Lanthanoid assisted self-assembly of imidazolium cations in organic bi-layers

Yatimah Alias, University of Malaya
Lanthanoid assisted self-assembly of imidazolium cations in organic bi-layers†

Irene Ling, a Yatimah Alias, a Alexandre N. Sobolev b and Colin L. Raston a

Received 8th January 2010, Accepted 15th January 2010
First published as an Advance Article on the web 1st February 2010
DOI: 10.1039/c000487c

Multi-component solutions containing 1-n-ethyl-3-methylimidazolium or 1-n-butyl-3-methylimidazolium cations, p-sulfonatocalix[4]arene and large mono- or bis-phosphonium cations, as well as lanthanide metal ions, afford self-assembled material incorporating all four components. The calixarenes and phosphonium cations are organized into bi-layers, with the imidazolium cations and gadolinium(iii) species incorporated between the bi-layers. The imidazolium cations are confined within essentially ‘molecular capsules’ based on two calixarenes from adjacent bi-layers, with these cations taking on different orientations, depending on the nature of the phosphonium cation, and whether the metal also binds to sulfonate moieties.

Introduction

Calixarenes are often used in engineering nano-materials, with their cavities able to include small molecules, and are generally referred to as cavatins. For example, the self-assembled solid state material based on p-tert-butylcalix[4]arene has been used in gas sorption studies, being able to trap gas molecules, including N₂, O₂, CO, CO₂, CF₃Br, CF₄ and CH₄, despite the porosity of the phenolic rings linked together in forming the macrocycles. In general terms, calix[n]arenes with variable internal cavities, depending on the value of n, can be used for confining molecules in the solid state and in solution, depending on the size and shape of the calixarene. This can involve binding larger organic molecules through to alkaline earth ions, by simply varying the value of n which corresponds to the number of phenolic rings linked together in forming the macrocycles. Calixarenes can be selectively functionalized at the upper or the lower rim, further adding to their utility, for example, in acting as receptors in molecular recognition, or recognition of Na⁺ and K⁺ ions at the air–water interface.

Calixarene functionalized at the upper rim with sulfonate groups, p-sulfonatocalix[n]arenes [n = 4, 5, 6 and 8], can act as versatile water soluble amphiphilic macrocyclic receptor molecules. They can bind organic molecules through weak non-covalent interactions, in building complex structures in the solid state, which is well documented. Moreover, sulfonated calixarenes provide anchoring points for the complexation of organic and inorganic moieties, with lanthanide metal ions, playing an important role in the stability and overall cohesion of the structures through charge balance, hydrogen bonding, bridging, and templating effects.

† CCDC reference numbers 728616–728619. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c000487c

Results and discussion

The reaction of a 1 : 1 : 1 ratio of 1 to 1-ethyl-3-methylimidazolium (2 or 3) or 1-butyl-3-methylimidazolium (4 or 5)
cations, and 1,4-bis(triphenylphosphonomethyl) benzene (6) or benzyltriphenyl phosphonium (7) cations, in aqueous solution (pH 3.5–4.9) in the presence of excess gadolinium(III) chloride afforded four discrete complexes as colorless crystals, Fig. 1. Complexes I–IV were characterized using single crystal X-ray diffraction data, with all four structures revealing the effective templating effects of lanthanide metal ion connecting the calixarenes from two adjacent bi-layers forming ‘molecular capsule’, with the imidazolium cations reside in the cavities. These ‘capsules’ are slightly skewed in the bi-layer arrangement, separated by a hydrophobic layer of phosphonium cations through common multiple phenyl embraces. The different alkyl chain lengths of the imidazolium cation are accommodated in different ways. For the shorter chain length, the imidazolium cation has a methyl or ethyl group directed into a calixarene cavity. In the case of butylimidazolium, the flexible longer \( n \)-butyl alkyl chain interplays with the calixarene cavity in different ways. It is also noteworthy that the mode of interaction of the lanthanide ions with the calixarenes is reflected in different interlayer thicknesses (distance measured between centres of neighboring bi-layers), with a more compact arrangement of ‘molecular capsules’ when the metal ion is directly bound to the calixarene sulfonate groups.

Complex I

Ions of 1, 2, 4 and gadolinium(III) come together in a crystalline solid with the asymmetric unit containing one calixarene (taking on a 5+ charge, with one proton removed from the lower rim) with a covalently bound aquated gadolinium(III) ion, one ethyl imidazolium cation, one bis-phosphonium cation, and included water molecules which form an extended H-bond network with O–O distances at 2.518(2) to 3.092(4) Å. A key feature of the structure is the centrosymmetric dimers of calixarenes which are bridged by aquated gadolinium(III) cations, where the gadolinium centres are bound to two adjacent sulfonate groups of calixarenes along with six water molecules. The bond distances of the O-atoms of sulfonate group to gadolinium are 2.330(1) and 2.381(2) Å. A compact ‘molecular capsules’ arrangement in the extended array is noted, which presumably arises from the coordination of the metal centres to some of the sulfonato moieties and this is manifested in the closer packing between the bi-layers, with the interlayer distance at 18.19 Å, Fig. 2.

The imidazolium ethyl group of the imidazolium cation is directed into the cavity of the calixarene and is involved in two C–H⋯\( \pi \) close distances to two phenolic rings of the calixarene,
with C–H···ring centroid distances at 2.66 and 2.94 Å. Two H-atoms of the five-membered ring are involved in C–H···O interactions with sulfonate groups with C···O distances at 3.36 and 3.59 Å, Fig. 3. The five-membered ring of the imidazolium cation is positioned parallel to one of the phenolic rings of the calixarene, and the distance between the centroids of the two encapsulated imidazolium cations is 4.65 Å, as measured between centroids of the five-membered ring. One of the phenolic rings of calixarene is splayed apart greater than the other phenolic rings with the angle between the basal plane and the phenyl ring at 38.9(1)°. Other angles are 53.7(1)°, 75.9(1)°, and 54.2(1)°, with two of the phenyl rings pinched around the imidazolium cation.

The trans-arranged bis-phosphonium cations have multiple C–H···π interactions between themselves with C–H···phenyl centroid distances at 3.0 to 3.7 Å. These cations are embedded in between calixarenes, having C–H···π interactions from an H-atom of the central ring of the bis-phosphonium cation to the centroid of a calixarene phenolic ring at 3.55 Å. Close C–H···O distances for an H-atom of phenyl rings of the cations to the hydroxyl groups at the lower rim of calixarene are evident, with distances ranging from 2.36 to 2.97 Å. There is a grid-like formation of bis-phosphonium cations which is revealed in projection along the c-axis, being effectively embedded in between the ‘capsules’, tucked in close to the lower rim of calixarenes within the bi-layers.

**Complex II**

Crystals are comprised of 1, 3, 5 and gadolinium(III), as for complex I, with the asymmetric unit containing two p-sulfonatocalix[4]arenes with covalently attached gadolinium(III) bearing seven coordinated water molecules, one butylimidazolium cation, distributed between cavities of two calixarenes, two benzyltriphenyl phosphonium cations, and solvent molecules. All water molecules are half-populated, and there are also included methanol molecules (residual solvent from recrystallization of p-sulfonatocalix[4]arene) which are involved in the H-bonding network, with O···O distances down to 2.50(2) Å.

The ‘molecular capsule’ is generated by an inversion centre, but electrical neutrality requires one of them taking on a 4+ charge, the other 5− charge within each ‘capsule’ (necessitating one proton being removed from the lower rim of calixarene). Two crystallographically unique gadolinium metal centres are bound to O-atoms of sulfonate groups with Gd−O at 2.371(4) and 2.429(9) Å and the direct coordination of the gadolinium cations with the calixarenes forms a compact arrangement with the interlayer thickness as at 18.07 Å, Fig. 4, which has approximately the same interlayer thickness in complex I.

The butylimidazolium cation residing in the ‘capsule’ is disordered with half population across the inversion centre having the methyl group directed into the calixarene cavity with a C···π close distance for the C-methyl group to centroid of a phenolic ring at 3.61 Å. Other close contacts involve an H-atom of the five-membered ring to the sulfonate group with the C···O distances at 3.01 to 3.20 Å. At the other end of the imidazolium cation, the butyl group is close to the calixarene phenolic rings with C···π close distances at 3.59 to 3.65 Å, and an H-atom of calixarene. Two crystallographically unique gadolinium metal centres are bound to O-atoms of sulfonate groups with Gd–O at 2.371(4) and 2.429(9) Å and the direct coordination of the gadolinium cations with the calixarenes forms a compact arrangement with the interlayer thickness as at 18.07 Å, Fig. 4, which has approximately the same interlayer thickness in complex I.

The butylimidazolium cation residing in the ‘capsule’ is disordered with half population across the inversion centre having the methyl group directed into the calixarene cavity with a C···π close distance for the C-methyl group to centroid of a phenolic ring at 3.61 Å. Other close contacts involve an H-atom of the five-membered ring to the sulfonate group with the C···O distances at 3.01 to 3.20 Å. At the other end of the imidazolium cation, the butyl group is close to the calixarene phenolic rings with C···π close distances at 3.59 to 3.65 Å, and an H-atom of calixarene. Two crystallographically unique gadolinium metal centres are bound to O-atoms of sulfonate groups with Gd−O at 2.371(4) and 2.429(9) Å and the direct coordination of the gadolinium cations with the calixarenes forms a compact arrangement with the interlayer thickness as at 18.07 Å, Fig. 4, which has approximately the same interlayer thickness in complex I.

The butylimidazolium cation residing in the ‘capsule’ is disordered with half population across the inversion centre having the methyl group directed into the calixarene cavity with a C···π close distance for the C-methyl group to centroid of a phenolic ring at 3.61 Å. Other close contacts involve an H-atom of the five-membered ring to the sulfonate group with the C···O distances at 3.01 to 3.20 Å. At the other end of the imidazolium cation, the butyl group is close to the calixarene phenolic rings with C···π close distances at 3.59 to 3.65 Å, and an H-atom of calixarene. Two crystallographically unique gadolinium metal centres are bound to O-atoms of sulfonate groups with Gd−O at 2.371(4) and 2.429(9) Å and the direct coordination of the gadolinium cations with the calixarenes forms a compact arrangement with the interlayer thickness as at 18.07 Å, Fig. 4, which has approximately the same interlayer thickness in complex I.
the butyl group is close to the sulfonate group at 2.69 Å (C–O distance at 3.65 Å). The calixarenes in complex II also have a pinched cone configuration associated with binding of the guest molecule, with the angles between the plane of the aromatic rings and the basal plane of the four hydroxyl groups at the lower rim being 70.2(2)°, 51.2(2)°, 64.6(2)°, and 46.3(2)°, Fig. 5.

Pairs of phosphonium cations embrace in an offset face-to-face manner with C–π (centroid) between the phenyl rings at 3.93 Å. Close contacts between calixarene and phosphonium cations are π···π interactions between the phenyl rings of calixarene and phosphonium with the centroid to centroid distance at 3.50 Å, and C–H···π interactions involving the methylene bridge of calixarene and the phenyl group of the phosphonium cation, the H-atom to centroid distance being 2.98 Å. Phosphonium cations link each other with common embraces as part of a grid network, with the calixarenes in the openings.

**Complex III**

The combination of components 1, 2, 5 and gadolinium(III) afforded colorless prisms of complex III. The asymmetric unit consists of one p-sulfonatocalix[4]arene, with one half-populated ethylimidazolium cation residing in the cavity of the calixarene molecule, two phosphonium cations surrounding the calixarene and a gadolinium(III) cation with half occupancy (disordered relative to an inversion centre), forming a secondary coordination sphere through hydrogen bonding with the calixarenes, effectively creating ‘molecular capsules’ in the extended structure. Fig. 6, rather than binding directly to calixarenes as opposed to complex I. Each adjacent ‘capsule’ is skewed presumably in maximizing electrostatic interaction between the sulfonate groups and the polyaquated lanthanide cations. This homogeneous ion is coordinated by eight water molecules, and has close contacts with the sulfonate groups with the upper rim of the calixarene through extensive hydrogen bonding, the GdO···OS distances ranging from 2.76(2) Å to 2.77(2) Å. The ‘molecular capsules’ interlayer distance is now slightly greater relative to complex I, with the interlayer thickness at 21.13 Å, Fig. 6.

The ‘molecular capsules’ contain one ethylimidazolium cation distributed between two positions, with the imidazolium cation having the methyl group directed into the cavity of a calixarene, the methyl C-atom having a short distance to the centroid of a phenyl ring at 3.47 Å. The imidazolium ring has a C–H···π interaction to the phenolic ring of calixarene, with C–H···π ring centroid distance at 2.74 Å, and two H-atoms on the five-membered ring are involved in C–H···O interactions with the sulfonate group, the C···O distances being 3.44 and 3.47 Å, Fig. 7. The calixarenes are slightly distorted from a symmetrical cone shape with two opposite 1,3-disposed aromatic rings pushed away, with the angles between the plane of the aromatic rings and the basal plane of the four hydroxyl groups at the lower rim of calixarene at 49.1(3)°, 65.9(3)°, 40.3(3)° and 62.7(3)°. One of the rings is splayed apart slightly greater and it is parallel with the five-membered ring of the imidazolium cation, the centroid to centroid distance being 3.97 Å. Disordered water molecules (albeit with no H-atoms located) are present within ‘molecular capsule’ along with the imidazolium cation, having H-bonds with O···O distances ranging from 2.44(2) to 3.28(5) Å.

**Complex IV**

Crystals are comprised of 1, 3, 5 and gadolinium(III), with the unit cell containing one p-sulfonatocalix[4]arene, one disordered butylimidazolium cation distributed between two positions, two benzyltriphenyl phosphonium cations and a half-populated gadolinium cation coordinated by eight water molecules, and a large quantity of disordered included water molecules (with no H-atoms located) filling the voids. The homoleptic metal centre is in close contact with the calixarene through extensive hydrogen bonding, as judged by the close proximity of the O-atom of the sulfonate group to the aquated gadolinium cations, O···O being 2.65(2) to 2.98(2) Å. The distance from the centre of the bi-layer to the next bi-layer is 20.92 Å, which is close to the size of the interlayer distance in complex III.

---

**Fig. 6** Projection along b-axis with some space filling of imidazolium guest molecules (blue) confined in the ‘molecular capsules’, and layers of phosphonium cations (orange) in the extended bi-layer of complex III.

**Fig. 7** (a) Stick representation showing close contacts between imidazolium and calixarene in complex III (H-bonds and C–H···π are shown as purple and green dashed lines, respectively) and (b) space filling showing the inclusion of imidazolium cation in the calixarene cavity (different orientation to (a)).
The calixarenes are arranged in slightly skewed ‘capsule’ forming bi-layers in the extended structure. Fig. 8, with each ‘capsule’ shrouding one imidazolium cation. In the present structure the half-populated imidazolium cation (also disordered between two positions) is folded into a ‘V’-shape, having multiple interactions with the walls of the ‘capsules’: (i) C–H⋯π from the butyl group to the phenolic ring of calixarene, C–H⋯ring centroid distances being 2.76 Å and 2.77 Å, (ii) an H-atom on the five-membered ring close to a sulfonate group, C⋯O distances being 3.28 Å to 3.54 Å, (iii) an H-atom of the methyl group close to the sulfonate group, C⋯O distance being 3.31 Å, and (iv) an H-atom of the butyl group close to the sulfonate group, C⋯O distance being 3.16 Å. As seen from the space-filling representation in Fig. 9, the butylimidazolium cation is positioned deep within the calixarene cavity, with the calixarene pinching around the guest. The angles of all four phenolic rings with the basal plane of the four hydroxyl groups at the lower rim of the calixarene are 40.0(3)°, 59.8(3)°, 49.6(3)°, and 66.6(3)°, for the pinching and splaying phenyl ring pairs (respectively) within each calixarene.

Phosphonium cations essentially form layers within the bi-layers with edge-to-face embrace, and are involved in two C–H⋯π (centroid) contacts, at distances of 3.0 Å and 3.2 Å. They are embedded in between calixarenes having multiple close contacts involving C–H⋯π (centroid) interactions between an H-atom at the phenyl ring of phosphonium and the centroid of the phenolic calixarene ring, at distances ranging from 2.71 to 2.98 Å.

**Conclusions**

Structural features arising from the assembly of multi-component materials containing water soluble sulfonated calix[4]arene, aquated gadolinium(III) ions, and a range of phosphonium cations have been established, with a common ‘molecular capsule’ or skewed ‘molecular capsule’ motif based on two calixarenes surrounding one or two imidazolium cations, depending on the choice of unsymmetrical 1-ethyl- or 1-n-butylimidazolium cations, as shown in cartoon form in Fig. 10. The shorter alkyl chain can afford ‘capsules’ containing one cation, with the ring methyl directed into a calixarene cavity, the ‘capsule’ also containing solvent molecules, complex III, Fig. 10(a). Alternatively two such cations can be in a ‘capsule’, complex I, but now with the ethyl groups directed into the calixarene cavities, Fig. 10(b). Thus the ‘capsules’ are flexible in confining the number and the orientation of the imidazolium cations, which are likely to depend in a subtle way on the choice of phosphonium cation, and how the metal centres interact with the calixarenes i.e. covalent bond versus H-bonding formation, for complexes I and III, respectively.

The longer n-butyl alkyl chain gives scope for the two ends of the imidazolium cation to reside in different calixarenes, as found in complex II, Fig. 10(d). The same cation can also be common to two calixarenes in a distinctly different way, complex IV, with the alkyl chain being V-shaped and snugly fitting into one cavity, the other cavity is presumably occupied by disordered solvent molecules, Fig. 10(e). Thus for the longer chain alkyl group, the number of cations in the ‘capsules’ is set at one, but the orientation and conformation of the alkyl chain can be varied, in a way depending on the choice of phosphonium cation, and also on how the metal centres interact with the calixarenes (covalent bond versus H-bonding formation), for complexes II and IV, respectively. Increasing the chain length further is likely to give ‘molecular capsules’ shrouding one imidazolium cation, but we note that the 1-n-octyl analogue results in the long alkyl chain penetrating the adjacent bi-layer, Fig. 10(e), rather than forming ‘capsules’.

The thickness of the bi-layer can be controlled by the choice of the imidazolium cation (alkyl chain length) and the coordination of lanthanide metal ions. Another design feature of the complexes is the packing of the phosphonium cations into layers or grid arrays around the aromatic rings of the calixarene within all the bi-layers. Overall the four components come together with selective interplay of the sulfonated calix[4]arene with either a mono-phosphonium or bis-phosphonium cation in forming bi-layers, even though the complexes can be of different composition. It is also noteworthy that the calixarene has some flexibility in its conformation, with subtle changes in forming pinched cones, for example, and it is also versatile in taking on a 4– or 5– charge for each ‘molecular capsule’, or indeed both of these within the same structure.

**Experimental section**

**General procedure**

p-Sulfonatocalix[4]arene (1), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate and bromide (2 and 3), and
1-butyl-3-methylimidazolium dicyanamide and chloride (4 and 5) salts were synthesized according to literature procedures. Bis-phosphonium and phosphonium chloride salts (6 and 7) were purchased from Sigma-Aldrich. A hot solution of a three fold excess of GdCl\textsubscript{3} \cdot 6H\textsubscript{2}O in water (19.0 mg, 0.5 ml) was added to a hot solution of equimolar imidazolium salt (4.9–5.6 mg) and phosphonium salt (9.3–16.1 mg) with p-sulfonatocalix[4]arene (25.2 mg) in a mixture of THF and water (1 : 1, 2 ml). The prepared solutions were left to cool, and slow-evaporate, affording colorless crystals of complexes which were suitable for X-ray diffraction studies after several days.

**X-Ray crystallography**

All data were measured from single crystals using Oxford Diffraction Xcalibur or Gemini CCD diffractometers with Mo-\(\text{K}\alpha (\lambda = 0.71073 \text{ Å})\) or Cu-\(\text{K}\alpha (\lambda = 1.54178 \text{ Å})\) radiation, at \(T = 100(2) \text{ K}\). Data was collected corrected for Lorentz and polarization effects and absorption correction applied, using multiple symmetry equivalent reflections. The structures were solved by direct method and refined with full matrix least-squares procedures on \(F^2\) using the SHELX-97 crystallographic package and X-seed interface. A full matrix least-squares refinement procedure was used, minimizing \(w(F_o^2 - F_c^2)\), with \(w = [\sigma^2(F_o^2) + (AP)^2 + BP]^\frac{1}{2}\), where \(P = (F_o^2 + 2F_c^2)/3\). Agreement factors \((R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|, wR2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}\) and \(GooF = [\Sigma[w(F_o^2 - F_c^2)^2](n - p)]^{1/2}\) are cited where \(n\) is the number of reflections and \(p\) is the total number of parameters refined. Non-hydrogen non-disordered atoms were refined anisotropically. The positions of hydrogen atoms were partly localized from difference Fourier synthesis, partly calculated and their atomic parameters were constrained to the bonded atoms during the refinement with \(C_{ph-H} = 0.95 \text{ Å}, C_{Me-H} = 0.98 \text{ Å} and 0.99 \text{ Å in CH}_2\).

**Complex I.** \(\text{C}_{56}\text{H}_{42}\text{Gd}_{5}\text{O}_{44}\text{S}_{8}^{2+}, \text{C}_{42}\text{H}_{38}\text{P}_{2}^{2+}\), \(2(\text{C}_{11}\text{H}_{11}\text{N}_{2}^{+})\), \(15(\text{H}_{2}\text{O})\); \(\text{C}_{112}\text{H}_{192}\text{Gd}_{5}\text{O}_{50}\text{P}_{2}\text{S}_{8}, M = 3131.30\), colorless prism, \(0.40 \times 0.28 \times 0.19 \text{ mm}^3\), triclinic, space group \(\text{P}1\) (no. 2), \(a = 12.7621(4), b = 15.4557(5), c = 19.2632(6) \text{ Å}, \alpha = 106.004(3), \beta = 93.474(3), \gamma = 112.632(3)\), \(V = 3311.07(18) \text{ Å}^3, Z = 1, D_{c} = 1.570 \text{ g cm}^{-3}, \mu = 1.240 \text{ mm}^{-1}, F_{000} = 1610, 2\theta_{max} = 76.4\), 128 317 reflections collected, 33 803 unique \((R_{int} = 0.0492)\). Final \(GooF = 1.001, |\Delta \rho_{max}| = 6.9(2) \text{ e Å}^{-3}, R1 = 0.0501, wR2 = 0.1436, R\) indices based on 25 260 reflections with \(I > 2\sigma(I)\), 847 parameters, 0 restraints.

**Complex II.** \(\text{C}_{26}\text{H}_{14}\text{Gd}_{2}\text{O}_{4}\text{S}_{8}^{2-}, \text{C}_{28}\text{H}_{33}\text{Gd}_{2}\text{O}_{23}\text{S}_{4}^{2-}, \text{C}_{46}\text{H}_{2}\text{N}_{2}^{2+}, 2(\text{C}_{25}\text{H}_{2}\text{P}_{2}^{+})\), \(8.5(\text{H}_{2}\text{O}), 0.5(\text{CH}_3\text{O})\); \(\text{C}_{114.50}\text{H}_{152}\text{Gd}_{2}\text{O}_{59}\text{P}_{2}\text{S}_{8}, M = 3062.25\), colorless prism, \(0.35 \times 0.30 \times 0.13 \text{ mm}^3\), triclinic, space group \(\text{P}1\) (no. 2), \(a = 12.8192(1), b = 18.6718(3), c = 28.8700(4) \text{ Å}, \alpha = 100.278(1), \beta = 99.635(1), \gamma = 98.348(1)\), \(V = 6593.41(15) \text{ Å}^3, Z = 2, D_{c} = 1.542 \text{ g cm}^{-3}, \mu = 1.241 \text{ mm}^{-1}, F_{000} = 3144, \lambda = 0.71073 \text{ Å}, 2\theta_{max} = 61.6\), 155 673 reflections collected, 37 896 unique \((R_{int} = 0.0512)\). Final \(GooF = 1.005, |\Delta \rho_{max}| = 5.7(2) \text{ e Å}^{-3}, R1 = 0.0869, wR2 = 0.2271, R\) indices based on 27 377 reflections with \(I > 2\sigma(I)\), 1591 parameters, 126 restraints.

**Complex III.** \(2(\text{C}_{25}\text{H}_{30}\text{O}_{16}^{4-}), 4(\text{C}_{25}\text{H}_{2}\text{P}_{2}^{+}). \text{Gd}^{3+}(\text{H}_{2}\text{O})_8, \text{C}_{6}\text{H}_{11}\text{N}_{2}^{2+}, 43(\text{H}_{2}\text{O}); \text{C}_{102}\text{H}_{341}\text{Gd}_{7}\text{N}_{28}\text{O}_{38}\text{P}_{28}, M = 4082.18\), colorless needle, \(0.45 \times 0.38 \times 0.14 \text{ mm}^3\), triclinic, space group \(\text{P}1\) (no. 2), \(a = 14.7508(8), b = 17.847(1), c = 22.1096(9) \text{ Å}, \alpha = 147.1093(4), \beta = 109.7212(4), \gamma = 85.7789(4)\), \(V = 3481.83(15) \text{ Å}^3, Z = 1, D_{c} = 1.509 \text{ g cm}^{-3}, \mu = 1.615 \text{ mm}^{-1}, F_{000} = 3170, \lambda = 0.71073 \text{ Å}, 2\theta_{max} = 69.3\), 159 137 reflections collected, 34 376 unique \((R_{int} = 0.051)\). Final \(GooF = 1.005, |\Delta \rho_{max}| = 8.6(2) \text{ e Å}^{-3}, R1 = 0.0899, wR2 = 0.2271, R\) indices based on 27 377 reflections with \(I > 2\sigma(I)\), 1591 parameters, 126 restraints.
α = 100.112(5), β = 102.224(4), γ = 97.190(5), V = 5519.9(5) Å³, Z = 1, Dc = 1.228 g cm⁻³, μ = 0.488 mm⁻¹, F(000) = 2143, 2θmax = 57.7°, 92 749 reflections collected, 25 866 unique (Rint = 0.1070). Final GooF = 1.003, |Δρmax| = 1.3(1) e Å⁻³, R1 = 0.1569, wR2 = 0.3047, R indices based on 12 311 reflections with I > 2σ(I), 1130 parameters, 135 restraints.

Complex IV. 2(C₈H₂₀O₁₆S₄)⁺, 4(C₅H₅N)⁺, C₃H₁₅N₂⁺, Gd³⁺(H₂O)₈, 36(H₂O); C₁₆₄H₂₃₁GdN₂O₇₆P₄S₈, M = 3984.12, colorless needle, 0.45 × 0.38 × 0.14 mm³, triclinic, space group P1 (no. 2), a = 14.7749(2), b = 17.8871(4), c = 21.7909(5) Å, α = 100.797(2), β = 100.493(2), γ = 97.627(2)°, V = 5478.7(2) Å³, Z = 1, Dc = 1.208 g cm⁻³, μ = 3.625 mm⁻¹, F(000) = 2089, 2θmax = 103.7°, 59 744 reflections collected, 11 972 unique (Rint = 0.0553). Final GooF = 1.009, |Δρmax| = 0.96(9) e Å⁻³, R1 = 0.1142, wR2 = 0.2475, R indices based on 8049 reflections with I > 2σ(I), 1140 parameters, 157 restraints.

Acknowledgements

We would like to thank the University of Malaya for financial support from Science Fund grant (03-001-03-SF0286), university research grant PS192/2008A, University of Malaya Centre for Ionic Liquids grant (TA009/2008A), The University of Western Australia, and the Australian Research Council for supporting this work.

References