Unlocking the elusive binding cavity in *p*-sulfonatocalix[8]arene

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For the first time the utility of *p*-sulfonatocalix[8]arene to form a chalice-like cavity for the solid state inclusion of a classical coordination complex $[Co(phen)_3]^{3+}$ has been demonstrated. In the presence of Yb^{3+} ions, a new crystalline material is formed which possesses large diameter, negatively charged channels which propagate through the material in three dimensions.

Introduction

Constructing helical or tubular structures of higher complexity is topical for the mimicry of macromolecular proteins and in building nanoporous materials for application in nanotechnology.[1] Cavitands can serve as a platform for preparing self-assembled multicomponent supramolecular architectures such as spheres and tubules at the nanometre scale.[2,3] Such molecular assemblies often contain large channels or voids which may provide suitable environments for controlled chemical transformations, and act as the basis for small footprint 'nanoreactors'. Further applications abound in separation science, with materials with tailored, specific monodisperse pore sizes being in high demand for nanofiltering of gaseous mixtures and in size-exclusion chromatography. New advances in the replacement of gels, membranes and sieves of random pore structure, and therefore poor guest specificity are of major interest in separation science, and catalysis.[4]

Inorganic and metal–organic porous[5] materials have found wide applications in many traditional fields such as catalysis, adsorption, electronics, and environmental technology because of their high surface area coupled with novel physical and chemical properties.[6] In contrast, the design and construction of organic nanotubes geared towards specific functions have been less well documented.[7] They present considerable synthetic challenges, and represent an exciting development in the field of separation science as a potential new class of molecular sieve, or chromatographic stationary phase. Formation of the latter may be achieved by tuning the hydrophobic/hydrophilic properties of the channel surfaces, or alternatively ion-channels may be formed by lining the surface with charged head groups. Electrostatic effects are important in ion-chromatography or charged-based filtering, which occurs in nature in the kidney where the negatively charged albumin is prevented from passing from the blood to the primary urine by the presence of negatively charged pores in the basal membrane.[8]

In striving for new-generation porous materials, we have recently reported the self-assembly of striking supramolecular arrays based on negatively charged *p*-sulfonatocalix[4]arene which contain large voids. Highlights include nanoscale spheroids as potential inorganic viral mimics,[2,9] tubules[2] and most recently a 'zeolite-like' material formed from helically arranged chains of the [{Co(diHOsar)$\cap${*p*-sulfonatocalix[4]arene}] supermolecule (diOHsar is dihydroxysarcophagine).[10] The rigid cone conformation of *p*-sulfonatocalix[4]arene provides a level of control for molecular capsule formation based on two calixarenes, and are subunits for the spheroidal arrays and those of 'Russian doll' inclusion complexes.[11] Prediction of arrays formed from other *p*-sulfonatocalix[n]arenes (n = 6, 8) is more difficult due to their higher flexibility. Indeed, *p*-sulfonatocalix[8]arene has only recently been structurally authenticated.[12,13]

p-Sulfonatocalix[8]arene has been used, in the presence of lanthanide (Ln^{3+}) ions, to form a complex 3D coordination polymer with 4,4′-bipyridine-*N*,*N*′-dioxide,[12] and an extended 2D porous array based on the partial inclusion of tetraphenylphosphonium (Ph_4P^+) cations.[13] In the polymer, the calixarene adopts the 'pleated loop' conformation, which does not contain a substantial molecular cavity and is the most commonly observed in calix[8]arene structures in general. A noteworthy feature of the structure of the 2D porous network obtained from *p*-sulfonatocalix[8]arene and Ph_4P^+ cations is that the presence of 'molecular capsules' based on two calixarenes with three encapsulated guest ions and the tethering of the calixarenes together through Ln^{3+} anion coordination. Moreover, the calix[8]arene adopts a conformation where three juxtaposed phenyl rings adopt a *pseudo* partial cone, which is occupied by a phenyl ring of one guest Ph_4P^+ cation. It would appear that the shape or size of the guest has the capacity to influence the shape of the calix[8]arene cavity adopted in the solid state. Such mutually-induced host–guest complex formation has recently been observed in solution with *p*-sulfonatocalix[8]arene.[14] This calixarene has a theoretically much larger molecular cavity, and thus has great potential for enveloping large spherical guest molecules such as fullerenes or globular shaped metal complexes in water soluble thin films,[15] in catalysis and ion transport,[16] or acting as a surfactant for nanoparticle stabilisation. Here, we report for the first time the structural authentication of the extended chalice-like

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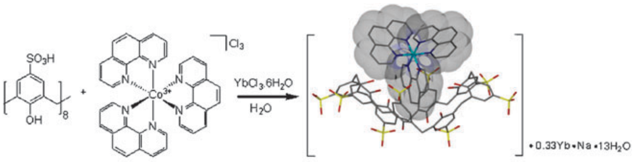

I

Scheme 1 Formation of complex **I**.

cavity in *p*-sulfonatocalix[8]arene, which wraps around the globular-shaped metal cation, tris(phenanthroline)cobalt(III), $[Co(phen)_3]^{3+}$ in the presence of Yb^{3+} ions to form a crystalline material containing large, *negatively charged* ion channels.

Results and discussion

Structure of the supermolecule I

Addition of excess $YbCl_3 \cdot 6H_2O$ to a hot aqueous solution of a 1 : 1 (pH = 1) mixture of calix[8]arene octasulfonic acid and $[Co(phen)_3]Cl_3$ resulted in the hydrated complex $[\{Co(phen)_3\} \cap \{$*p*-sulfonatocalix[8]arene$\} \cdot Yb_{0.33} \cdot Na \cdot 13H_2O]$ **I**, Scheme 1.

Single crystal X-ray analysis shows that **I** has an intricate structure, which is based on the $[\{Co(phen)_3\} \cap \{$*p*-sulfonatocalix[8]arene$\}]$ supermolecule. The crystals were of poor quality, leading to a very low number of 'observed' reflections (~30% of all data). This, and the refinement methods used account for the reasonably high *R* factors in the structure, although the gross atom–atom connectivities have been established.

The encapsulation of the spherical $[Co(phen)_3]^{3+}$ cation results in a disruption of the calixarene hydrogen bond network associated with the phenolic moieties, and the wrapping of the flexible host around the guest, Fig. 1. The calixarene adopts a novel conformation, which is distinctly different to that in previously reported structures of calix[8]arene clathrates and coordination polymers.[12,13] In the case of the 2D-polymer, the calixarene adopts the pleated loop conformation in which the phenolic oxygen atoms are essentially coplanar and are knitted together *via* hydrogen bonding. The calixarene in **I** is best described as a distorted version of the pleated loop conformation, with the phenolic hydrogen bond network breaking such that a C_2 symmetrical chalice is formed, Fig. 2. This conformation is unique to structures containing *p*-sulfonatocalix[8]arene, although a similar situation has been reported recently for a bismuth cluster complex of a *p-tert*-butylcalix[8]arene.[17] The upper, wider 'rim' of the chalice is delineated by the two pairs of aryl rings *a* and *b*, whose equatorial alignment resembles that of half a laterally positioned calix[4]arene (*pseudo* calix[4]arene), and which is reminiscent of the pleated loop arrangement in the 2D-calix[8]arene octasulfonate coordination polymer. Aryl rings *c* and *d* are rotated away from the plane containing rings *a* and *b*, which results in them assuming the conical 'walls' of the chalice. Interestingly, rings *c* and *d* are in a 1,2-alternate conformation, with the sulfonate group of ring *c* protruding across the lower rim of the cavity and forming a hydrogen bond with the phenolic oxygen atom of ring *d* from the second symmetry-related ring *c* and *d* pair (O22···O1 2.47 Å). The C_2 symmetry of the calixarene dictates an identical hydrogen bonding interaction with the other ring *c,d* pair, such that the lower-rim of the chalice is 'stitched' together through the two hydrogen bonding interactions. Hydrogen bonding interactions between phenolic units, which define the majority of calix[8]arene octasulfonate structures reported to date, are absent.

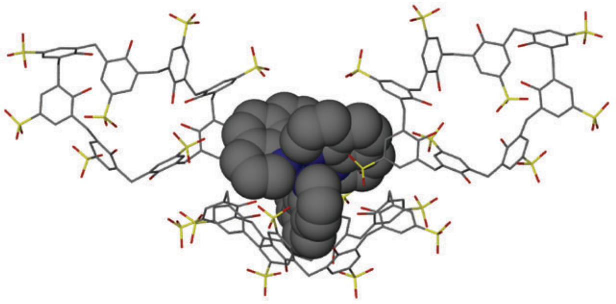

Fig. 1 Inclusion of $[Co(phen)_3]^{3+}$ within the *p*-sulfonatocalix[8]arene cavity and interactions with neighbouring calixarene molecules.

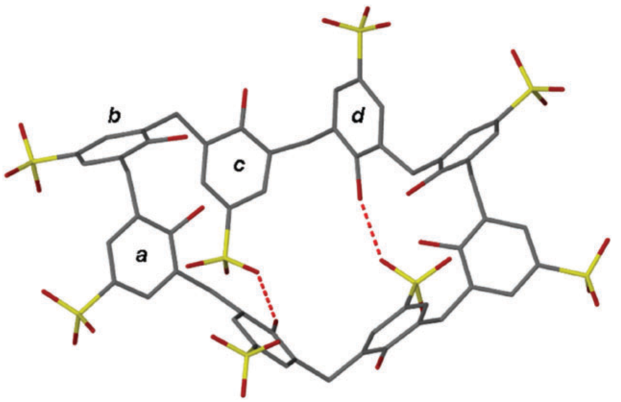

Fig. 2 The *p*-sulfonatocalix[8]arene molecule showing intramolecular hydrogen bonding (dotted lines). Rings *a*–*d* are as indicated in the text.

The $[Co(phen)_3]^{3+}$ guest cation is centrally located within the calixarene cavity, with the Co^{3+} centre being located on the two-fold axis which runs centrally through the calixarene cavity. The complex crystallizes in an achiral space group $R\bar{3}c$ and thus both guest enantiomers (Δ and Λ) are present in a 1 : 1 ratio. In the absence of intramolecular aryl host–guest $\pi \cdots \pi$ interactions, it appears that the guest is retained primarily through OH–π, and CH–π interactions. The former relates to the interplay of water in the cavity of *p*-sulfonatocalix[4]arene.[18] The hydroxyl groups of rings *a* and *b* are oriented towards the enshrouded phen ligand of the guest, which exhibits some disorder, with distances of 3.43 Å and 3.66 Å with the centroid of ring *c* to O3, and O4, respectively and an additional contact of 3.59 Å from the centroid of ring *d* to O4. The other phen rings of the guest are ordered, with a close contact between one of the protons of the methylene group connecting rings *a* and *b* to one of the 'pyridine' rings of the phenanthrolines (C–H···centroid 3.12 Å, C–H···centroid 133.1°).

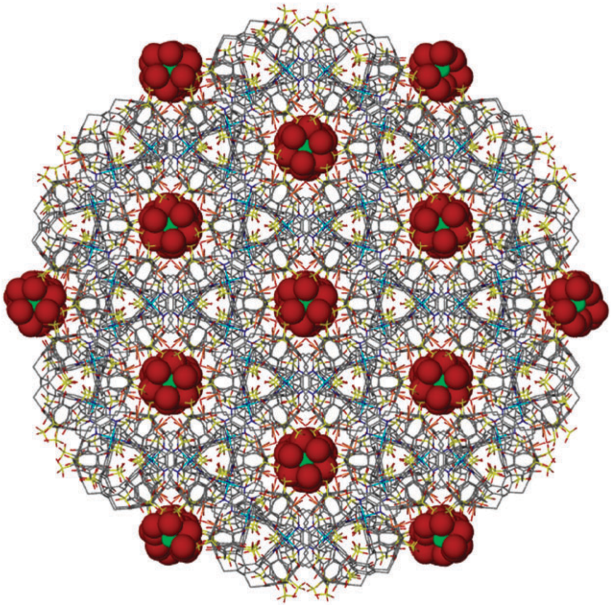

Fig. 3 A view of the supramolecular array down the *c* axis, showing the occupation of the channels by $[Yb(H_2O)_9]^{3+}$ ions (space filling).

Interplay of adjacent supermolecules

The chalice defined within the $[\{Co(phen)_3\} \cap \{$*p*-sulfonatocalix[8]arene$\}]$ supermolecule contains an upper rim delineated by the two lateral pairs of aryl rings *a* and *b*. These rings form clefts which are exterior to the calixarene chalice, and are each occupied by one of the phen ligands from the $[Co(phen)_3]^{3+}$ cation in an adjacent supermolecule. Therefore, two $[Co(phen)_3]^{3+}$ cations are associated externally to each supermolecule, and each of these have opposite chirality to that included within the supermolecule. The guest cations are held distant from each other through encapsulation by three calixarenes, with each calixarene behaving as a heterotritopic receptor for $[Co(phen)]^{3+}$, Fig. 1. Similar inclusion behavior is also observed in the two recently reported *p*-sulfonatocalix[8]arene arrays,[12,13] although in these cases the binding regions act independently of each other such that multiple guest molecules are associated with each calixarene. This contrasts with the inclusion of related $[Ni(phen)_3]^{2+}$ within *p*-sulfonatocalix[4]arene, in which adjacent cations interact strongly by π–π stacking interactions.[19] We attribute this association to a CH–π interaction (closest contact C–H···centroid ring *b* 3.78 Å) and an OH–π interaction from a sulfonate oxygen of ring *a* to the centroid of the phen 'benzene' ring. The distance (3.15 Å) and the positioning of the oxygen centre directly above the centroid are consistent with this, assuming that protonation of the oxygen centre occurs. This is expected on the basis of the low pH, and the need to address charge imbalance within the system.

The packing of the $[\{Co(phen)_3\} \cap \{$*p*-sulfonatocalix[8]arene$\}]$ supermolecules in **I** is complex, with the asymmetric unit being comprised of half a supermolecule, and ytterbium ions, sodium ions, and water molecules in the ratio 0.17 : 0.5 : 6.5. As mentioned previously,[11] the discrepancy in charge balance can be addressed through partial protonation of the calixarene sulfonates, or the presence of oxonium ions, which are not uncommon in supramolecular arrays involving *p*-sulfonatocalix[*n*]arenes.[11]

On first inspection the structure is comprised of a spectacular honeycomb lattice of parallel, tubular assemblies which propagate down the *c* axis, Fig. 3, with the centre of each tube being occupied by aquated Yb^{3+} ions. A projection of one of the tubules down the *b* axis reveals the presence of two distinct regions, one section containing the aquated Yb^{3+} ions and another which is devoid of these ions. This partitioning is commensurate with the low distribution level of the Yb^{3+} ions within the structure (0.17 per asymmetric unit), and is analogous to the recently reported zeolitic structure comprised of $[\{Co(diHOsar)\} \cap \{$*p*-sulfonatocalix[4]arene$\}]$ supermolecules (Yb···Yb distance 11.28 Å).[10] As in this former case, the residence of the lanthanide ions coincides with a narrowing in this part of the channel. The channel is irregular, with minimum and maximum diameters of approximately 4.55 and 10.2 Å, respectively. In addition to two aquated Yb^{3+} ions, the void is occupied with numerous disordered water molecules. No coordination of the Yb^{3+} ions with any of the sulfonate oxygen atoms occurs, however the $[Yb(H_2O)_9]^{3+}$ coordination sphere closes the channel through extensive hydrogen bonding to calixarene sulfonate, and phenolic groups. Each centre shows close contacts with six neighbouring calixarenes, with each calixarene bridging the two Yb^{3+} centres. Three of these calixarenes each form two hydrogen bonds to the $[Yb(H_2O)_9]^{3+}$ sphere, with both hydrogen bonds arising from one aquated oxygen donor and showing contacts to a sulfonate oxygen atom of ring *c* (O···O 2.72 Å), and the phenol of ring *d* (O···O 2.93 Å). The other three calixarenes each form one sulfonate hydrogen bond (O···O 2.75 Å), giving a total of nine hydrogen bonds per $[Yb(H_2O)_9]^{3+}$ sphere.

Channel structure

Moving along the *c* axis, the channel diverges to give a substantial, loosely-filled void containing disordered sodium ions and water molecules. The dimensions of this void are approximately 24 × 23 Å, and it is largely hydrophilic due to the calixarene sulfonate groups which point towards the interior. Closer inspection reveals large openings in the tubule walls, such that the internal space forms part of a large channel which propagates throughout the crystal lattice at an angle of 57.4° to the Yb^{3+} containing channel (*c* axis), Fig. 4(a). These openings are large enough (minimum diameter 12 Å) for possible ingress of gases, and globular guest species such as carboranes and fullerene C_{60}. Another, identical channel runs nearly orthogonal (86.2°) to the previous one and again at an angle of 57.4° from the *c* axis, giving the structure a 3D-network of interconnecting channels. These channels are lined predominantly with negatively charged sulfonate groups, and it is noteworthy that these channels are largely unfilled apart from water molecules. Two other smaller channels run orthogonally to the major channels, one of these being defined by rows of oppositely stacked (lower rim to lower rim) calixarene chalices, Fig. 4(b). The included $[Co(phen)_3]^{3+}$ cations predominate the structure of the second channel, which lies directly parallel to and above the first one.

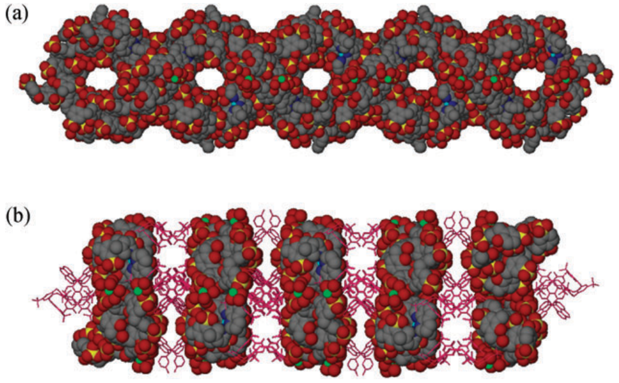

Fig. 4 A depiction of the major (**a**) and minor (**b**) channels within the structure. The surfaces of the minor channels are separated by supermolecules of **I** (depicted in wire frame).

Both channels are again partially occupied, containing disordered Na^+ ions and water molecules.

Helical arrangement of tubules

Another striking feature of the structure is the helical assembly of the *p*-sulfonatocalix[8]arenes which define each tubule. When isolated tubules are considered, containing only complete calixarene and guest molecules, the widest point of each tubule is defined by three calixarenes, whose lower-rims point directly into the hydrophilic void. Each of these calixarenes can be viewed as the backbone of a helix, whose adjacent members are generated by the interplay of two $[\{Co(phen)_3\} \cap \{p\text{-sulfonatocalix[8]arene}\}]$ supermolecules with the clefts created by aryl rings *a* and *b*. The helix propagates in each direction through the inclusion of further supermolecules within the external clefts, resulting in a spiraling of the calixarenes to form the outer surface of the tube, Fig. 5. The propagation of each helix in this fashion terminates every 71.1 Å, which corresponds to the length of the *c* axis, with further packing in this fashion extending the strand into adjacent tubules.

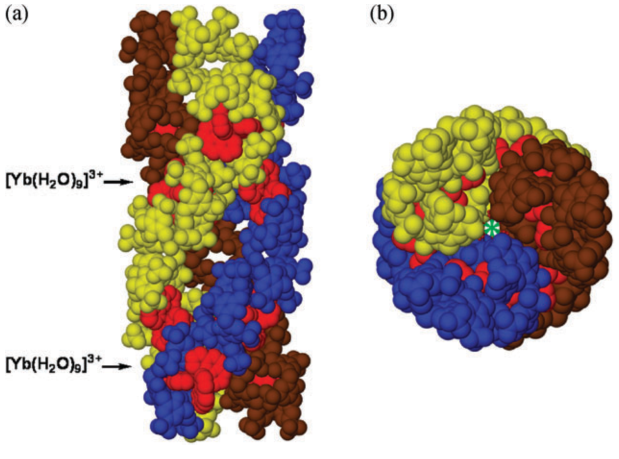

Fig. 5 A view of a tubule comprised of three individual calixarene helices. The helices are in shown in different colours, with the guests depicted in red. The wide and narrow regions in each tubule are highlighted in (**a**), with the arrows indicating the narrow regions containing the aquated Yb^{3+} ions (omitted for clarity). The view down the *c* axis shows the interplay of the helices (**b**).

Conclusions

We have established the structure of a complex system at a resolution sufficient for a detailed understanding of the interplay of the various components. In doing so we have demonstrated the feasibility of using the extended cavity of *p*-sulfonatocalix[8]arene to form a supramolecular array, based on the first example of inclusion of a classical coordination complex within the calixarene chalice. The preorganisation requirement of the calixarene in forming the complex results in the formation of large diameter, negatively charged channels within the crystal lattice. Exerting conformational control over the flexible *p*-sulfonatocalix[8]arene host molecule through inclusion complex formation highlights its remarkable versatility and exciting potential as a building block for new nanomaterials. We are currently undertaking investigations into assessing the degree of porosity[5] in this material.

Experimental

General procedures

Calix[8]arene octasulfonic acid[20] and $[Co(phen)_3]Cl_3 \cdot 7H_2O$[21] were synthesised according to literature procedures.

Synthesis of I

A hot solution of $YbCl_3 \cdot 6H_2O$ (13 mg, 3.35×10^{-5} mol) in water (0.5 cm^3) was added to a hot solution of $[Co(phen)_3]Cl_3 \cdot 7H_2O$ (5.6 mg, 6.71×10^{-6} mol) and calix[8]arene octasulfonic acid (10 mg, 6.71×10^{-6} mol) in water (2 cm^3). A cloudy and as yet ill-defined suspension immediately formed, and the hot mixture (pH ~1) was left to cool. In addition to the cloudy material, orange prismatic crystals of **I** formed on the surface of the solution after several days. Yield 4.0 mg, 25%. Microanalysis (CHN) was not feasible due to the highly hydrated nature of the complex.

X-Ray crystallography

The X-ray diffracted intensities were measured from single crystals at 153 K on a Bruker ASX CCD diffractometer with rotating anode using monochromatized Mo-Kα radiation (λ = 0.71073 Å.) Data were corrected for Lorentz and polarization effects and absorption correction applied using multiple symmetry equivalent reflections. The structure was solved using direct methods and refined on F^2 using the Bruker SHELXTL crystallographic package.[22] A full matrix least-squares refinement procedure was used, minimizing $w(F_o^2 - F_c^2)$, with $w = >\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. Agreement factors ($R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ and GOF $= \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ are cited, where *n* is the number of reflections and *p* the total number of parameters refined).

Crystal/refinement details for compound I. $C_{92}H_{90}CoN_6NaO_{45}S_8Yb_{0.33}$, M = 2395.78, $F(000)$ = 22 200 e, trigonal, $R\bar{3}c$, Z = 18, T = 153 K, a = 32.197(10), c = 71.112(14) Å, V = 63 842(18) Å^3; D_c = 1.122 g cm^{-3}; $\sin\theta/\lambda_{max}$ = 0.5723;

N(unique) = 10807 (merged from 47095, $R_{\text{int}} = 0.231$, $R_{\text{sig}} = 0.242$), N_o ($I > 2\sigma(I)$) = 3279; $R = 0.1801$, $wR2 = 0.4213$ (A,B = 0.2, 650.0), GOF = 1.178; $|\rho_{\max}| = 1.9(2)$ e Å^{-3}.

Compound **I** crystallizes in the trigonal space group $R\bar{3}c$, $Z = 18$ (hexagonal setting), comprising $[\text{Co(phen)}_3]^{3+}$ cations encapsulated within *p*-sulfonatocalix[8]arene molecules. Both are sited on a two-fold axis, with the aquated $[\text{Yb(H}_2\text{O)}_9]^{3+}$ ion located on a three-fold axis, one Na^+ ion with disordered water molecules, and a number of crystalline water molecules, mainly disordered at general positions in the asymmetric unit. One of the phen-ligands of the $[\text{Co(phen)}_3]^{3+}$ cation is disordered (50 : 50 ratio) around a 2-fold symmetry axis. One of the *p*-sulfonatophenyl groups of the calix[8]arene is disordered over two positions, and this could be related with symmetry breaking, which is not unusual for macromolecular complexes in its crystalline state. H-atom positions, where possible, were calculated from geometrical considerations and were constrained during refinement to the appropriate positional and thermal parameters of bonded atoms.

The crystals were of poor quality, leading to a very low number of 'observed' reflections (∼30% of all data). This dictated applying anisotropic displacement parameters for the metal atoms and non-disordered molecular fragments. The disordered non-hydrogen atoms were refined isotropically and hydrogen atom parameters were constrained to the bonded atoms during the refinement. These refinement conditions account for the reasonably high R factors in the structure. Attempts to refine all non-hydrogen atoms anisotropically resulted in unrealistic displacement parameters, due to the low reflection/parameter ratio.

CCDC reference number 298640. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604513h

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