



Stereochemistry of cage amine complexes – control of conformations via hydrogen bonding

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ARTICLE

Stereochemistry of cage amine complexes –probing the ligand conformational flexibility with hydrogen bonds

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Structure determinations for some Co(III) complexes of simple derivatives of the cage hexamine 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane (“sarcophagine”) show that there is no evidence that the H-bonding involving the NH centres of the complex cations is influenced by electronic effects due to the substituents. “H-bond chelation” of chloride anions or water molecules results in retention of the symmetrical *lel*₃ conformation.

Introduction

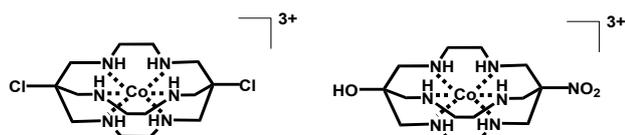
Complexes of polycyclic, encapsulating (« cage ») ligands have frequently proven to have exceptional properties leading to their applications in various domains.¹⁻³ Derivatives of the cage hexamine 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane, known as « sarcophagine »,^{3,4} are particularly effective complexants of heavy metal ions and applications of this property have been widely investigated, for example, in theranostic use of the radioisotopes ⁶⁴Cu and ⁶⁸Ga.^{5,6} Since the complexes are chiral, their interactions with biological systems may be influenced by this factor and thus it is important to have a detailed understanding of their stereochemistry.³

Structural investigations involving complexes of the cage hexamine sarcophagine and its derivatives are extensive⁷ and have involved a variety of metal ions but have provided only a few examples^{4,7-11} of species where the ligand conformation is not one or other of the extreme forms designated *lel*₃ and *ob*₃.^{3(b)} This nomenclature derives from the consideration of the central C-C bonds of the ligand arms forming five-membered chelate rings as lying either *parallel* or *oblique* to the threefold rotation axis of the complex.^{8,12} At least in complexes where the ligand framework as in the parent sarcophagine is retained, these conformational preferences for *lel*₃ or *ob*₃ may reflect their control by H-bonding interactions involving the secondary, coordinated NH centres,^{7,8,13,14} interactions of an energy which considerably exceeds that estimated to be the difference between the conformers.^{15,16} The only recognised case of such a complex showing a “mixed” conformation (that is, either *lel*₂*ob* or *ob*₂*lel*) is that of *lel*₂*ob*-[Ni(NH₃)₂sar]Cl₄•H₂O,³ where the relatively low charge on the metal ion may have rendered the NH entities less effective as H-bond donors, although an unpublished study of the Co(III) cage complex Δ-[Co(NO₂)₂sar][Gd(dipic)₃]•12H₂O has shown the crystal lattice to contain some *ob*₂*lel* species.

In earlier investigations of inclusion of cationic Co(III) cage amine complexes by (Scheme 1) *p*-sulfonatocalix[4]arene,¹⁷ the ligand conformations were not the focus of the analysis of the crystal structures of the isolated inclusions. In fact, the structures described for the 1:1 and 1:2 (Co:calix[4]arene) inclusions of the complex of 1,8-dichlorosarcophagine (Cl₂sar) (Scheme 1), and sulfonatocalix[4]arene are interesting in that the first contains the complexed ligand in the very familiar *lel*₃ conformation, while the second contains inequivalent species with the *ob*₂*lel* and *ob*₃ conformations. An obvious difference between the two structures is that in the 1:1 species the cation is only partially enveloped by the anionic calixarene, whereas in the 1:2 species it is effectively contained within a capsule formed by two facing calixarene units. Thus, in the former it is possible for three water molecules to approach the cation in a way which results in NH···O···HN bridging in a manner analogous to that observed in all other known structures of *lel*₃ Co(III) complexes.^{7,8} The conformation therefore appears to be determined by interactions other than those with the calixarene.

The difference in symmetry between the chiral *D*₃ cation and the *C*_{2v} sulfonated calixarene anion of course means that there is an inherent incompatibility in regard to maintaining either symmetry within their associate, which is in fact a chiral species of *C*₁ symmetry. An *ob*₂*lel* species, however, has *C*₂ symmetry and in this sense might be considered better fitted for interactions with the calixarene. If this is so, then for the capsule containing this conformer in the 1:2 species the interactions involving H-bond donor NH units and sulfonate-O atoms (water being absent from the vicinity of the cation) are still quite limited, since only two contacts (N13B···O112 3.21(1) Å) lie below 3.50 Å and are indicated to be significant by CrystalExplorer.¹⁸ For the capsule involving the *ob*₃ cation, there are no N···O contacts below 3.50 Å and cation···anion interactions appear to be of the CH···O type instead.¹⁷ Given

that the structure of a simple salt of $[\text{Co}(\text{Cl}_2\text{sar})]^{3+}$ is unknown and the possibility that the chloro substituent might induce different properties to those seen in the numerous cases where the substituent is an H-bond donor/acceptor species, characterisation of a simple species appeared desirable to better understand the cation properties. Some suitable crystals were in fact available as the unintended products of other efforts to obtain calixarene inclusates where the cation crystallised with anions present other than the sulfonated calixarene, and so were used in the present work. In addition to two structures involving $[\text{Co}(\text{Cl}_2\text{sar})]^{3+}$, a similar structure of a simple salt involving $[\text{Co}(\text{NO}_2)(\text{HO)sar}]^{3+}$ (Scheme 1), a cation also characterized previously but in an extensively disordered form as an inclusate,¹⁷ is given for comparison.



Scheme 1. Structures of the $[\text{Co}(\text{Cl}_2\text{sar})]^{3+}$ and $[\text{Co}(\text{NO}_2)(\text{HO)sar}]^{3+}$ cations.

Results and discussion

The X-ray structure determinations on single crystals of $[\text{Co}(\text{Cl}_2\text{sar})]\text{Cl}_3 \cdot 3.67\text{H}_2\text{O}$ (complex **1**), $[\text{Co}(\text{Cl}_2\text{sar})]_2\text{Cl}_3\text{Br} \cdot 5\text{H}_2\text{O}$ (complex **2**) and $[\text{Co}(\text{NO}_2)(\text{HO)sar}]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (complex **3**), have shown that the cation in all three cases adopts the intrinsically favored $1el_3$ conformation. Relatively large trigonal twist angles for all three complexes were observed ($\phi = 54.3^\circ$ to 56.4°), close to the ideal octahedral arrangement regardless of the variation of functional groups at the terminal trigonal cap. The Co-N bond lengths and angles are in the ranges found for Co(III) cage complexes (Table 1).

Complex 1

Complex **1** crystallizes in the triclinic space group, $P\bar{1}$, $Z = 4$, with the asymmetric unit comprising two $1el_3$ (but inequivalent) $[\text{Co}(\text{Cl}_2\text{sar})]^{3+}$ cations, six chloride anions and $3\frac{2}{3}$ water molecules. The cations, defined in detail in Table 1, can be considered to lie in sheets parallel to the ab plane, the closer pairs of sheets (separation of the mean Co planes 7.2 \AA) sandwiching the partially occupied water molecule sites involving O(2), while the chloride ions and other water molecules (one of which, involving O(1) and O(1'), is disordered over two sites) lie partly within the sheets and partly between the more distant sheet units (Co mean plane separation 9.5 \AA ; Figure 1). In any given sheet, both inequivalent cations are present in a 1:1 ratio but all are of the same absolute configuration, opposite to that in the closer adjacent sheet, so that the sheet chirality alternates along the c direction.

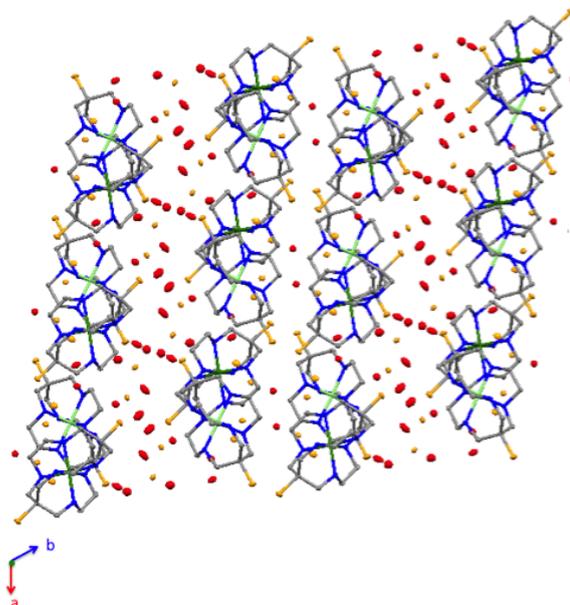


Figure 1 A partial view, down b , of the lattice of **1**. Co(1) atoms are shown in green, Co(2) in light green, H atoms are omitted.

The partial occupancy and partial disorder of the oxygen atom sites prohibit the application of CrystalExplorer to analysis of the lattice interactions but atom...atom separations are consistent with H-bonding being pervasive. Thus, both the inequivalent but closely similar cations are involved in NH-bond chelation of three chloride ions each, as long known for complexes of this type (Figure 2).¹⁰ Each open octahedral edge of the cations is spanned by a nearly symmetrically bound chloride ion $\{\text{Cl}(1)\cdots\text{H}(13\text{B}, 16\text{A}) 2.223(2), 2.325(3); \text{Cl}(2)\cdots\text{H}(13\text{C}, 16\text{B}) 2.228(3), 2.162(3); \text{Cl}(3)\cdots\text{H}(13\text{A}, 16\text{C}) 2.285(2), 2.203(2); \text{Cl}(4)\cdots\text{H}(23\text{B}, 26\text{A}) 2.329(2), 2.207(2); \text{Cl}(5)\cdots\text{H}(23\text{C}, 26\text{B}) 2.221(2), 2.326(3), \text{and } \text{Cl}(6)\cdots\text{H}(23\text{A}, 26\text{C}) 2.244(2), 2.260(2) \text{ \AA}\}$. Within a given cation sheet, the inequivalent cations (containing Co1 and Co2) lie in parallel rows along a , each second pair of rows being linked through the infinite chain (along a) of water molecules involving $\cdots\text{O}(1)(\text{O}(1'))\cdots\text{O}(6)\cdots\text{O}(5)\cdots\text{O}(8)\cdots\text{O}(3)\cdots\text{O}(4)\cdots\text{O}(7)\cdots$ (mean $\text{OH}\cdots\text{O} 1.89(8) \text{ \AA}$), specifically involving $\text{Cl}(1)\cdots\text{H}(1\text{A}), \text{Cl}(1)\cdots\text{H}(8\text{A}), \text{Cl}(3)\cdots\text{H}(3\text{A}), \text{Cl}(4)\cdots\text{H}(4\text{A}), \text{Cl}(5)\cdots\text{H}(5\text{A})$ and $\text{Cl}(5)\cdots\text{H}(7\text{A})$ contacts averaging $2.39(5) \text{ \AA}$. Were the site of O(2) to be fully occupied, each cation containing Co(1) would form a centrosymmetric unit with its enantiomer in the closer cation sheet ($\text{Co}(1)\cdots\text{Co}(1') 9.307(2) \text{ \AA}$) as a result of $\text{NH}\cdots\text{Cl}\cdots\text{HOH}\cdots\text{Cl}\cdots\text{HN}$ links ($\text{Cl}(2)\cdots\text{H}(2\text{A}) 2.11, \text{Cl}(3)\cdots\text{H}(2\text{B}) 2.20 \text{ \AA}$) but seemingly this must only occur for two thirds of these cations.

Other contacts observed are possibly consistent with some contribution from $\text{CH}\cdots\text{O}$ and $\text{CH}\cdots\text{Cl}$ interactions, and perhaps even halogen bonding, to the lattice interactions but there is no real evidence to suggest that they would exceed dispersion force effects. While Coulombic forces may be largely responsible for the form of the lattices, they gain directionality through specific contacts such as H-bonding.²⁰

Table 1: Selected Bond Lengths and Angles

| | [Co(Cl ₂ sar)]Cl ₃ •3.67H ₂ O (1•3.67H ₂ O) | [Co(Cl ₂ sar)] ₂ Cl ₅ Br•5H ₂ O (2•5H ₂ O) | [Co((NO ₂)(HO)sar)]Cl ₃ •2H ₂ O (3•5H ₂ O) |
|-------------------------|--|--|--|
| Bond Lengths (Å) | | | |
| <Co – N> | 1.981(8) [1.974(8) - 1.988(8)] | 1.978(28) [1.971(29)-1.983(28)] | 1.979(17) [1.975(17) - 1.987(17)] |
| N(–H) ...Cl | 2.162(3) - 2.329(2) | 2.116(23) - 2.429(18) | 2.226(5)-2.392(5) |
| Angles (deg) | | | |
| <N – Co – N> (intracap) | 86.39(3) [85.88(3) - 86.99(3)] | 86.70(14) [86.29(14)-86.91(14)] | 86.51(7) [86.35(7) - 86.73(7)] |
| <N – Co – N> (intercap) | 90.58(3) [89.88(3)-91.07(3)] | 90.49(13) [89.96(12)-91.10(15)] | 90.54(7) [89.81(7)-91.51(7)] |
| <N – C – C – N> | 55.24 (54.85-55.85) | 55.97 (55.34-57.35) | 55.03 (54.76-55.38) |
| <twist angle> (ϕ) | 54.5, 56.4 | 56.3 | 54.3 |

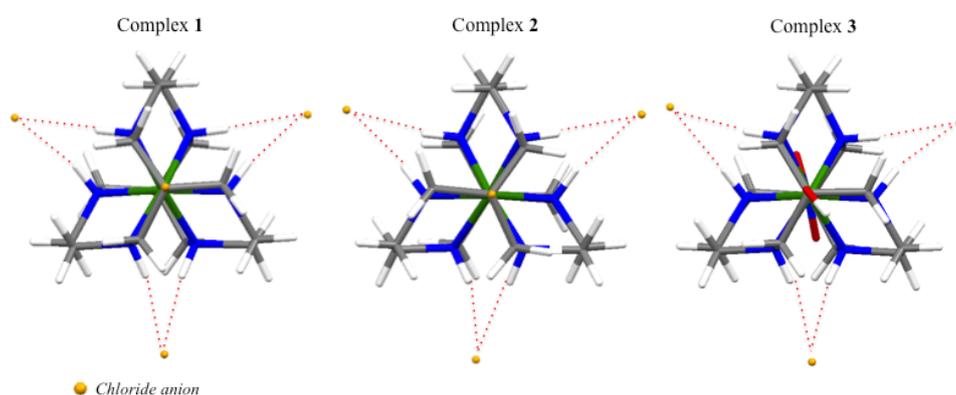


Figure 2 Equatorial chelation of a triad of chloride anions by the cobalt(III) sarcophagine cations in the complexes **1**, **2** and **3**. Each cation is arbitrarily shown in its Δ configuration and, for **1**, only one (involving Co(1)) of the two very similar cations is shown while for **2**, chloride disorder (Cl(3)/Cl(4)) is not shown.

Complex 2

Complex **2** crystallizes in the monoclinic space group $P2_1/c$, $Z = 2$, the crystal unit comprising two $[\text{Co}(\text{Cl}_2\text{sar})]^{3+}$ components in their lel_3 conformation, accompanied by five chloride and one bromide anions and five water molecules. Viewed down a (Figure 3) the lattice can be seen to contain homochiral sheets of cations lying parallel to the ac plane, with the chirality alternating from one plane to the next. Water molecules lie between these sheets, chloride ions both within and between, while bromide ions lie between every second pair of sheets. Fractional occupancies and partial disorder once again limit the application of CrystalExplorer to analysis of the lattice interactions but, as for **1**, H-atom contacts provide evidence for extensive H-bonding. Here, there is but one cation site and, interestingly, the chloride “deficiency” in terms of the ratio Co:Cl of 1:3 which would be required for each lel_3 cation to have its own separate sheath of H-bonded chloride ions is not compensated for by bromide, so that one chloride (Cl(2)) forms a bridge as a result of its chelation by pairs of NH units on separate cations. There is, as in **1**, a threefold chelation of

chloride by the NH units of the lel rings (Figure 2; Cl(1)⋯H(3A, 6C) 2.242(7), 2.235(9); Cl(2)⋯H(3B, 6A) 2.31(1), 2.218(1), Cl(3)⋯H(3C, 6B) 2.116(23), 2.429(18) and Cl(4)⋯H(3C, 6B) 2.116(23), 2.278(1) Å) and the lattice water molecules do not compete for this role. The apparent coordination geometry of the bridging chloride is close to square planar, not tetrahedral, possibly indicating a dynamic situation involving equivalent forms of three-coordination, consistent with the extruded probability displacement ellipsoid on Cl(2). The cations linked by this bridge are enantiomeric. H-bonding of chloride to water (mean Cl⋯HO 2.56(17) Å) and water to water (mean O⋯O 2.09(27) Å) results in a three-dimensional network linking all the cations together. The bromide ions are presumably involved in this network also but there are some anomalously short Br⋯H and Br⋯O contacts which indicate that there may be some unresolved disorder associated with these anions and their adjacent water molecules. As for **1**, there are some relatively short CH⋯O and CH⋯Cl contacts, which may indicate that forces other than conventional H-bonding contribute to the lattice construction.

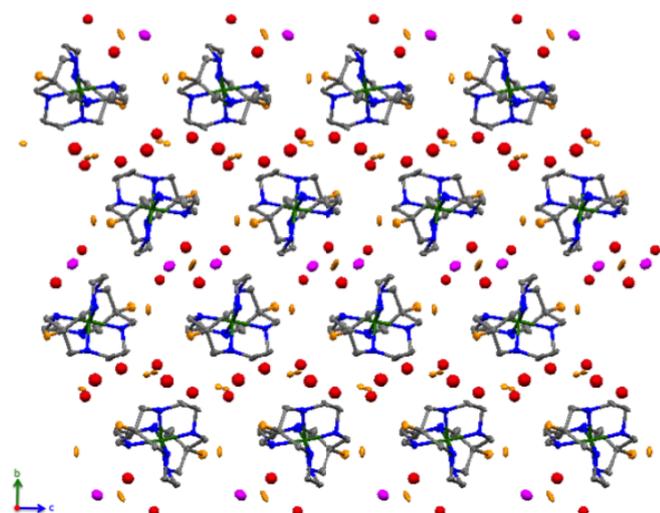


Figure 3 Partial view, down *a*, of the lattice of complex **2**. Probability ellipsoids are shown at the 50 % level; H atoms are omitted. Bromide ions are shown in pink.

Complex 3

Complex **3** crystallizes in the orthorhombic space group $P2_12_12_1$, $Z = 4$, with the asymmetric unit comprising one $[\text{Co}(\text{NO}_2)(\text{HO})\text{sar}]^{3+}$ cation, three chloride anions and two water molecules. Despite its unsymmetrical substitution and the presence of one substituent capable of hydrogen-bond donation, the simplest situation of all arises in that there is but one cation site, all cations necessarily being of the same chirality under the given space group, and there is no disorder or partial site occupancy. Examination of the Hirshfeld surface of the complex obtained by using CrystalExplorer (Figure 4) confirms the occurrence once more of the strong H-bonding chelation of three chloride ions by the lel_3 cation (Figure 2; $\text{Cl}(1)\cdots\text{H}(3\text{A}, 6\text{C})$ 2.338(5), 2.276(5); $\text{Cl}(2)\cdots\text{H}(3\text{B}, 6\text{A})$ 2.392(5), 2.226(5); $\text{Cl}(3)\cdots\text{H}(3\text{C}, 6\text{B})$ 2.267(5), 2.240(5) Å) but shows also that there are significant (beyond dispersion effects) $\text{CH}\cdots\text{O}$ (mean 2.48(7) Å) and $\text{CH}\cdots\text{Cl}$ interactions, only in part associated with the two polar substituents (Figure 5).

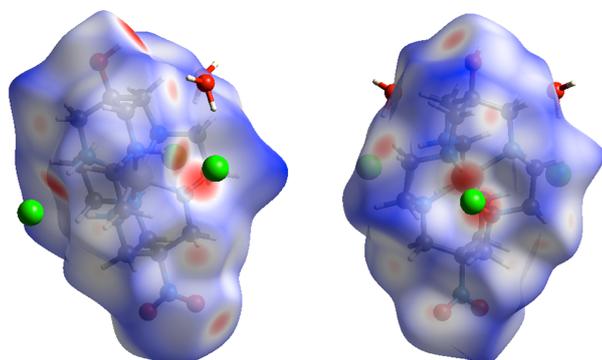


Figure 4 Different views of the asymmetric unit of complex **3**, showing the Hirshfeld surface of the cation. Red indicates regions where interactions exceed dispersion forces.

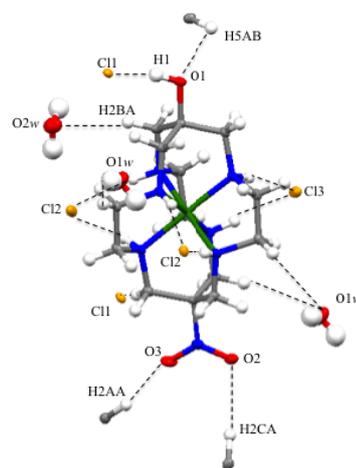


Figure 5 Contacts (dashed lines) indicated by the Hirshfeld surface properties to be significant bonding interactions of the cation present in complex **3**. For CH contacts, only one C atom of the additional complex unit involved is shown.

While the oxygen atoms of the hydroxyl and nitro substituents appear to act exclusively as CH bond acceptors, the water molecules of the lattice also act as conventional H-bond donors to chloride ($\text{Cl}(2)\cdots\text{H}(2\text{wA})$ 2.352(5) Å, $\text{H}(2\text{wB})\cdots\text{Cl}(1)$ 2.827(5) Å, $\text{Cl}(1)\cdots\text{H}(1\text{wA})$ 2.390(5) Å, $\text{H}(1\text{wB})\cdots\text{Cl}(2)$ 2.404(5) Å), providing a network which, in association with the $\text{NH}\cdots\text{Cl}$ interactions, leads to a three-dimensional linking of all the cations (Figure 6). The detailed analysis of the lattice of **3** which is possible, coupled to the close general similarities of the three lattices presently discussed, indicates that while conventional H-bonding interactions may be the dominant lattice forces for all three, $\text{CH}\cdots\text{O}$ interactions, in particular, are also of general significance.

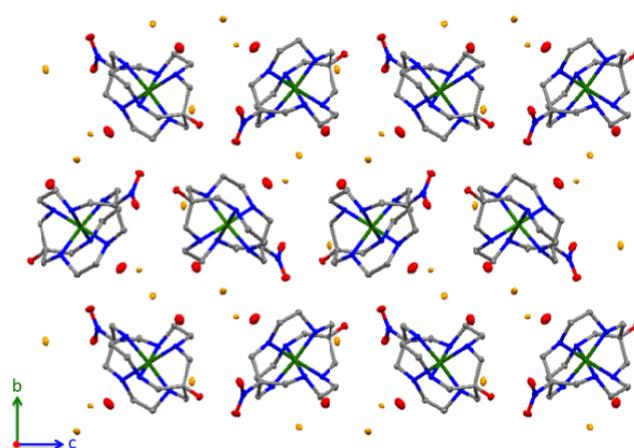


Figure 6 Partial view, down *a*, of the lattice of complex **3**. Probability ellipsoids are shown at the 50 % level; H atoms are omitted.

Conclusions

Taken together, the present structures do not indicate that the different substituents, particularly Cl, here have a significant influence on the observed tendency of Co(III) sarcophagine complexes of 3+ overall charge to adopt a *lel*₃ conformation when a small bridging hydrogen-bond acceptor species such as chloride or water is available. Since molecular mechanics calculations^{15,16} indicate that energy differences between all the possible conformers are very small, it is unsurprising that relatively strong and multiple hydrogen-bonds can lead to a single conformer being favoured but that different conformers may be observed nonetheless when the pattern of hydrogen bonds is altered by changes in the composition of the crystalline solid containing the cage cation.⁷

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Experimental

Synthesis of complexes 1, 2 and 3

Simple chloride salts of [Co(Cl₂sar)]³⁺ and [Co(NO₂)(HO)sar)]³⁺ were available from earlier work.⁵

Crystals of complex **1** were grown by slow evaporation of a hot aqueous solution of [Co(Cl₂sar)]Cl₃.

Slow evaporation of an equimolar combination of [Co(Cl₂sar)]³⁺ or [Co(NO₂)(HO)sar)]³⁺, sulfonated calix[8]arene or calix[6]arene, and tetraphenylphosphonium bromide, in a mixture of water and THF (1:1, 2 mL) in the presence of a three-fold excess of gadolinium(III) chloride, afforded crystals of complexes **2** and **3** respectively, which were suitable for X-ray diffraction studies.

Crystallography

All data were measured using an Oxford Diffraction Xcalibur-S, Sapphire CCD diffractometer at T = 100(2) K with monochromatic Mo-K α radiation (λ = 0.71073 Å). The images were interpreted and integrated with the program CrysAlisPRO, Oxford Diffraction Ltd. 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-97¹⁹ crystallographic package,

and X-seed²⁰ interfaces. Non-hydrogen non-disordered atoms were refined with anisotropic displacement parameters. The positions of hydrogen atoms were partly localized from difference Fourier synthesis, partly calculated and their atomic parameters constrained to the bonded atoms during the refinement with C_{Ph}-H = 0.95 Å, C_{Me}-H = 0.98 Å, and 0.99 Å for CH₂ groups. CCDC deposition numbers are 1025431-1025433.

Crystal/refinement details for complex 1

C₁₄H₃₀Cl₂CoN₆³⁺, 3(Cl⁻), 3.67(H₂O), C₁₄H_{37.33}Cl₅CoN₆O_{3.67}, M = 584.69, orange prism, 0.32 \times 0.29 \times 0.26 mm³, triclinic, space group $P\bar{1}$ (No. 2), a = 9.4847(2), b = 16.2433(3), c = 16.9867(3) Å, α = 97.456(1)°, β = 101.802(2)°, γ = 102.069(2)°, V = 2464.05(8) Å³, Z = 4, D_c = 1.576 g/cm³, μ = 1.270 mm⁻¹. F_{000} = 1219, $2\theta_{max}$ = 74.8°, 93752 reflections collected, 24665 unique (R_{int} = 0.0239). Final $Goof$ = 1.004, $|\Delta\rho_{max}|$ = 0.70(7) e Å⁻³, R_I = 0.0286, wR_2 = 0.0727, R indices based on 22189 reflections with $I > 2\sigma(I)$ (refinement on F^2), 541 parameters, 0 restraints.

Crystal/refinement details for complex 2

2(C₁₄H₃₀Cl₂CoN₆³⁺), 5Cl⁻, Br⁻, 5(H₂O), C₂₈H₇₀BrCl₉Co₂N₁₂O₅, M = 1171.78, yellow needle, 0.34 \times 0.21 \times 0.04 mm³, monoclinic, space group $P2_1/c$ (No. 14), a = 9.7649(4), b = 27.6067(8), c = 9.5645(4) Å, β = 117.183(5)°, V = 2293.59(15) Å³, Z = 2, D_c = 1.697 g/cm³, μ = 2.170 mm⁻¹. F_{000} = 1208, $2\theta_{max}$ = 61.5°, 40659 reflections collected, 6677 unique (R_{int} = 0.0543). Final $Goof$ = 1.019, $|\Delta\rho_{max}|$ = 1.5(1) e Å⁻³, R_I = 0.0543, wR_2 = 0.1532, R indices based on 4501 reflections with $I > 2\sigma(I)$ (refinement on F^2), 270 parameters, 0 restraints.

Crystal/refinement details for complex 3

C₁₄H₃₁CoN₇O₃³⁺, 3Cl⁻, 2(H₂O), C₁₄H₃₅Cl₃CoN₇O₅, M = 546.77, orange prism, 0.37 \times 0.23 \times 0.11 mm³, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 8.9691(1), b = 15.3233(2), c = 16.3516(2) Å, V = 2247.30(5) Å³, Z = 4, D_c = 1.616 g/cm³, μ = 1.162 mm⁻¹. F_{000} = 1144, $2\theta_{max}$ = 64.6°, 48711 reflections collected, 7579 unique (R_{int} = 0.0341). Final $Goof$ = 1.005, $|\Delta\rho_{max}|$ = 1.10(9) e Å⁻³, R_I = 0.0326, wR_2 = 0.0872, R indices based on 7323 reflections with $I > 2\sigma(I)$ (refinement on F^2), 272 parameters, 0 restraints. Absolute structure parameter = 0.077(10) (Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876-881).

Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

- 1 J.-M. Lehn *Acc. Chem. Res.* 1978, **11**, 49-xx
- 2 Y. Z. Voloshin, N. A. Kostromina, R. Krämer *Clathrochelates: Synthesis, Structure and Properties*, Elsevier Science, Amsterdam, 2002.
- 3 (a) A. M. Sargeson, *Coord. Chem. Rev.*, 1996, **151**, 89-114; (b) A. M. Sargeson, *Pure Appl. Chem.* 1986, **58**, 1511-1519.
- 4 R. J. Geue, T. W. Hambley, J. M. Harrowfield, A. M. Sargeson and M. R. Snow, *J. Am. Chem. Soc.*, 1984, **106**, 5478-5488.
- 5 B. M. Paterson, P. Roselt, D. Denoyer, C. Cullinane, D. Binns, W. Noonan, C. M. Jeffery, R. I. Price, J. M. White, R. J. Hicks, P. S. Donnelly *Dalton Trans.* 2014, **43**, 1386-1396 and references therein.
- 6 M. T. Ma, O. C. Neels, D. Denoyer, P. Roselt, J. A. Karas, D. B. Scanlon, J. M. White, R. J. Hicks, P. S. Donnelly *Bioconjugate Chem.* 2011, **22**, 2093-2103.
- 7 I. J. Clark, A. Crispini, P. S. Donnelly, L. M. Engelhardt, J. M. Harrowfield, S-H. Jeong, Y. Kim, G. A. Koutsantonis, Y. H. Lee, N. A. Lengkeek, M. Mocerino, G. L. Nealon, M. I. Ogden, Y. C. Park, C. Pettinari, L. Polanzan, E. Rukmini, A. M. Sargeson, B. W. Skelton, A. N. Sobolev, P. Thuéry and A. H. White, *Aust. J. Chem.*, 2009, **62**, 1246-1260 and references therein.
- 8 J. M. Harrowfield, *Supramolecular Chem.* 2006, **18**, 125-136.
- 9 L. M. Engelhardt, J. M. Harrowfield, A.M. Sargeson and A. H. White *Aust. J. Chem.* 1993, **46**, 127-143.
- 10 I. J. Clark, R. J. Geue, L. M. Engelhardt, J. M. Harrowfield, A. M. Sargeson and A. H. White *Aust. J. Chem.* 1993, **46**, 1485-1505.
- 11 P. M. Angus, A. M. Sargeson and A. C. Willis *Chem. Commun.* 1999, 1975-1976.
- 12 This nomenclature is discussed in a more general context in J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry*, 4th Edn 1993, p. 501 ff (Harper and Collins, New York, NY).
- 13 P. V. Bernhardt, A. M. T. Bygott, R. J. Geue, A. J. Hendry, B. R. Korybut-Daszkiewicz, P. A. Lay, J. R. Pladziejewicz, A. M. Sargeson and A. C. Willis *Inorg. Chem.* 1994, **33**, 4553-4561.
- 14 J. Harrowfield and D. Matt *J. Incl. Phenom. Macrocyclic Chem.* 2004, **50**, 133-150.
- 15 (a) P. Comba *Inorg. Chem.* 1989, **28**, 426-431; (b) P. Comba and T. W. Hambley, *Molecular Modelling of Inorganic Compounds*, VCH, Weinheim, 1995.
- 16 A. M. T. Bygott and A. M. Sargeson *Inorg. Chem.* 1998, **37**, 4795-4806.
- 17 (a) I. Ling, Y. Alias, A. N. Sobolev, B. W. Skelton and C. L. Raston *Dalton Trans.* 2011, **40**, 10337-10344; (b) A similar study involving $[\text{Co}(\text{HO})_2\text{sar}]^{3+}$ and where the cation is probably in its lel_3 conformation is C. B. Smith, L. J. Barbour, M. Makha, C. L. Raston and A. N. Sobolev *Chem. Commun.* 2006, 950-952.
- 18 (a) CrystalExplorer 3.1, S.K. Wolff, D.J. Grimwood, J. J. McKinnon, M. J. Turner, D. Jayatilaka, M. A. Spackman, University of Western Australia, 2012; (b) M. A. Spackman, D. Jayatilaka *CrystEngComm.* 2009, **11**, 19-32.
- 19 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.
- 20 L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189.