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Inclusion complexes of imidazolium carboxylate-metal species in the water-soluble sulfonated calix[4]arene system

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Dedicated to Prof. Jerry L. Atwood on the occasion of his retirement from the University of Missouri

Keywords: Calixarenes, coordination chemistry, self-assembly, encapsulation, host-guest chemistry

Abstract

Two multi-component crystal structures comprising a carboxylic acid-functionalized imidazolium zwitterion, a *p*-sulfonatocalix[4]arene anion and aquated metal ion (Na^+ or Y^{3+}) with or without an auxiliary component (the 3-methoxyphenyl-triphenylphosphonium cation) are reported. The carboxylic acid-functionalized imidazolium ion binds either as a monodentate or a bidentate ligand depending on the nature of the metal ions, and a bi-layer arrangement prevails in the extended structure regardless of the type of metal ion employed or presence / lack of auxiliary component.

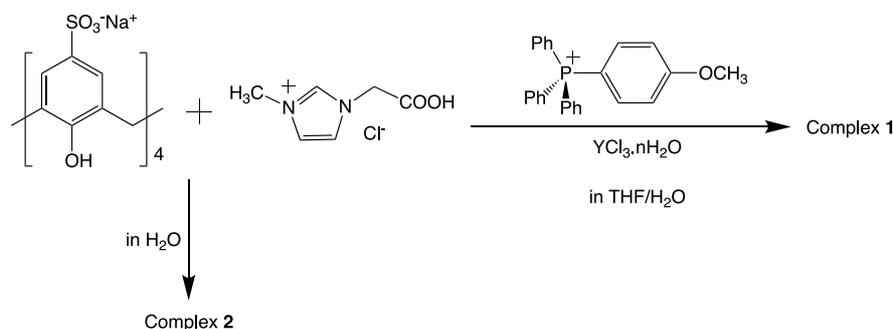
1. Introduction

Task-specific ionic liquids (TSILs) have functional groups such as sulfonic acid¹, amino acid², terpyridine³, carboxylic acid⁴, hydroxyl⁵ and ether⁶ (to name but a few) covalently tethered to a cationic or anionic moiety; many involve the incorporation of functionality appended to the imidazolium cation. Carboxylic acid-functionalized imidazolium ionic liquids contain either one, two or multi carboxylic acid substituents appended to the cationic five-membered imidazole ring, and exhibit zwitterion character in the deprotonated form.⁷ This type of TSIL has attractive applications in materials processing as they are efficient for dissolving metal oxides and hydroxides due to a strong coordination ability.⁸ Binnemans and co-workers have reported on the TSIL bearing a carboxyl group that has a selective solubilizing ability for various (alkali, alkali earth, transition, lanthanide and actinide) metal oxides and hydroxides in the presence of water.⁹ Li and co-workers directly dissolved lanthanide oxides and organic ligands into carboxylic acid-functionalized TSILs and fabricated distinctive luminescent soft materials.¹⁰ Being able to understand and to visualize the way TSILs and metal ions aggregate

or self-assemble in the solid-state is essential in material or device manufacturing, as different assemblies may exhibit disparate performance or characteristics. If the packing order of the molecules within the system is fully understood, it is envisaged that consistency in material or device manufacture / performance can be achieved.

Several crystal structures of metal complexes of carboxylic acid-functionalized imidazolium zwitterions have been reported.¹¹⁻¹⁶ The carboxylate group can act as a mono-, bi-, or multidentate ligand when coordinated to a metal center, affording coordination polymers with wide-ranging topologies and conformations. Fei and co-workers synthesized imidazolium salts with two carboxylic acid substituents and prepared metal complexes with different group I (Cs^+), II (Ca^{2+} , Sr^{2+} , Ba^{2+}) and transition metal (Co^{2+} , Zn^{2+}) ions; these complexes form either the 2-D or helical coordination polymers.¹⁷⁻¹⁹ We have explored the complexation ability of imidazolium salts appended with one carboxylic acid substituent with lanthanide ions (Y^{3+} and Gd^{3+}), and have used these metal complexes as guest species to construct complex self-assembled structures in the presence of a cavity containing host, *p*-sulfonatocalix[4]arene ($\text{SO}_3[4]$).²⁰ In doing so we have found that the guest species comprised of either two trivalent Ln^{3+} ions bridged by two carboxylic acid-functionalized imidazolium moieties, or one carboxylic acid-functionalized imidazolium moiety bridging two Ln^{3+} ions.

Here we describe the structural characterization of two multi-component assemblies comprising carboxylic acid-functionalized imidazolium zwitterion complexes with two different aquated metal ions (sodium(I), Na^+ or yttrium(III), Y^{3+}) and $\text{SO}_3[4]$, Scheme 1. Both complexes crystallized as hydrated material with $\text{SO}_3[4]$ s assembled in an anti-parallel bilayer arrangement, as is frequently observed for this particular host.²¹ The type of the metal ion (size and valency) is seen to influence the interaction between the metal ion and the carboxylate group. Crystals formed as a product of the complexation between the carboxylic acid-functionalized imidazolium and Y^{3+} (large ionic radius) cation along with the presence of a monophosphonium salt are closely related to a previously reported structure (CCDC refcode: ZAVWUQ),²⁰ where Y^{3+} bridges to two carboxylic acid-functionalized imidazolium moieties yielding a dimeric arrangement. Two $\text{SO}_3[4]$ host molecules encapsulate a dimeric guest species with monophosphonium cations embedded within the extended bilayer structures. Distinct differences found between the present structure relative to ZAVWUQ include space group, number of waters of crystallization, and disparate metal coordination modes between Y^{3+} and the carboxyl groups. As for the crystals formed from the complexation between carboxylic acid-functionalized imidazolium and Na^+ (small ionic radius) cation, the monodentate carboxyl group bridges to two Na^+ cations and points away from the calixarene, whilst the positively charged imidazole ring is drawn into the cavity. There is consistency of the up-down antiparallel bilayer arrangements of $\text{SO}_3[4]$ s with the positively charged species included between the alternating layers, again highlighting the prevalence of this assembly mode in the context of previously reported structures.²¹



Scheme 1. Synthesis of complexes 1 and 2.

2. Materials and method

2.1 Synthesis of complexes 1 and 2

Crystals of complex **1** were formed in the vial that originally produced ZAVWUQ.²⁰ Crystals appeared after allowing the vial to sit at ambient conditions for several months (i.e. crystals of ZAVWUQ and complex **1** form in sequence). Crystals in the form of thin plates (as opposed to rods in ZAVWUQ) were inspected and characterized using SCXRD where upon identifying that the cell dimensions (as well as crystal morphology) had changed. Diffraction studies revealed these crystals to be different to ZAVWUQ in both space group and cell dimensions. The arrangement of molecules in the crystals is seen to transform or self-adjust with respect to the further decrease of solvent during crystallization. This type of transformation mechanism is close to a model introduced by Petit and Coquerel related to the dehydration mechanism of molecular crystals,²² noting also the complex nature of hydrates of SO₃[4].²³

The synthesis of complex **2** involves *p*-sulfonatocalix[4]arene sodium salt and *N*-carboxymethyl-*N*-methylimidazolium chloride, both of which were purchased from Sigma Aldrich and used as received. A hot aqueous solution of equimolar (0.01 M) *p*-sulfonatocalix[4]arene with *N*-carboxymethyl-*N*-methylimidazolium (0.01M) in distilled water (2 mL) was prepared. The solution was left to cool and evaporate slowly at room temperature, with suitable quality crystals forming over several days. Cell dimensions were checked for several crystals in order to establish homogeneity of the sample; the crystals were found to be solvent dependent, thus limiting the use of PXRD to check for bulk homogeneity.

2.2 X-Ray Crystallography

All data were measured from a single crystal using an Oxford Diffraction Gemini-R Ultra CCD and an Oxford Diffraction Xcalibur-S, Sapphire3 CCD diffractometer at T = 100(2)K with monochromatic CuK α (λ = 1.54178 Å) and MoK α (λ = 0.71073 Å) radiation for the compounds **1** and **2** respectively. Data were corrected for Lorentz and polarization effects, and absorption correction applied using multiple symmetry equivalent reflections. The structures were solved by direct methods and refined against F^2 with full-matrix least-squares using the program suite SHELX.²⁴ Anisotropic displacement parameters were employed for the non-hydrogen atoms. Some water molecule hydrogen atoms were not located. All remaining hydrogen atoms were added at calculated positions and refined by the use of a riding model with isotropic displacement parameters based on those of the parent atom. Anisotropic displacement parameters were employed for the non-hydrogen atoms. Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre. Copies of data with CCDC numbers 2016498-2016499 can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax+ 441223336033; email deposit@ccdc.cam.ac.uk).

Crystal data for complex **1**: C₁₁₈H₁₃₆N₄O₅₇P₂S₈Y₂, M = 3018.54, colorless plate, $0.39 \times 0.21 \times 0.09$ mm³, monoclinic, space group $P2_1/c$ (No. 13), a = 12.5068(6), b = 14.2338(10), c = 39.8349(16) Å, β = 90.492(4)°, V = 7091.1(7) Å³, Z = 2, D_c = 1.414 g cm⁻³, μ = 3.182 mm⁻¹. F_{000} = 3128, CuK α radiation, λ = 1.54178 Å, $2\theta_{\max}$ = 134.8°, 31146 reflections collected, 12536 unique (R_{int} = 0.0704). Final $Goof$ = 1.003, $R1$ = 0.1048, $wR2$ = 0.2421, R indices based on 7389 reflections with $I > 2\sigma(I)$, $|\Delta\rho|_{\max}$ = 1.1(1) e Å⁻³, 907 parameters, 124 restraints. CCDC number: 2016498

Crystal data for complex **2**: C₃₄H₃₆N₂Na₄O₂₂S₄, M = 1044.85, colorless prism, $0.28 \times 0.11 \times 0.06$ mm³, triclinic, space group $P-1$ (No. 2), a = 10.7038(4), b = 12.5496(6), c =

15.1265(5) Å, $\alpha = 92.435(3)$, $\beta = 92.841(3)$, $\gamma = 102.178(4)^\circ$, $V = 1980.83(14)$ Å³, $Z = 2$, $D_c = 1.752$ g cm⁻³, $\mu = 0.380$ mm⁻¹. $F_{000} = 1076$, MoK α radiation, $\lambda = 0.71073$ Å, $2\theta_{\max} = 64.3^\circ$, 23342 reflections collected, 12667 unique ($R_{\text{int}} = 0.0339$). Final $Goof = 1.002$, $R1 = 0.0680$, $wR2 = 0.1571$, R indices based on 9736 reflections with $I > 2\sigma(I)$, $|\Delta\rho|_{\max} = 1.1(1)$ e Å⁻³, 604 parameters, 0 restraints. CCDC number: 2016499

3. Results and Discussion

3.1 Complex 1: $\{[Y_2(H_2O)_{13}(C_6H_8N_2O_2)_2]^{8+} \cdot 2[(SO_3)\text{calix}[4]\text{-H}]^{5-}\} \cdot 2[Ph_3P(PhOMe)]^+ \cdot 6H_2O$

Complex **1** crystallizes in the monoclinic space group $P2/c$ ($Z = 2$). The asymmetric unit (ASU) contains one calixarene anion (with one sulfonate group disordered), one phosphonium cation and one imidazolium cation with carboxylate oxygen atoms connected to Y^{3+} aquatic cations, along with three waters of crystallization (all of which are poorly defined and disordered, and as such have been refined without H-atoms located). Charge balance necessitates deprotonation of one of the phenolic oxygens of the calixarene, rendering it a penta-anion which is not unusual for this host. The formation of a continuous bilayer structure prevails with the interstices between neighboring bilayers containing phosphonium cations (approximate bilayer thickness of 14.8 Å, inter-bilayer distance of 20.0 Å). The water molecules remain uncoordinated in the hydrophilic region.

Complex **1** shows a new self-assembled structure that has different carboxylato-lanthanoid coordination modes relative to ZAVWUQ as shown in Figure 1. The Y1 center is located on a 2-fold axis, has six aquo ligands (Y1–O distances ranging from 2.356(6) Å to 2.424(6) Å), and bridges to two independent carboxylate oxygen atoms of two carboxyl-functionalized imidazolium moieties (Y1–O1 distance at 2.256(6) Å to 2.424(6) Å), thus forming a relatively different dimer compared to the previously reported structure. The C–O bond lengths in the carboxylate group range between 1.236(12) Å and 1.242(11) Å and indicate a uniform delocalization of the negative charge in contrast to the C–O bond lengths found in ZAVWUQ (1.239(8) Å and 1.29(1) Å). The coordination environment around Y1 in **1** is best described as a square anti-prism with angles between 69.49(19) ° to 147.6(2) °. The Y2 center was found to be half-populated and disordered across two positions (Fig. 1A) and is also eight-coordinate, however it is bound to only one carboxyl-functionalized imidazolium moiety (Y2–O2 distance at 2.269(8) Å) with the immediate coordination sphere around the metal ion fulfilled by seven aquo ligands (Y2–O distances ranging from 2.461(13) Å to 2.486(12) Å). The C–O bond lengths and angles of the carboxylic acid-functionalized imidazolium zwitterion are only marginally different to those found in ZAVWUQ. The coordination around the Y2 metal center is best described as a bicapped trigonal prismatic. All metal ions interact with the hydrophilic species (water molecules and calixarene sulfonate groups) through aquo ligands in the secondary coordination sphere.

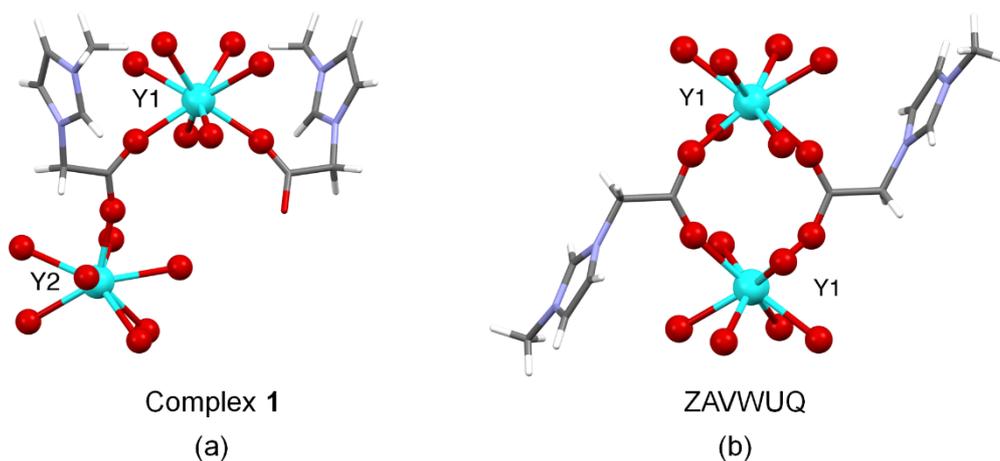


Figure 1. (a) Partial ball and stick representation showing the arrangement of Y^{3+} ions and carboxyl-functionalized imidazolium species in different coordination environments as opposed to the binuclear Y^{3+} metal center in ZAVWUQ (b). In complex **1** only one of four possible positions of Y2 with its aqua ligands is depicted.

The binuclear species is encapsulated by the skewed ‘molecular capsule’ (capsule size ~ 16 Å), Figure 2, built by two calixarenes in the cone conformation (dihedral angles calculated from the planes of the phenolic rings and the basal plane comprised of the four methylene carbon atoms are 49.9° , 49.5° , 62.2° , 64.32°). In **1**, the terminal imidazolium moieties are included in the cavities of calixarenes with the *N*-methyl group pointing directly into the cavity in attaining the most favorable orientation with the host molecule, having close (i) $C \cdots \pi_{(\text{centroid})}$ distances at 3.36 and 3.49 Å and (ii) $C \cdots O$ distance at 3.35 and 3.50 Å Fig. 2. The angle between the plane of the imidazolium cation and the methylene bridge plane of the calixarene is 45.5° , which is less than the previously reported structure, presumably due to the different metal coordination experienced by the carboxylic-functionalized imidazolium species.

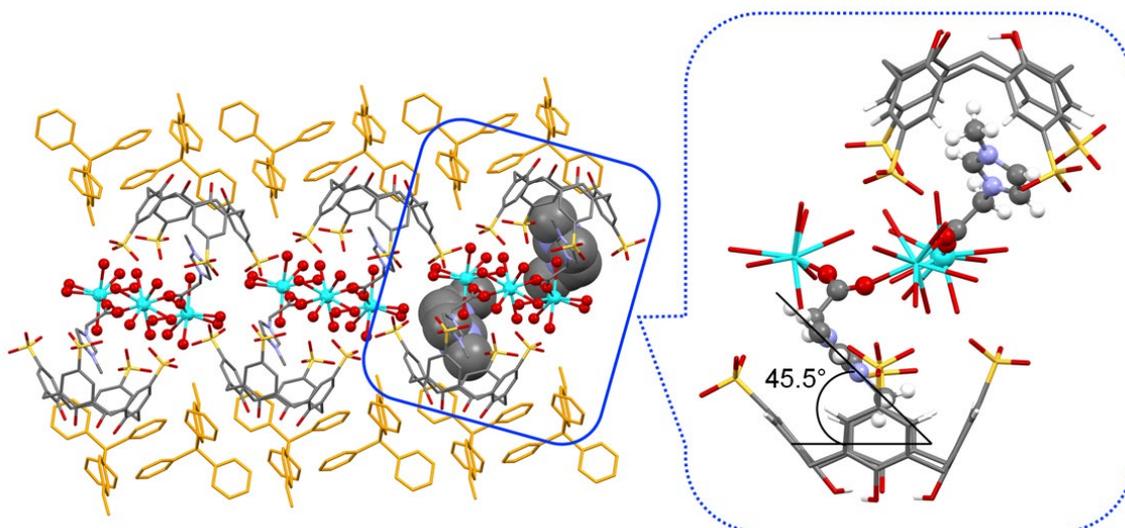


Figure 2. Partial space filling and ball and stick representations of **1** showing the skewed molecular capsule arrangement. Inset: The inclusion complex of carboxylic-functionalized imidazolium- Y^{3+} within a molecule capsule.

The interposing bilayer arrangement of calixarenes, an offset back-to-back array with embedded phosphonium cations, is different when compared ZAVWUQ (Figure 3). The packing of the capsules within the crystal lattice is associated with hydrogen bonding between calixarenes and other weak interactions involving mutual interplay with the phosphonium ions. These two components have close C–H $\cdots\pi$ (centroid) contacts (C $\cdots\pi$ (centroid) 3.30 to 3.60 Å) and the methoxy group of the phosphonium ion has C–H \cdots OS contacts at 3.10 to 3.30 Å. The phosphonium ions are organized as two-dimensional hydrophobic layers within the compact bilayers of calixarenes, devoid of the common phenyl embrace arrangement with the larger distribution of P \cdots P distances (range from 9.7 to 12.5 Å) and these are relatively shorter compared to the previously reported structure. Thus, the organization of the phosphonium ions is also affected by the nature of the complexation of the carboxylate-lanthanoid species.

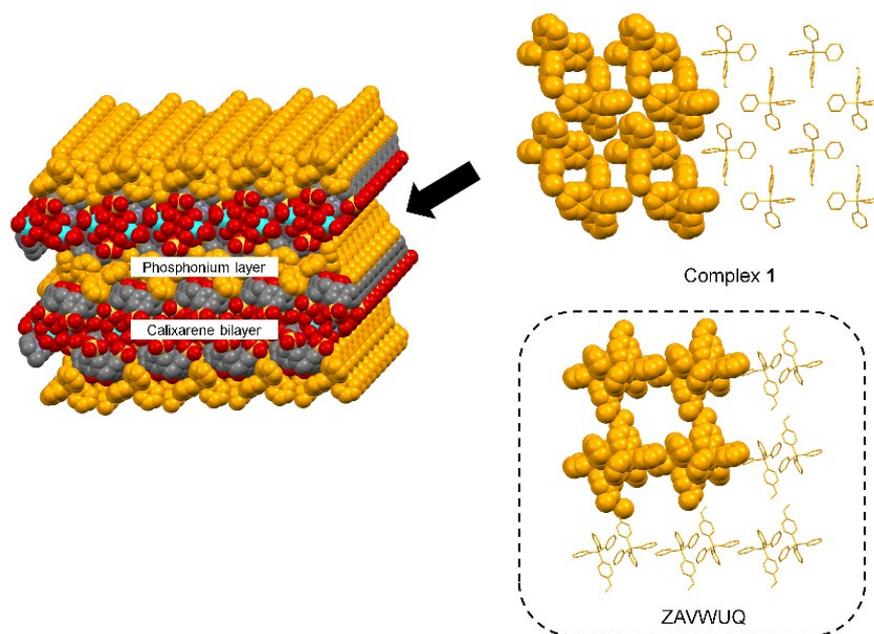


Figure 3. The extended structure in **1** with alternating calixarene bilayers and phosphonium layers. The phosphonium ions are assembled into two-dimensional layers (right top) devoid of the common phenyl embrace as seen in ZAVWUQ (inset).

3.2 Complex 2: $[\text{Na}_4\text{-(SO}_3\text{)calix[4] c C}_6\text{H}_8\text{N}_2\text{O}_2] \cdot \text{H}_2\text{O}$

The sodium complex, **2**, crystallizes as hydrate in the triclinic space group $P\bar{1}$ ($Z = 2$). The ASU comprises one tetra-anionic $\text{SO}_3[4]$, one imidazolium molecule, four Na^+ cations (Na_4 is poorly defined and disordered), and one uncoordinated water of crystallization in close proximity to a calixarene sulfonate group and an aquo ligand. The $\text{SO}_3[4]$ s are arranged back-to-back into antiparallel bilayers that are stabilized in part by the electrostatic interaction of the sodium ions with the calixarenes' sulfonate and hydroxyl groups, but also by the favorable C $\cdots\pi$ (centroid) interaction involving aromatic rings that are positioned close to each other (calculated C $\cdots\pi$ (centroid) distance at 3.46 Å, Figure 4). As a result, a three-dimensional polymeric bilayer network is obtained with the inter-bilayer distance is 13.7 Å and bilayer thickness of 10.7 Å.

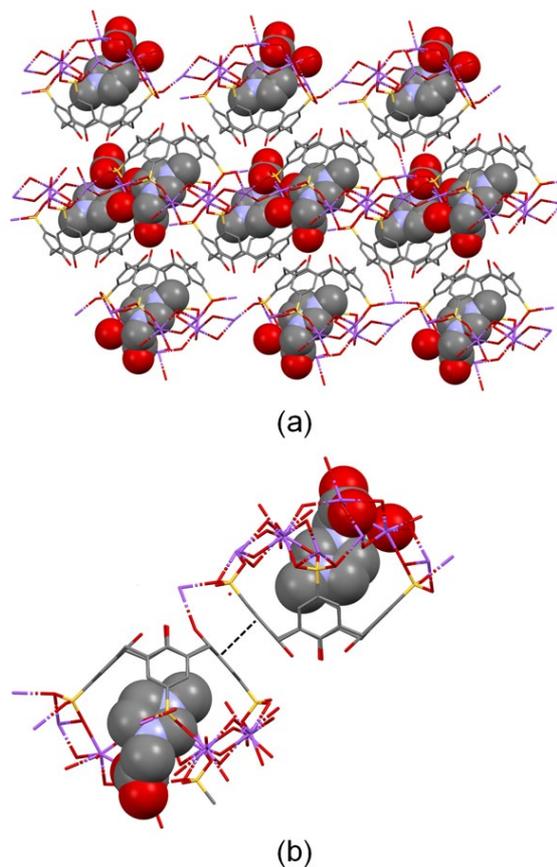


Figure 4. (a) Bilayer arrangement in **2**. (b) Interactions between the neighboring calixarene aromatic rings.

The coordination environments of the sodium ions are somewhat more complicated (Figure 5). Na1 is bound to one sulfonate group (Na1-O13 = 2.235 (3) Å). Na2, as a six-coordinate ion with three symmetry generated O-atoms, is bound to one aquo ligand (Na2-O3W = 2.540(3) Å) and bridges to a sulfonate and carboxylate group (Na2-O21 = 2.363(2) Å; Na2-O1 = 2.435(2) Å). Na4 is two coordinate and is also bound to the same carboxylate O-atom (Na4-O1 = 2.363 (12) Å) and an aquo ligand (Na2-O4W = Å). Na3 forms chelate with a sulfonate group (Na3-O31 = 2.536(2) Å; Na3-O33 = 2.460(2) Å) and the remaining coordination is fulfilled by an aquo ligand (Na3-O1W = 2.336 (3) Å).

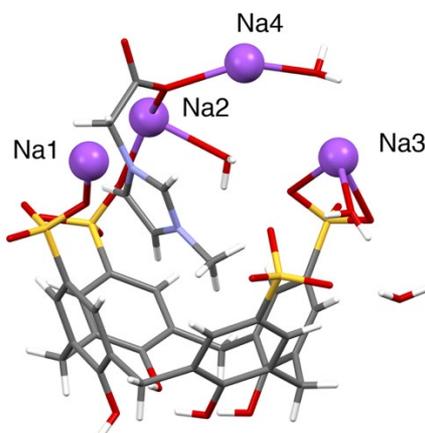


Figure 5. Partial ball and stick representation of the coordination environments found for the sodium ions within the ASU of complex **2**.

The overall structure also features the complicity of the calixarene slightly pinching the imidazolium ring of the carboxylic acid-functionalized imidazolium zwitterion (corresponding dihedral angles formed by the calixarene phenolic rings are 51.0 °, 65.6 °, 42.7 ° and 67.6 °). The methyl group points towards one of the calixarene aromatic rings, while the carboxylate terminal is directed away from the cavity. The complementarity of interaction of the carboxyl-functionalized imidazolium cation with the calixarene cavity is dominated by both C–H $\cdots\pi_{(\text{centroid})}$ (C $\cdots\pi_{(\text{centroid})}$ at 3.34 Å) and C–H \cdots O hydrogen bonding interactions (C \cdots O distance at 3.50 Å). The carboxylate group of the carboxylic acid-functionalized imidazolium zwitterion coordinate as monodentate to Na⁺. The C–O bond lengths (1.226(4) Å and 1.287(3) Å) and bond angle (125.8(3) °) of the carboxylate group are within the range found in other carboxylic acid-functionalized imidazolium salts.

4. Conclusion

The structural characteristics of the carboxylic acid-functionalized imidazolium ligand are crucial in the formation of coordination complexes with different topologies. In the solid state, the crystalline structures are found to be largely dependent on the size of the metal ion, with a small cation (Na⁺) favoring a polymeric network, whilst a larger cation (Y³⁺) favors dimeric cluster formation. The presence of the imidazole ring appears to drive the formation of a host-guest supermolecule through the inclusion of the positively charged five-membered ring. Although the bilayer arrangement persistently formed in the present and previously reported structures, it appears that the alignment of the bilayer depends on the nature of the complexed carboxylate moieties. The reported complexes may serve as i) a base model to work from towards the development of bioimaging and drug delivery using calixarene-based nanovehicles, as yttrium is known to be a good candidate for radiotherapy²⁵ and antibacterial²⁶ applications and ii) a model in the development of conducting material involving sodium-oxygen species interlocked by calixarenes as supporting layer to build nanodevices.²⁷

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