.6.6]icosane and commonly abbreviated to ‘sar’). These carbon-bridgehead macrobicyclic hexamines form more stable complexes with metal ions relative to analogous sepulchrates-type complexes. Further modification of sarcophagines is associated with introducing functionality at these quaternary carbon centres, and such complexes have been used as imaging and therapeutic agents, in metal ion capture and toxicity treatment, and in intercalation and binding to DNA.

Co(III) complexes are ubiquitous with sarcophagines. The complex with each of the quaternary carbon centres bearing an hydroxyl group, Co(diHOsar))\textsuperscript{3+}, is a potential synthon in supramolecular chemistry for forming complex structures through electrostatic, hydrogen bonding and \(\pi\)-stacking interactions, especially for negatively charged cavatands, for example calixarenes bearing sulfonate groups on their upper rims. Smith et al. have shown that [Co(diHOsar)]\textsuperscript{3+} binds in the rigid cavity of \(p\)-sulfonated calix[4]arene, \(1\), with the 1 : 1 supermolecule of the two components assembling in the presence of aquated praseodymium(III) ions in the solid state into infinite helical chains with large hydrophilic channels. In another study by Castro et al. the larger ring size \(p\)-sulfonated calix[6]arene, which is conformationally more flexible, forms stable inclusion complexes with cobalt(III) sepulchrate, with hydrogen bonding and electrostatic interactions dominating the interactions. Interestingly, the complexes show different guest: host stoichiometries in the solid state and also in aqueous media.

The host–guest chemistry of calixarenes with molecules of different types and shapes has been widely studied. We have previously reported on the inclusion chemistry of large organic cations such as tetraphenylphosphonium cations with \(p\)-sulfonatocalix[4]arene, where there is the formation of pseudopolymorphic complexes. Here one of the phenyl groups of the cation resides in the cavity of the calixarene with each calixarene surrounded by phosphonium cations engaged in phenyl embrace interactions. Other investigations on the interplay of the larger bis-phosphonium cation with the same calixarene shows that the cation can be positioned either \textit{exo} and/or \textit{endo} with respect to the cavity, and this essentially creates porosity and a scaffold between bilayers of calixarenes and other bis-phosphonium cations in the extended structures. Subsequently we developed a series of host–guest complexes based on ionic liquid components, imidazolium and pyrrolidinium type cations, as additional cations to build up multicomponent complexes. Here the rigid cone-shaped...
Co(III) complexes in the cavity of the calixarene. Importantly these same calixarenes, a phosphonium cation, and two different Co(III) sarcophagine cations, which form in the presence of lanthanide ions; the sarcophagines bear two chloro groups in the 1,8-positions, [Co(diCLsar)]³⁺, 2, or a hydroxo and a nitro group in the same positions, [Co(HONOsar)]²⁺, 3. Also reported, are solution ¹H NMR studies in establishing the nature of the binding of the Co(III) complexes in the cavity of the calixarene. Importantly these types of secondary coordination interactions for metal ions are becoming increasingly important in controlling the reactivity of transition metal centres.¹³

Results and discussion
The multi-component complexes I, II and III were grown from an acidic aqueous solution containing equimolar amounts of the globular-like Co(III) sarcophagine cations, 2 and 3, and water soluble p-sulfonatocalix[4]arene, 1, as its sodium salt, Scheme 1, in the presence of phosphonium cations, benzyltriphenylphosphonium, 4, or tetraphenylphosphonium, 5. The ratio of the calixarene to the Co(III) sarcophagine is either 1:1 where the two components are built of a perched inclusion complex, or 1:2 where two calixarenes encapsulate the Co(III) sarcophagine, essentially as a molecular capsule. In all complexes the coordination sphere of Co(III) takes on the expected octahedral arrangement of the N-centres (trigonal twist angle along the principal axis of the CoN₆ core, θ = 60°) in a rigid (left), conformation which is stabilized by hydrogen bonding of the coordinated amines. There are no subtle geometric distortions of the primary coordination environment that could be a manifestation of the secondary coordination interactions with the calixarenes.

All the complexes contain the hydrophobic phosphonium cations, self assembled in their common phenyl embrace mode of interaction, positioned in interstices within bilayer arrangements of calixarene. This type of arrangement is comparable to our previously reported studies involving imidazolium based cations as the guest molecules.¹⁰ Although the synthesis of the present complexes requires the presence of aquated lanthanide metal ions, these species are not incorporated in the final structure. This phenomena has been noted for other complexes of p-sulfonated calix[4]arene.¹⁴

Complex I, [p-sulfonatocalix[4]arene-Co(diCLsar)-benzyltriphenylphosphonium] crystallises in the monoclinic space group P₂₁/n, with the asymmetric unit consisting of one calixarene anion (with a disordered SO₃– group), one Co(III) sarcophagine cation and two benzyltriphenylphosphonium cations, 4, (all in general positions) along with some disordered water molecules. Complex II, [p-sulfonatocalix[4]arene-Co(diCLsar)-tetraphenylphosphonium] crystallises in the monoclinic space group P2₁/c with the asymmetric unit containing two calixarene moieties, three tetraphenylphosphonium cations, 5, and two half Co(III) sarcophagine cage cations, with Co1 and Co2 lying on independent two-fold axes along with sodium ions and some included water molecules. In complex III, [p-sulfonatocalix[4]arene-Co(HONOsar)-tetraphenylphosphonium], the asymmetric unit consists of two calixarene anions, two Co(III) sarcophagine cations, four tetraphenylphosphonium cations, 5, and some included water molecules, crystallising in the triclinic space group P1. The two Co(III) sarcophagine cations are significantly disordered and one of the tetraphenylphosphonium cations has been assigned half-occupancy. In both complexes I and III, the calixarenes take on a 5– charge associated with removal of one proton on the lower rim, which is commonly encountered in solid state structures containing the calixarene.¹⁵ However for complex II, the calixarenes take on the other common level of charge, as the 4– species. Hydrogen bonding and electrostatic interactions dominate the interplay of the Co(III) sarcophagine and calixarene ions. All three complexes crystallise in chiral space groups, so that both enantiomers of the metal complex are present.

Calixarene–sarcophagine interactions
A striking feature of these complexes is the difference in orientation of the Co(III) sarcophagine cations in the calixarene cavity, with the cation either positioned vertically with the principal axis of the molecule coincidental with that of the calixarene, complex I and II, or positioned with the cation orientated laterally with respect to the host molecule, as in complex III, Fig. 1.

The Co(III) sarcophagine cage molecule in complexes I and II, has a chloro group on each terminal, with one of them directed close to the midpoint of the calixarene cavity, at 3.4 to 3.8 Å from the centroids of the four calixarene phenolic rings. In both structures the associated calixarene has a distorted bowl shape with the corresponding dihedral angles at 118.8° to 134.9° between the planes of the phenyl rings and the basal plane of the four methylene carbon atoms of the calixarene. There are the expected hydrogen bonds between the calixarene phenolic oxygen atoms, as defined by the short O···O distances, in the range of 2.45 to 2.60 Å. Intermolecular interactions between Co(III) sarcophagine...
and calixarene in both complexes I and II are dominated by C–H and N–H protons from the cation with the sulfonate groups of the calixarene (corresponding C⋯O distances 3.20 to 3.59 Å, and N⋯O distances 3.21 to 3.63 Å). Indeed for complex I these interactions contribute almost 80% in the overall host–guest formation, as revealed from fingerprint plots generated from the Hirshfeld surface analyses for complex I, Fig. 2. Hirshfeld surface analysis was not undertaken for the other complexes because of disorder associated with the sarcophagine cation. The cation also has weak methylene C–H⋯p interactions with the phenyl rings of the calixarene (C⋯p(centroid) close contact at 3.76 to 4.10 Å). In complex I, the Co(III) sarcophagine cation has short N–H⋯O hydrogen bonding distances with disordered water molecules (H⋯O from 1.83 to 2.08 Å). A striking feature of complex II is the formation of ‘molecular capsules’ based on two calixarenes, which effectively shroud the Co(III) sarcophagine. These 1:2 supermolecules are situated on crystallographic 2-fold axes.

The supermolecule in complex III consists of a Co(III) sarcophagine molecule which is disordered over two sites, and is ‘perched’ with respect to the calixarene cavity in a lateral mode where an ethylene group is directed into the cavity, the C⋯p(centroid) contacts being 3.62 and 3.69 Å. The calixarene is in a slightly pinched cone conformation with dihedral angles of 129.1°, 102.0°, 138.4° and 124.0°. The restricted cavity size constraint optimises the shape of the calixarene surface in interacting with the sarcophagine. Multiple hydrogen bonding between the cation protons and the calixarene sulfonate groups are evident with the corresponding C⋯O and N⋯O distances ranging from 3.12 to 3.38 Å and 2.93 to 3.61 Å respectively. The presence of a terminal hydroxyl group on one end of the sarcophagine in complex III presumably directs the orientation of the molecule with respect to the calixarene via hydrogen bonding with the sulfonate groups, with an O⋯O close contact at 2.90 Å. As for the nitro group at the other end, the oxygen atom is directed towards a sulfonate group with a close O⋯O distance of 3.33 Å to the oxygen atom of the sulfonate group. There are some disordered water molecules (with a partial occupancy of 0.50) which are in close proximity to the oxygen atoms of the sulfonate groups, which are presumably involved in extended hydrogen bonding with the close O⋯O distances in the range of 2.46 to 3.05 Å.

**Multi-component self assembly**

Further examination of the crystal packing in complex I reveals that the calixarenes form an offset up down anti-parallel bilayer arrangement, Fig. 3, with an inter-bilayer spacing of 20.0 Å, the closest approach between the lower rims of the calixarenes being 5.1 Å (calculations made based on the four oxygen atoms from the phenolic groups). The upper rims of the calixarenes are aligned in the head-to-head fashion, essentially creating hydrophilic regions
interposed with disordered water molecules and both components presumably involved in mutual hydrogen bonding, there being short O⋯O contacts at 2.74 to 2.92 Å. The hydrophobic phosphonium cations are arranged in the self-assembled multiple phenyl embrace manner close to the lower rim of the calixarenes, rather than residing in the cavity of the calixarenes. They are between back-to-back arrangements of the calixarenes and this expands the distance between the centres of the bilayers to 14.0 Å, Fig. 3. The phosphonium cations are also involved in self-association through attractive edge-to-face (ef) interactions,16 with C⋯π(centroid) contacts at 3.58 to 3.74 Å. The interactions of the phosphonium cations with the calixarenes involve C⋯π(centroid) interactions involving the calixarene aromatic moieties and its methylene bridges, with the closest distances at 3.57 to 3.62 Å and 3.66 to 3.88 Å respectively. The phosphonium cations are also engaged in weak hydrogen bonding with oxygen atoms of the calixarene molecules, for both the sulfonate and hydroxyl groups, with short contacts at 2.70 to 2.87 Å and 2.48 to 2.95 Å (corresponding C⋯O distances are 3.60 to 3.69 Å and 3.34 to 3.43 Å) respectively.

In complex II, the end capping of a Co(III) sarcophagine cation by two calix[4]arene molecules takes on a form of ‘molecular capsules’, with the centroids of the three components arranged linearly, in a way comparable to structures involving bis-imidazolium capsules, with the centroids of the three components arranged linearly, in a way comparable to structures involving bis-imidazolium cations.17 Within each capsule, the calixarene upper rims are aligned close to each other with O⋯O distances at 5.1 to 6.2 Å. The ‘molecular capsules’ are shrouded with endo-cavity tetraphenylphosphonium cations which fill the interstices of the calixarene bilayers, forming rigid open networks (see below) with the distance between the layers of the ‘molecular capsule’ at 19.2 Å, Fig. 4. As for complex I, the phosphonium cations are involved in weak hydrogen bonding with the oxygen atoms of the calixarene molecules, involving both the sulfonate and hydroxyl groups, with short contacts at 3.39 to 3.43 Å and 2.78 to 2.95 Å (corresponding C⋯O distances are 3.75 to 3.78 Å and 3.37 to 3.85 Å) respectively. The phosphonium cations are also involved in C⋯H⋯π (centroid) contacts to the calixarene phenyl rings, at 2.65 and 2.86 Å (corresponding C⋯π(centroid) distance 3.48 and 3.51 Å). It is noteworthy that open channels in the networks contain some water molecules which are involved in extended H-bonding interactions with the sulfonate groups of the calixarenes, along with the other included water molecules, with O⋯O distances ranging from 2.69 to 2.75 Å. There are also sodium ions in the channels.

For the overall crystal packing in complex III, the super-molecules are self-assembled into a complicated arrangement where the calixarene sulfonate groups are directed towards each other and are organised into infinite stranded chains in a zig-zag motif, Fig. 5. The chains are stabilised by hydrogen bonds between (i) the included Co(III) sarcophagine cation and the sulfonate groups, and (ii) two included Co(III) sarcophagine cations. The oxygen atoms from the sulfonate groups have close O⋯H contacts to the Co(III) sarcophagine protons at 2.22 to 2.66 Å (corresponding C⋯O distances are 3.13 to 3.46 Å), whilst the terminal nitro group has close O⋯H contacts to the adjacent Co(III) sarcophagine protons at 2.35 to 2.73 Å (corresponding C⋯O distances are 2.7 to 3.41 Å), Fig. 5. The stranded chains are made up of alternating enantiomers with respect to the chirality of the metal centres. The interplay between the two chains is governed by the CH⋯π (centroid) interaction involving the methylene bridge and the phenolic aromatic rings with the C⋯π(centroid) distance at 3.50 Å, Fig. 6. The extended structure contains hydrophobic regions made up of phosphonium cations in their common multiple phenyl embrace arrangement, in the form of grooves sandwiching the zig-zag chain pairs, running parallel with respect to the chains, Fig. 7.

Fig. 4 Extended structure of complex II showing ‘molecular capsules’ confined in the open network above and below the bilayer arrangement of calixarenes and phosphonium cations (pink), viewed down the b-axis. (Co(III) sarcophagine cations are labelled in blue).

Fig. 5 (a) Stick representation showing hydrogen bonds (dotted lines) between the Co(III) sarcophagine cation and the calixarene molecule, and (b) space filling representation of the zig-zag infinite chains, in complex III.

Solution studies

In the UV-visible spectra, Fig. 8, the cobalt sarcophagines have two almost symmetric absorption bands at ~475 nm (1A1g → 1T2g) and ~345 nm (1A1g → 1T1g), which correspond to the d–d electronic transitions of an octahedral Co(III)N6 chromophore in the UV region.18 On addition of Co(III) sarcophagine to a solution of...
Fig. 6 Stick representation showing C–H⋅⋅⋅π interactions (dotted lines) between calixarene pairs in complex III.

Fig. 7 (a) Cartoon representation of the two zig-zag chains (blue and green) in III, which are arranged in opposite directions; (b) and (c) space filling representations showing the phosphonium cations (pink) wrapping each zig-zag chain.

p-sulfonatocalix[4]arene, the Co(III) sarcophagine–calix[4]arene complexes experience a hyperchromic shift with successive increases in intensity observed for both Co(III) sarcophagine–calix[4]arene complexes, Fig. 8, due to formation of the host–guest complexes of Co(III) sarcophagine with calixarene. Importantly the increase in intensity is consistent with the solid state structures. The stoichiometry of the Co(III) sarcophagine–calixarene complex was determined by the Job’s plot (see the ESI†) using UV-visible absorption titration measurements. A series of samples were made which contained both components, calixarene (constant host concentration) and [Co(diCLsar)]³⁺ or [Co(HONOsar)]³⁺ in varying amounts, but such that the volume, and concentration of the total species in solution (7.5 mM) remained constant. The data from the Job’s plots for both Co(III) sarcophagine–calix[4]arene complexes were fitted to a 1 : 1 host–guest complex and the titration experiments, Fig. 9 (a plot of the absorbance intensity changes after addition of different equivalents of Co(III) sarcophagine), gave an association constant of 50.3 ± 0.1 M⁻¹ for [Co(diCLsar)]³⁺–calix[4]arene and 60.3 ± 0.1 M⁻¹ for [Co(HONOsar)]³⁺–calix[4]arene.

¹H NMR spectra are provided in Fig. 10 and Fig. 11. For [Co(diCLsar)]³⁺ there are two sets of chemically disparate methylene protons on the apical rings of the sarcophagine cage with a single AB doublet pair centered at δ = 3.1 ppm. The methylene protons of the NCH₂CH₂N units give rise to two multiplets centered at δ = 2.6 ppm and 3.3 ppm. Rapid exchange on the NMR time scale with respect to the sarcophagine cage molecules residing in the calixarene cavity in solution is evident, with these peaks experiencing significant upfield chemical shifts with subsequent addition of calixarene. It is also noteworthy that the methylene protons close to the terminal of the sarcophagine experience the greatest shift, which suggest that the Co(III) sarcophagine is included in the host molecule, like that established in the solid state where one of the apical rings is positioned in the hydrophobic cavity of the calixarene. The cone conformation of the calixarene in solution is also evident by the appearance of the well-resolved peaks for the methylene protons (asterisk), at 3.0 to 4.5 ppm, and this suggests a strong host–guest interaction between the two components involving the cavity of the calixarene. For supermolecules of [Co(HONOsar)]³⁺–calix[4]arene, the multiplets assigned to the protons of the cobalt cage molecules similarly
Fig. 9  Titration curves for determining the association constants of (a) 50.3 ± 0.1 M⁻¹ for [Co(diCLsar)]⁺⁻–calix[4]arene and (b) 60.3 ± 0.1 M⁻¹ for [Co(HONOsar)]⁺⁻–calix[4]arene.

Fig. 10  ¹H NMR spectra for [Co(diCLsar)]⁺⁻, and [Co(diCLsar)]⁺⁺ with p-sulfonated calix[4]arene, 1:1 and 1:2, measured in D₂O.

experience upfield chemical shifts, which confirms comparable host–guest interactions in aqueous solution. The rigid cone conformation of the calixarene is evident by the AB spin system of the methylene protons (asterisk).

Fig. 11  ¹H NMR spectra for [Co(HONOsar)]⁺⁺, and [Co(HONOsar)]⁺⁺ with p-sulfonated calix[4]arene, 1:1 and 1:2, measured in D₂O.

Conclusions

Globular-like Co(III) sarcophagine cations form host–guest complexes in solution with water soluble p-sulfonated calix[4]arene, with the nature of the interactions evident from NMR studies, and from structures of the solid state inclusion complexes, which readily form in the presence of phosphonium cations, and aquated gadolinium(III) ions, although the latter are not incorporated into the three dimensional arrays. In the solid state there are different orientations of the principal axis of the Co(III) sarcophagine cations relative to the calixarene, in a manner depending on the functional groups on the cations, which is a design strategy for building the multicomponent systems. There is flexibility in the formation of assemblies of 1:1 supermolecules in the solid state, or 1:2 molecular capsules. An important feature of the solid state structures is the uptake of the large phosphonium cations, forming hydrophobic regions separating bilayers of calixarene, or assemblies into 1-D arrays, wrapping around continuous arrays of 1:1 supermolecules.

Experimental

p-Sulfonatocalix[4]arene sodium salt¹⁹ and cobalt(III) sarcophagine ([Co(diCLsar)]⁺⁺ and [Co(HONOsar)]⁺⁺) were synthesized according to the literature procedures²⁰ [Ph₃PBz]Cl and [Ph₄P]Br were purchased from Sigma Aldrich and used as received. Slow evaporation of an equimolar combination of calixarene, cobalt complex and phosphonium salt, in a mixture of water and THF (1:1, 2 mL) in the presence of a three-fold excess of gadolinium(III) chloride, afforded yellow crystals which were suitable for X-ray diffraction studies after several days.

Aqueous samples of cobalt sarcophagines and calixarene were characterized using a Shimadzu UV-2500PC spectrometer within 10-mm quartz cuvette with a spectral range of 700 to 300 nm. ¹H NMR spectra were collected on a JEOL Lambda 400 MHz spectrometer using D₂O at 25 °C: [p-sulfonatocalix[4]arene]: δ 7.2
Crystallography

All data were measured using an Oxford Diffraction Gemini CCD diffractometer at $T = 100(2)$ K with monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) (I and III) or Cu-Kα radiation ($\lambda = 1.54178$ Å) (II). The data were corrected for Lorentz and polarization effects, with absorption corrections applied using multiple symmetry equivalent reflections. The structures were solved by direct methods and refined using full matrix least-squares on $F^2$ with the SHELX-97 crystallographic package, via the WinGX,24 and X-seed23 interfaces. Except for III, non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of hydrogen atoms were partly localized and their atomic parameters were constrained to the bonded atoms during the refinement with $C_{ph}$–H = 0.95 Å, C–Me–H = 0.99 Å, and 0.99 Å for CH$_2$ groups. CCDC deposition numbers are 809412 (I), 809410 (II), 809411 (III).†

Crystal/refinement details for complex I

$\text{C}_3\text{H}_8\text{O}_4\text{Si}_5^-$, $\text{C}_3\text{H}_8\text{CoNiCl}_2$, 2(C$_2$H$_5$P$^+$), $\text{H}_2\text{O}$, $\text{C}_{42}\text{H}_{116}\text{O}_2\text{P}_{2}\text{S}_4$; $M = 2072.22$, yellow plate, 0.52 $\times$ 0.33 $\times$ 0.13 mm$^3$, monoclinic, space group $P2_1/n$ (No. 14), $a = 25.9289(5)$, $b = 18.4847(3)$, $c = 27.6134(6)$ Å, $\beta = 96.836(2)$°, $V = 10556.6(4)$ Å$^3$, $Z = 4$, $D_0 = 1.303$ g cm$^{-3}$, $\mu = 0.395$ mm$^{-1}$, $F_{max} = 4356$, 26590 unique reflections collected, 26352 unique ($R_{int} = 0.0513$). Final Goof = 1.107, $|\Delta F_{max}| = 1.83$ e Å$^{-3}$, $R_1 = 0.1172$, $wR$_2 = 0.3335, $R$ indices based on 26352 reflections with $I > 2\sigma(I)$, 1271 parameters, 200 restraints.

One SO$_3^-$ group on the calixarene was disordered over two positions with occupancies set at 0.5 after trial refinement. Geometries of the disordered atoms were restrained to ideal values and refined with isotropic displacement parameters. Water molecule oxygen atoms were modelled with occupancies of either 1.0 or 0.5 after trial refinement, their hydrogen atoms not being located. Remaining electron density could not be modelled sensibly and was effectively removed by the use of the program Squeeze.24

Crystal/refinement details for complex II

2(C$_2$H$_5$O$_4$Si$^-$), (C$_2$H$_5$CoCl$_2$Co$_2$), 3(C$_3$H$_7$P$^+$), 2Na$^+$, 5.5(H$_2$O), $\text{C}_{16}\text{H}_{41}\text{Cl}_2\text{CoN}_2\text{O}_{17.96}\text{P}_{3.54}$; $M = 3056.81$, yellow plate, 0.28 $\times$ 0.13 $\times$ 0.11 mm$^3$, monoclinic, space group $P2_1/c$ (No. 10), $a = 38.578(2)$, $b = 15.6651(11)$, $c = 30.6281(19)$ Å, $\beta = 95.483(6)$°, $V = 18425(2)$ Å$^3$, $Z = 4$, $D_0 = 1.102$ g cm$^{-3}$, $\mu = 2.667$ mm$^{-1}$, $F_{max} = 6364$, 26083 reflections collected, 32647 unique ($R_{int} = 0.9977$). Final Goof = 0.742, $|\Delta F_{max}| = 2.011$ e Å$^{-3}$, $R_1 = 0.1191$, $wR_2 = 0.2998$, $R$ indices based on 32647 reflections with $I > 2\sigma(I)$, 1835 parameters, 1616 restraints.

It is assumed that the structure contains two Na ions per asymmetric unit for charge balance although, from the residual electron density, only a total of one could be assigned as such. Na1 is on a crystallographic 2-fold axis and Na2 has a site occupancy of 0.5 being close to a crystallographic inversion centre. The atoms of the Co(III) sarcophagine and some of the sulfonate groups exhibited high displacement parameters. Attempts to model these as disordered were not successful. Geometries and displacement parameters of the phenyl rings and Co(III) sarcophagine were restrained to ideal values. Some residual electron density was modelled as water molecules. The remaining electron density could not be modelled sensibly as such and was effectively removed by use of the program Squeeze.24

Crystal/refinement details for complex III

3(C$_2$H$_7$O$_2$Si$^-$), (C$_2$H$_5$O$_2$Si$^-$), 4(C$_3$H$_7$P$^+$), 7(C$_3$H$_7$P$^+$), 16(H$_2$O), $\text{C}_{136}\text{H}_{250}\text{CoN}_2\text{O}_{27.9}\text{P}_2\text{S}_4$; $M = 7241.09$, yellow plate, 0.40 $\times$ 0.16 $\times$ 0.12 mm$^3$, triclinic, space group $P1$ (No. 2), $\alpha = 18.2887(2)$, $b = 20.4581(7)$, $c = 25.7583(9)$ Å, $\alpha = 67.104(3)$, $\beta = 77.787(3)$, $\gamma = 84.702(3)$°, $V = 8676.2(5)$ Å$^3$, $Z = 1$, $D_0 = 1.386$ g cm$^{-3}$, $\mu = 0.40$ mm$^{-1}$, $F_{max} = 3790$, $2\theta_{max} = 58.7°$, 93887 reflections collected, 40592 unique ($R_{int} = 0.0769$). Final Goof = 1.004, $|\Delta F_{max}| = 1.13$ e Å$^{-3}$, $R_1 = 0.1035$, $wR_2 = 0.2597$, $R$ indices based on 12797 reflections with $I > 2\sigma(I)$, 1971 parameters, 468 restraints.

Two Co(III) sarcophagine cations were modelled as being disordered over two sets of sites with occupancies set at 0.5 after trial refinements. Two SO$_3^-$ groups on the calixarene are disordered over two sites with occupancies set at 0.5 for one of them and 0.75 : 0.25 for the other.

Two of the four tetraphenylphosphonium cations have some phenyl rings disordered and one cation is present with half-occupancy. Geometries of the disordered atoms were restrained to ideal values.

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