DALTON
FULL PAPER

Dihydroxybenzoquinone and chloranilic acid derivatives of rare earth metals†

Brendan F. Abrahams, Joseph Coleiro, Karen Ha, Bernard F. Hoskins, Simon D. Orchard and Richard Robson*

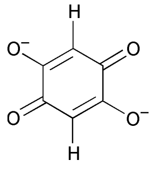
School of Chemistry, University of Melbourne, Victoria 3010, Australia

Received 11th October 2001, Accepted 29th January 2002
First published as an Advance Article on the web 15th March 2002

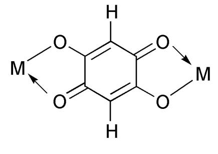
The crystal structures of lanthanide complexes involving the dianions of dihydroxybenzoquinone (H_2dhbq) or chloranilic acid (H_2can) are presented. The complexes, $Ln_2dhbq_3\cdot 24H_2O$ (Ln = Y, La, Ce, Gd, Yb and Lu) are 2-D coordination polymers with metal centres linked by $dhbq^{2-}$ ligands. Each of these species contain a $Ln_2(H_2O)_{18}$ pentagonal dodecahedral cage. Despite the variation in the radii of lanthanide ions this series is isostructural. In contrast, the hydrated structures of Ln_2can_3 (Ln = Sc, Y, La, Pr, Nd, Gd, Tb, Yb and Lu) show considerable structural variation. The crystal structures of the diamond-like networks $Ycan_2^-$ and $Thcan_2$ are also presented.

Introduction

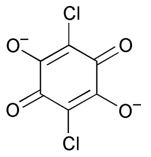
The construction of extended coordination frameworks formed by linking rod-like or slab-like ligands with metal centres is an area receiving considerable attention.[1] Out of this work has arisen a diverse range of structures of varied topology. Many of these have used non-chelating ligands to link metal centres into a polymeric network, however a common problem encountered with such structures is that the single crystal character is lost upon solvent removal from channels within the network. In an attempt to produce more stable networks we have been exploring the use of bridging ligands that can chelate at two ends. Although there are many examples in the literature[2–6] of the use of chelating-bridging ligands to form a variety of polymers, our original goal was the formation of diamond-like networks. In such a structure we envisaged an eight coordinate metal linked to four others by four bridging chelating ligands.



A



B



C

Our original investigations into this area focused on the use of the dianion of dihydroxybenzoquinone ($dhbq^{2-}$) (A) which has the potential to bridge and chelate metal centres (B). In order to attain electrical neutrality in a diamond net, a +4 ion was required and it was anticipated that the ceric ion would be a good candidate as its ability to bind to four chelating catecholate ions had already been demonstrated.[7] In 1996 we reported the results of a reaction between a ceric salt and dihydroxybenzoquinone in aqueous solution. X-Ray analysis of the resulting crystalline product showed that the ceric ion had been reduced to the cerous (+3) ion.[8] The compound which had the formula: $Ce_2(dhbq)_3\cdot 24H_2O$ may also be prepared directly from the cerous ion. The structure is a 2-D coordination polymer with each cerous ion linking to three other cerous ions through chelating dhbq ligands (Fig. 1). Three water molecules complete a nine-coordinate, tri-capped trigonal prismatic coordination environment around the cerous ion. The topology of the coordination network is 6,3 meaning that 3-connecting centres link to form six-membered rings in this two-dimensional network. The structure shares this topology with graphite although unlike graphite the network is undulating with the six-membered rings adopting a cyclohexane, chair-like conformation. While the 2-D structure is not surprising the hydrogen bonding within the crystal led to an unexpected and novel structural feature. Lattice water molecules, hydrogen bond to the coordinated water molecules of a pair of symmetry related cerous ions from different sheets resulting in the formation of a pentagonal dodecahedral $Ce_2(H_2O)_{18}$ cage. The cage passes through a hexagonal hole of a $[Ce_2dhbq_3]_n$ sheet that lies half way between the two cerous ions of the pentagonal dodecahedron (Fig. 2). The twelve water molecules in the central "equatorial belt" of each $Ce_2(H_2O)_{18}$ cage are hydrogen

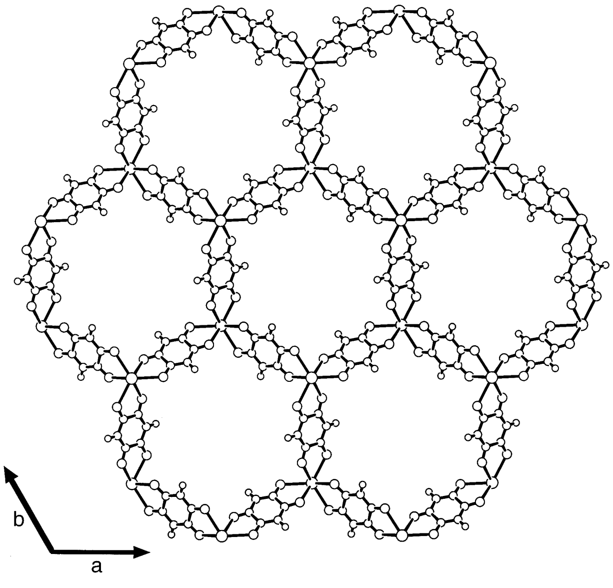


Fig. 1 The two-dimensional sheet structure of $Ce_2dhbq_3\cdot 24H_2O$.

---

† Electronic supplementary information (ESI) available: views of $La_2can_3\cdot 13H_2O$ and $Lu_2can_3\cdot\approx 12H_2O$. See http://www.rsc.org/suppdata/dt/b1/b109296k/

DOI: 10.1039/b109296k

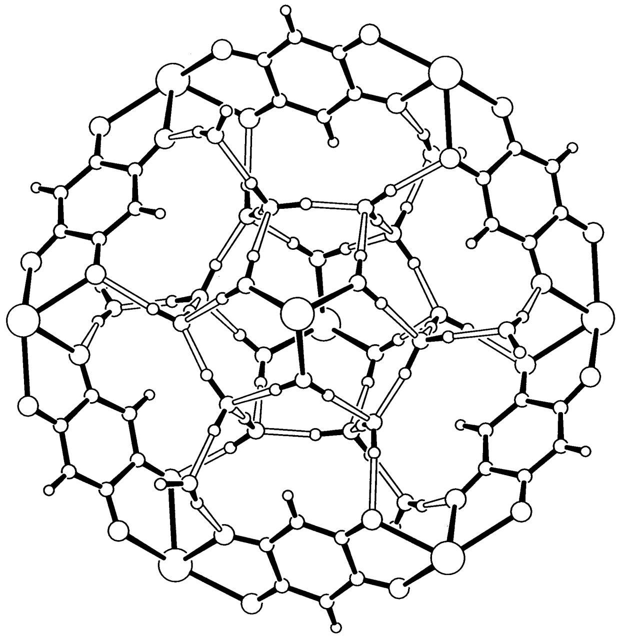


Fig. 2 The $Ce_2(H_2O)_{18}$ cage and the encompassing Ce_6dhbq_6 ring to which it is hydrogen bonded.

bonded, either directly or *via* six other intermediary lattice water molecules, to the dhbq atoms of the encompassing $Ce_6(dhbq)_6$ ring through which the cage passes.

An interesting topological feature of this structure is that if the pair of cerous atoms belonging to each cage is considered as linked then the structure has the connectivity of two interpenetrating diamond networks (Fig. 3).

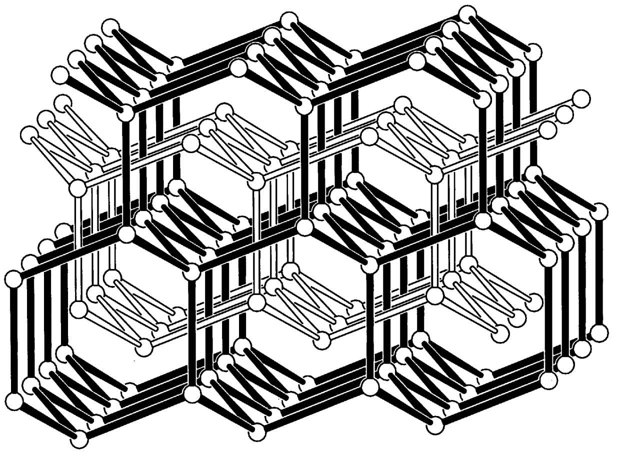


Fig. 3 The connections between Ce atoms in $Ce_2dhbq_3{\cdot}24H_2O$. "Filled bonds" belong to one diamond-like network while "open bonds" belong to a second interpenetrating network. All vertical connections represent hydrogen-bonded $(H_2O)_{18}$ links, while all other connections represent $dhbq^{2-}$ links.

In this present work we have extended our investigations by fully characterizing dihydroxybenzoquinone complexes of other lanthanide elements. In order to gauge the effect of substitution on the quinone ring, structural studies of lanthanide complexes of the chloranilate ion (can, C) have also been undertaken and have provided very different outcomes to the studies involving dhbq. The structural results are reported here.

We also report achievement of the original goal of this work—the synthesis of a diamond related network using bridging-chelating ligands.

Table 1 Cell volume for crystals of the type: $Ln_2dhbq_3{\cdot}24H_2O$ and associated nine-coordinate metal ionic radii[a]

Ln	Ionic radii (Ln^{3+})/Å	Cell volume/Å^3
La	1.356	3289(2)
Ce	1.336	3254(2)
Gd	1.247	3162.7(7)
Y	1.215	3120.6(12)
Yb	1.182	3087.1(4)
Lu	1.172	3074.2(4)

[a] From ref. 19.

Results and discussion

Full crystal structure analysis of compounds of the type $M_2dhbq_3{\cdot}24H_2O$ (M = La, Gd, Y, Yb and Lu) show these compounds to be isostructural with the cerous analogue. The metals selected span the full range of ionic radii found for lanthanides including the pseudo-lanthanides, yttrium and lanthanum. The persistence of the nine-coordinate tri-capped trigonal prismatic geometry (Fig. 4a) and indeed the gross structural features, despite the lanthanide contraction, is remarkable and strongly suggests that the hydrogen bonding within the crystal plays a major stabilizing role.

The effect of the lanthanide contraction within this series is reflected in cell dimensions (Table 1). Not surprisingly the cell volumes show an expected correlation with the radius of the ion (nine-coordinate ionic radius). The diameter of the cyclohexane-type M_6dhbq_6 ring is also strongly dependent upon the size of the lanthanide ion. For small lanthanides this has the effect of constricting the $M_2(H_2O)_{18}$ cage to a greater extent around the equatorial plane.

Earlier it was recognized[8] that the $Ce_2(H_2O)_{18}$ pentagonal dodecahedral cage resembled the $(H_2O)_{20}$ cage found in some gas hydrates. The $(H_2O)_{20}$ cages are capable of encapsulating a range of species such as noble gas atoms, O_2, N_2, Cl_2 and H_2S. Although there is an obvious geometrical similarity, the substitution of two water molecules with the lanthanide ions at the "poles" of the cage brings the now coordinated water molecules closer together than the corresponding molecules in the $(H_2O)_{20}$ cage. This has the effect of reducing the size of the cage void relative to the $(H_2O)_{20}$ case (see Fig. 5). The van der Waals void volumes (calculated using the PLATON[9] program) ranged from 38 Å^3 (Lu) to 44 Å^3 (La) compared to a volume of 64 Å^3 found for the pentagonal dodecahedron found in the double hydrate of tetrahydrofuran and hydrogen sulfide.[10] Given the reduced cage size one may expect greater difficulty in incorporating guest molecules into the cage compared with the so-called gas hydrates, nevertheless on the basis of the calculation it would not be surprising if monoatomic and small diatomic molecules could be included. Preliminary attempts have failed to incorporate a guest into the cage.

The existence of this isostructural series prompted an examination of lanthanide complexes with the closely related chloranilate ligand (C). Prior to this investigation the crystal structures of $Y_2can_3{\cdot}12H_2O$[3] and $Pr_2can_3{\cdot}8CH_3CH_2OH$[4] had already been reported. In both cases a two-dimensional polymer with 6,3 topology is formed with ethanol or water molecules completing a nine-coordinate geometry about the metal centre. In contrast to the dhbq analogues, no metal–solvent cages are found. EXAFS studies of hydrated Pr(III), Nd(III), Tb(III) and Er(III) chloranilates indicated a variable number of coordinated water molecules, however, these samples had been dried under vacuum prior to examination.[11]

Crystalline samples of a number of lanthanide chloranilate complexes including scandium, yttrium and lanthanum chloranilates were prepared by mixing an aqueous solution of the metal nitrate with an aqueous solution of chloranilic acid. The metal to ligand mole ratio was 2 : 3. From each

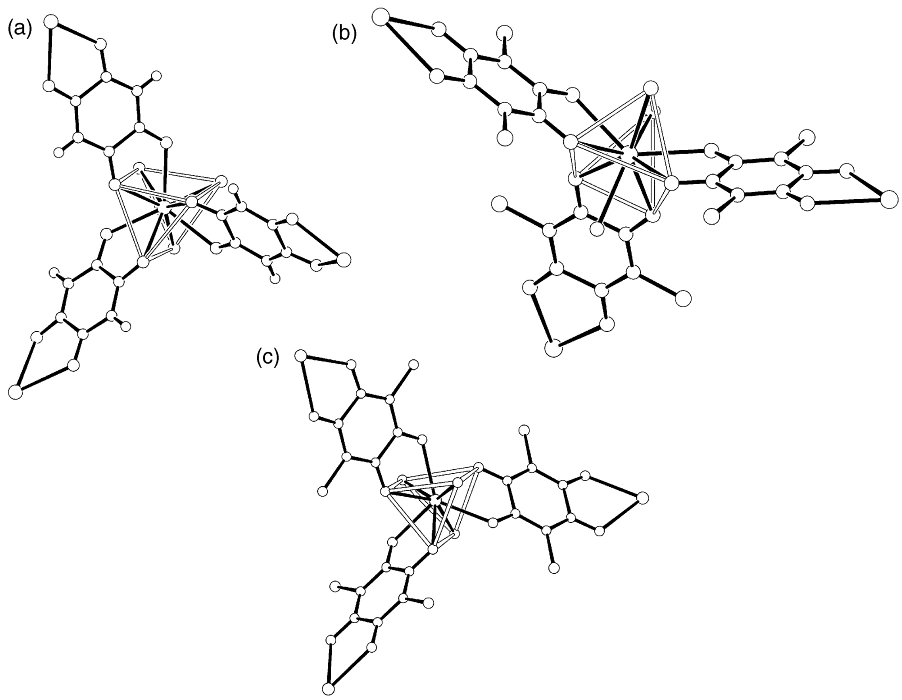


Fig. 4 The tri-capped trigonal prismatic metal coordination environments in (a) $Ce_2dhbq_3{\cdot}24H_2O$, (b) $Ce_2can_3{\cdot}{\approx}18H_2O$ ($P\bar{1}$) and (c) $Y_2can_3{\cdot}{\approx}16H_2O$.

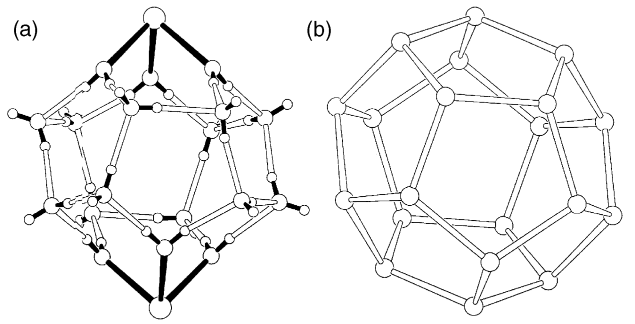


Fig. 5 (a) The hydrogen bonded pentagonal dodecahedral cage found in $La_2(H_2O)_{18}$. (b) The cage in gas hydrate structures.

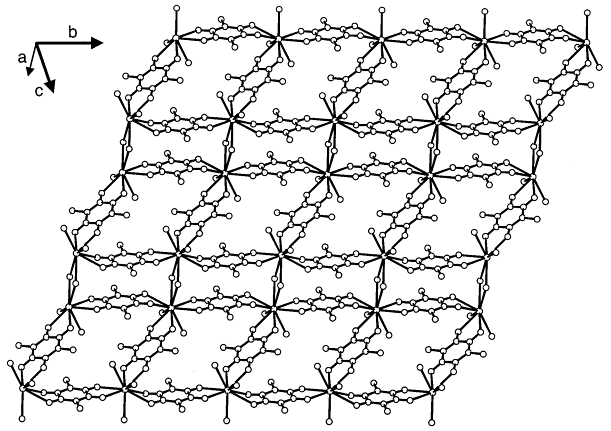


Fig. 6 The sheet structure of $La_2can_3{\cdot}13H_2O$.

solution dark crystals were obtained, all with the general formula $M_2can_3{\cdot}xH_2O$ (M = Sc, Y, La, Ce, Pr, Nd, Eu, Gd, Tb, Yb and Lu). According to either full crystal structure determinations or cell dimensions the crystalline materials may be divided into four structural types. Each structural type is discussed below.

Type I — $La_2can_3{\cdot}13H_2O$ — ten coordinate metal

In this structure a ten-coordinate lanthanum centre links to four other equivalent lanthanum centres through either a pair of bridging water molecules or one of three chloranilate ions. Two terminal water molecules complete the coordination environment on each lanthanum. The resulting network is a 2-D coordination polymer as shown in Fig. 6. The sheet structure which extends in the *b–c* plane has the same topology as the square grid net with lanthanide centres acting as the 4-connecting centres. Two types of four-membered rings are observed in the sheet; a La_4can_4 and a $La_4can_2[(H_2O)_2]_2$ ring.

Linear chains of lanthanum atoms linked by chloranilate dianions extend in the *b*-direction. Somewhat surprisingly the plane of these chloranilate ligands is inclined relative to the *b*-axis. This leads to the lanthanum atom at one end of the chloranilate lying out of the mean plane of the bridging ligand. This deviation allows close contact between chloranilate ligands of the $La_4can_2[(H_2O)_2]_2$ rings with C ··· C contacts of 3.35 Å and C ··· Cl contacts of 3.50 Å. These contacts are indicated in a diagram included in the ESI.†

Type II — 6,3 nets — nine-coordinate metal

As in the dihydroxybenzoquinone complexes a 2-D coordination network with the 6,3 topology is formed but unlike the dhbq complexes no water cages are present. The 6,3 nets may be divided into three sub-classes (IIa, IIb and IIc) which differ in regard to the coordination environment of the metal and the orientation of the chloranilates relative to the plane of the polymeric sheet.

Type IIa — $Ln_2can_3{\cdot}{\approx}18H_2O$ (Ln = Ce, Pr, Nd, Tb). Full crystal structure analyses were performed on Ce, Pr and Tb products. Data were measured on crystals exposed to the atmosphere. These crystals were triclinic and on the basis of cell dimensions $Nd_2can_3{\cdot}{\approx}18H_2O$ was identified as a member of this isostructural series.

The coordination geometry may be best described as a nine-coordinate tri-capped trigonal prism with water molecules occupying one position on each trigonal face and capping a

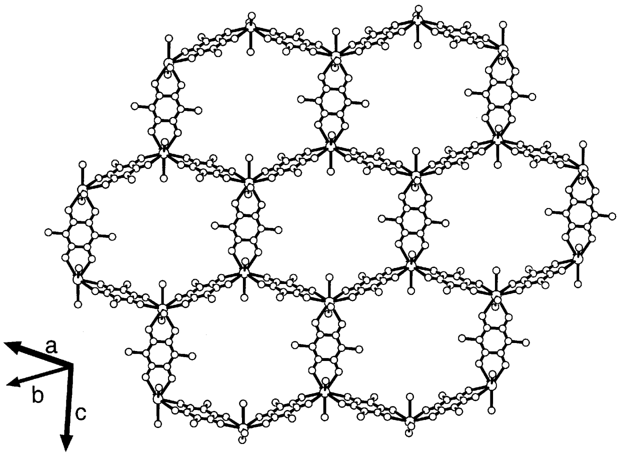


Fig. 7 The sheet structure of $Pr_2can_3 \cdot \approx 18H_2O$.

rectangular face (Fig. 4b). As can be seen in Fig. 7, each six-membered Ln_6can_6 ring is comprised of two "face-on" and four "edge-on" ligands relative to the reader. The sheets stack in the [1 −1 1] direction with ordered and disordered water molecules filling the voids within the crystal.

In the case of the cerium product a data collection was also performed with the crystal protected against water loss by placing it in a Lindeman glass capillary tube containing a small amount of mother liquor. The protected crystal is monoclinic with space group *C*2/*m*, in contrast to the crystal exposed to air which was triclinic. There is a similarity between the reduced cell of the *C*-centred form and the exposed triclinic crystal although the cell volume is almost 28 Å^3 less in the triclinic crystal. This is consistent with the loss of a small amount of water of solvation on exposure to the air but with retention of the single crystal character. Structural analysis of the monoclinic form shows a similar sheet structure (Fig. 8) but with mirror symmetry perpendicular to the plane of the coordination polymer.

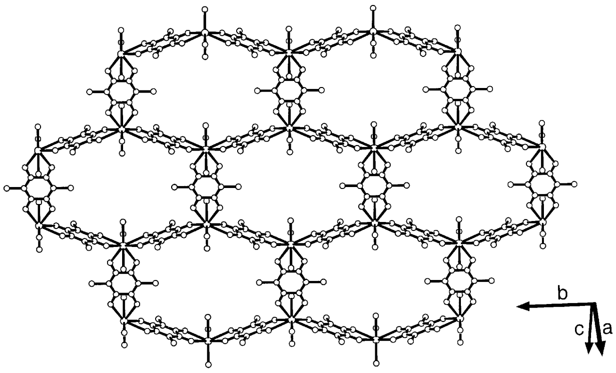


Fig. 8 The monoclinic sheet structure of $Ce_2can_3 \cdot \approx 18H_2O$.

Type IIb — $Ln_2can_3 \cdot \approx 16H_2O$ (Ln = Y, Gd, Eu) — nine-coordinate. Full crystal structure analyses were performed on Gd and Y products. On the basis of cell dimensions $Eu_2can_3 \cdot \approx 16H_2O$ was identified as a member of this isostructural series.

These structures are similar to the type IIa class with nine-coordinate metal centres linked together through bridging chloranilate ligands to give the two-dimensional sheet structure. As can be seen in Fig. 9 the major structural difference is related to the orientation of the chloranilate ligands relative to this sheet. In this class each six-membered Ln_6can_6 ring comprises four "face-on" and two "edge-on" bridging units. The nine-coordinate metal again gives rise to a tri-capped trigonal prism geometry but with coordinated water molecules occupying three of the vertices of the trigonal prism although not all on the one face (Fig. 4c). Once again ordered and disordered solvent water molecules occupy voids within the crystal structure.

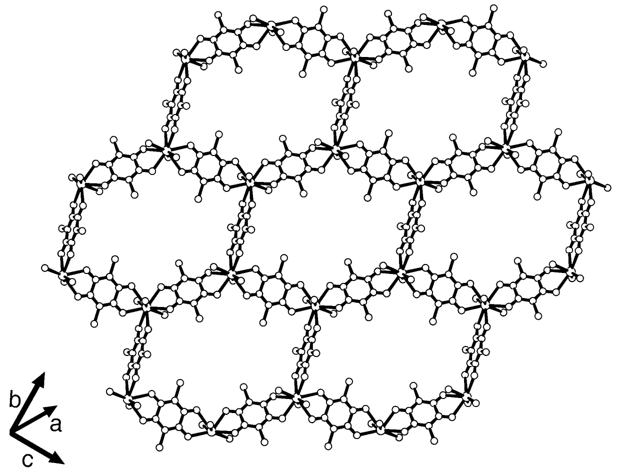


Fig. 9 The sheet structure of $Y_2can_3 \cdot \approx 16H_2O$.

The structural differences between type IIa and type IIb structures do not appear to be solely related to the size of the ion. It may be argued that the larger lanthanides that form the 2-D hexagonal sheet are more likely to form type IIa structures but this fails to explain why Tb falls into class IIa while the larger Gd ion gives rise to a type IIb structure. It thus seems likely that very subtle influences determine whether the hexagonal net is a type IIa or type IIb structure.

Type IIc — $Y_2can_3 \cdot 12H_2O$ — nine-coordinate. The type IIb structure provides an interesting contrast to the original $Y_2can_3 \cdot 12H_2O$ reported by Robl[3] which we have classified as type IIc. Although the nine-coordinate yttrium centre and 6,3 topology are shared by both structures the shape of the "hexagonal holes" is quite different (Fig. 10a). Robl's crystals were grown in aqueous silica gel whereas our crystals were from an aqueous solution. It seems likely that the reduced availability of water in the silica gel gives a less hydrated crystal with smaller hexagonal holes. It is also worth noting that Robl's yttrium structure bears a resemblance to the structure of $Pr_2can_3 \cdot 8CH_3CH_2OH$[4] (Fig. 10b) which suggests that restricting the access to water during crystal growth leads to compression of the network structure.

Type III — $Ln_2can_3 \cdot \approx 12H_2O$ (Ln = Yb, Lu) — eight-coordinate

Although cell dimensions and space group symmetry indicated that the Yb and Lu products were isostructural, data sets were collected on both materials. Unfortunately, problems relating to large ripples of electron density on ytterbium metal centres could not be treated satisfactorily and as a consequence the full crystal structure determination is not reported here. The refinement that was performed on the Yb structure left no doubt that the structure was the same as the Lu structure which is reported in detail.

The type III structures represent a departure from the 2-D coordination polymers characteristic of the earlier structural types. In this structure a $Lncan_2(H_2O)_4$ monoanion is the counterion for a 1-D polymeric cationic chain of formula $Lncan(H_2O)_4$. In the discrete anion and the polymeric cation the metal centre is in a remarkably similar eight-coordinate environment. The metal centres each lie on a mirror plane (parallel to the *a*–*c* plane) along with coordinated water molecules. In the case of the cation, one coordinated water molecule is disordered across the mirror plane. In both the anion and the cation the metal is coordinated to two chloranilates related to each other by mirror symmetry but in the /anion, the chloranilate ligands are non-bridging.

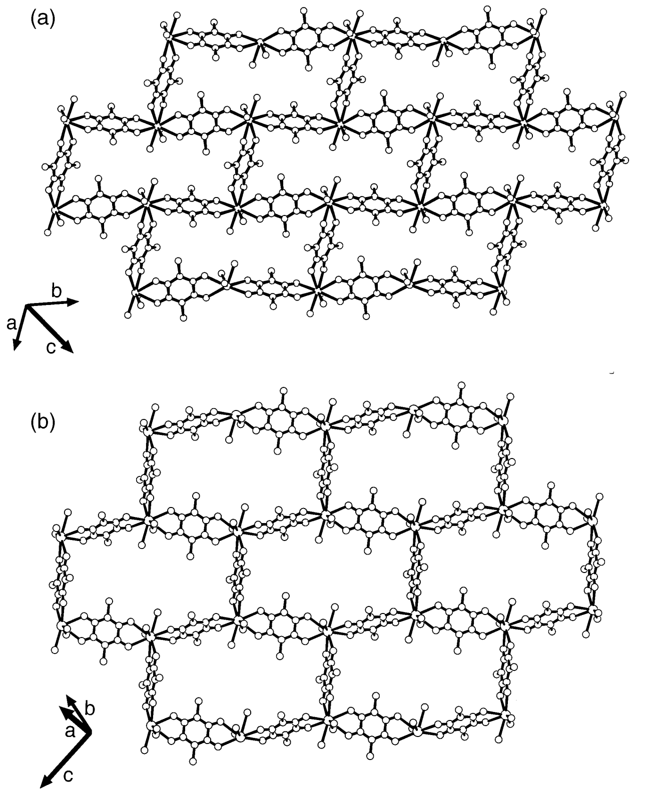


Fig. 10 (a) The sheet structure of $Y_2can_3·12H_2O$ reported by Robl.[3] (b) The sheet structure of $Pr_2can_3·8CH_3CH_2OH$ reported by Raymond and co-workers.[4]

The anions lie with terminal anionic ligands essentially parallel to the *a–b* plane (Fig. 11a). Hydrogen bonding involving water molecules yields a sheet-like structure that extends in the *a–b* plane. The cationic chain polymer is involved in a hydrogen bonded sheet parallel to the anionic sheets (Fig. 11b). There are twice as many metal centres in the cationic sheets as in the anionic sheets and as a consequence there are two anion sheets for every cation sheet. The anion sheets (An) and the cation sheets (Cat) stack in a –An–An–Cat–An–An–Cat–An–An–Cat– sequence along the *c*-direction. A colour representation of the sheets and the stacking is supplied in the ESI.† While cation sheets are related to each other by a pure translation in the *c*-direction, neighbouring anion sheets are centrosymmetrically related.

Type IV — $Sc_2can_3·16H_2O$ — seven-coordinate

Like the type III structures this compound features both terminal and bridging chloranilates, however this time they are part of a discrete bimetallic neutral molecule (Fig. 12). The coordination geometry of the scandium atom is best described as a pentagonal bipyramid with water molecules occupying the axial positions. Despite the difference in coordination number the coordination environment of the scandium is similar to that observed for the eight-coordinate Yb and Lu structures. The difference between the two geometries is that instead of the metal ion lying in a plane of four water molecules with chelating chloranilates on either side, the scandium only shares a plane with three water molecules.

Structural inter-relationships

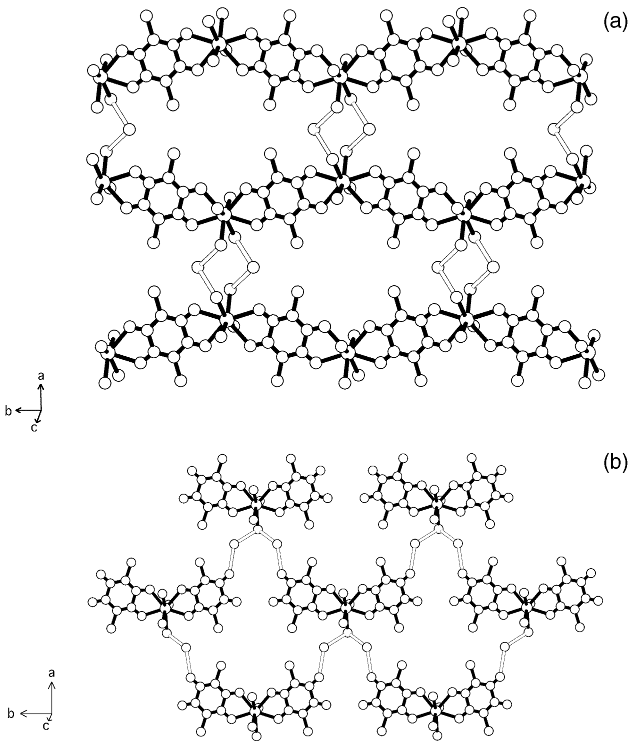


Fig. 11 (a) The hydrogen bonded sheet structure of the anion layer in $Lu_2can_3·{\approx}12H_2O$. (b) The hydrogen bonded sheet structure of the cation layer in $Lu_2can_3·{\approx}12H_2O$. "Unfilled" bonds represent hydrogen bonds.

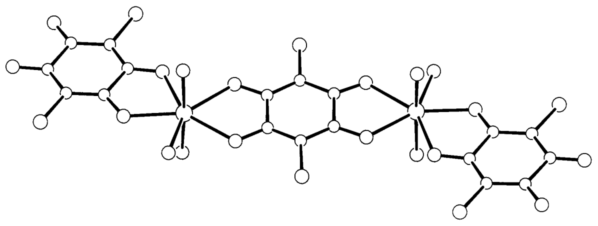


Fig. 12 The bimetallic structure of $Sc_2can_3·{\approx}13H_2O$.

To a large extent the variation in structural types may be attributed to the size of the metal ion. Thus we see the ten-coordinate lanthanum giving rise to the 4-connecting sheet structure, the nine-coordinate metals in the hexagonal sheets, the eight-coordinate Yb and Lu atoms in the anion–cation structures and the seven-coordinate scandium in the bimetallic molecule as the radius of the +3 cation is reduced. An interesting aspect of this trend towards lower coordination numbers is that the number of coordinated water molecules is always at least 3. It does seem surprising to us that in cases where the coordination number drops below nine, water molecules are in some instances able to compete more effectively for coordination sites than the second binding site on the dianionic ligands. This perhaps reflects a strong contribution from the orthoquinone canonical form that is also apparent in a hydrated ferric chloranilate complex.[12]

The structural variation apparent with the hydrated lanthanide chloranilates provides a stark contrast with the isostructural dihydroxybenzoquinone derivatives. The persistence of the nine-coordinate geometry from lanthanum to lutetium (including Y) is truly remarkable and reflects the stability imparted by the hydrogen bonding interactions of the water cage. The absence of the water cage in the chloranilate structure is attributed to the chlorine atoms that would protrude into potential hexagonal holes and thus block any possible formation of a water cage.

Diamond networks

Our original interest in the lanthanide dhihroxybenzoquinone and chloranilic acid derivatives was sparked by the attempt to synthesise a neutral diamond network involving ligands that chelate at each end. There are examples of 4-connected coordination polymers with oxalates as bridging units formulated as $M(C_2O_4)_2H\cdot3H_2O$ (M = Er, Y) that have a two-dimensional square-grid structure.[5] Other 4-connected coordination polymers also based on oxalates,[6] we have noticed, have the quartz (6^48^2b) topology. Given these examples, a diamondoid network constructed from bridging ligands which chelate at *each* end seemed to us to be an important structural target in the rapidly growing field of coordination polymers. This prompted us to further explore coordination polymers based upon the aforementioned dianions, can^{2-} and $dhbq^{2-}$.

As indicated earlier we had hoped to use a +4 ion to act as an eight-coordinate 4-connecting node with metals ions linked by the bridging ligands. An alternative approach to the neutral diamond net is an anionic coordination polymer with +3 lanthanide ions serving as topological 4-connectors. The aforementioned work provides an indication that water molecules may be expected to offer strong competition for coordination sites on lanthanide metal ions in any attempt to form a diamond network. For this reason it seemed sensible to employ a synthetic approach involving non-aqueous solvents. Yttrium(III) was selected as the potentially 4-connecting metal centre because of its ability to readily achieve eight-coordination. The reaction between $Y(NO_3)_3\cdot6H_2O$ and chloranilic acid in a 1 : 2 proportion in the presence of base (triethylamine) gave rise to an anionic polymer with the required composition of $Ycan_2^-$. Single crystal X-ray structural analysis confirmed the formation of a diamond-related net. Each yttrium centre lies on a $\bar{4}$ position and is coordinated by four crystallographically equivalent chelating ligands which link to equivalent yttrium centres at the corners of a tetrahedron, elongated along a two-fold axis (Fig. 13). Each ligand lies on a centre of symmetry. The coordination of the chloranilate is slightly asymmetric with Y–O bond distances of 2.306(7) and 2.396(6) Å. The Y ⋯ Y separation along a bridging ligand is 8.5911(8) Å. The two unique Y ⋯ Y ⋯ Y angles are 84.728(11)° (between yttrium atoms related by the two-fold axis which in Fig. 13 is vertical) and 123.089(6)°. The extended structure is represented in Fig. 14a and the underlying diamond connectivity of the structure can be seen in Fig. 14b.

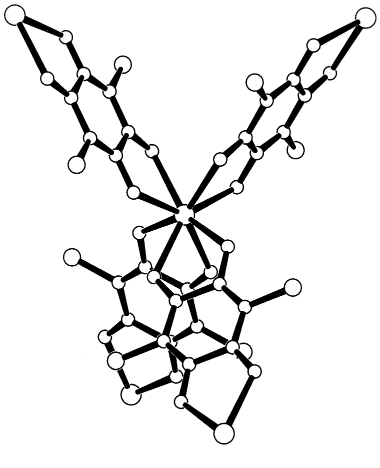


Fig. 13 The coordination environment of the yttrium atom in the $Ycan_2^-$ network. The chloranilate bridges extend to yttrium atoms that lie at the vertices of a tetrahedron that has been elongated along a vertical two-fold axis.

Although it was not possible to unambiguously identify the cation in this crystal, it is clear from microanalysis and an infrared spectrum that the cation is not the anticipated triethylammonium ion. We tentatively propose that the cation is the hydronium ion (H_3O^+). This assignment is supported by a neutron diffraction study of a 2-D yttrium oxalate network $[Y(C_2O_4)_2^-]$ that clearly showed the diaquahydronium ion within the crystal.[13]

A preliminary report of this compound appeared in a Dalton Perspective[14] in 2000 and to the best of our knowledge this compound represents the first structure with the diamond topology constructed solely from ligands that chelate at each end. Its formation encouraged us to re-explore the possibility of forming neutral networks with the diamond topology. For this reason we turned our attention to the non-redox active +4 thorium ion to avoid the problems encountered with the ceric ion. We recognised that thorium readily achieves coordination numbers in excess of eight however it seemed likely in aqueous solution that extra coordination sites could be occupied by water molecules as they are for the lanthanide series.

The reaction of hydrated thorium nitrate with chloranilic acid in a 1 : 2 proportion in aqueous solution yields crystals of composition $Thcan_2\cdot6H_2O$. Single crystal X-ray structural analysis indicated that the thorium ion was coordinated by four chelating ligands each bridging to a crystallographically identical thorium ion. The coordination sphere of the ion was completed by two water molecules to give a ten-coordinate thorium ion (Fig. 15a). Interestingly the immediate coordination environment bears a resemblance to that of the lanthanum ion in $La_2can_3\cdot13H_2O$ (Fig. 15b).

From a topological perspective each Th centre serves as a 4-connecting centre in a diamondoid network. An adamantane-type unit in this structure is shown in Fig. 16a and may be compared with the adamantane-type unit present in diamond (Fig. 16b). The gross geometrical distortion of the network from the ideal diamond net may be attributed to the ten-coordinate geometry making it impossible for the metal ion to serve as a tetrahedral 4-connector. In fact given the very irregular 4-connecting geometry it is perhaps surprising that a diamond network is formed at all.

Conclusion

Although there are some obvious geometrical differences one cannot help but be struck by the topological similarities of lanthanide chloranilates and carbon allotropes. Both carbon and lanthanide chloranilates form a structure based on 6,3 nets and anionic lanthanum chloranilates can form a diamond network. Extrapolating these results one may imagine through the use of appropriate molecular templates that lanthanide chloranilates may yield discrete molecular cages as carbon does with Buckminster fullerenes. The geometry of the cage formed will be determined to a large extent by the angle at the 3-connecting centre. In the case of the hydrated dhbq and can structures the Ln ⋯ Ln ⋯ Ln angle is determined by the sites occupied by the water molecules on the nine-coordinate metal. If water molecules occupy a trigonal face of the tri-capped trigonal prism as in the $Ln_2dhbq_3\cdot24H_2O$ series then an Ln ⋯ Ln ⋯ Ln angle of ≈107° is obtained. This angle matches closely the angle of 108° required for the 3-connecting centres in the beautifully symmetrical pentagonal dodecahedron. Such a molecule would have the formula $Ln_{20}L_{30}(H_2O)_{60}$ (L = can or dhbq). Occupation of alternative sites by the water molecules would lead to a larger angle leading to a larger cage, perhaps even analogous to C_{60} itself.

Experimental

The synthesis of the isostructural series: $Ln_2dhbq_3\cdot24H_2O$ (Ln = Y, La, Gd, Yb, Lu) followed the method employed for the cerous complex.[8] Analysis for the cerium complex on a dried sample: Calc. for $Ce_2dhbq_3\cdot22H_2O$ ($C_{18}H_{50}Ce_2O_{34}$): C, 19.8; H, 4.6. Found:[8] C, 19.8; H, 4.5%.

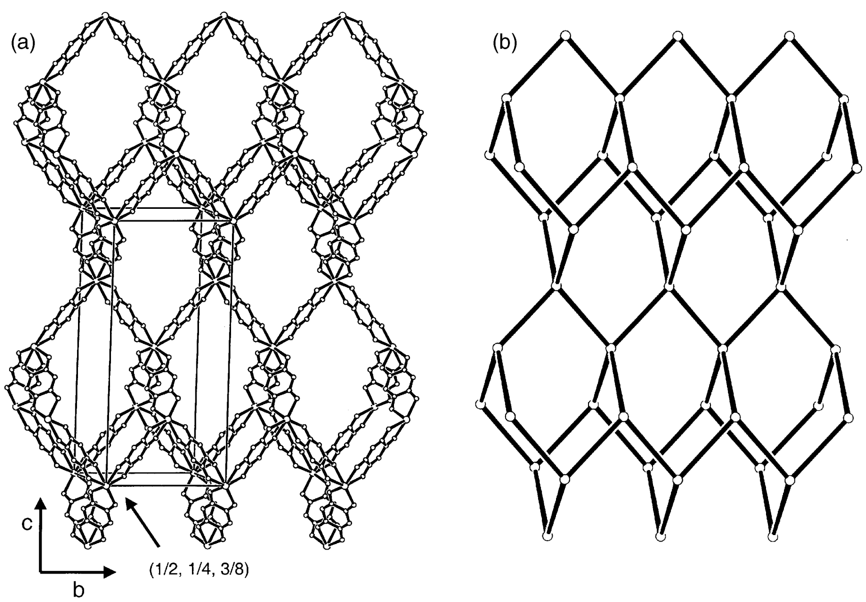


Fig. 14 (a) The extended structure of the $Ycan_2^-$ network. Chlorine atoms have been omitted for clarity. A unit cell is indicated. (b) The underlying diamond-like connectivity of the $Ycan_2^-$ network.

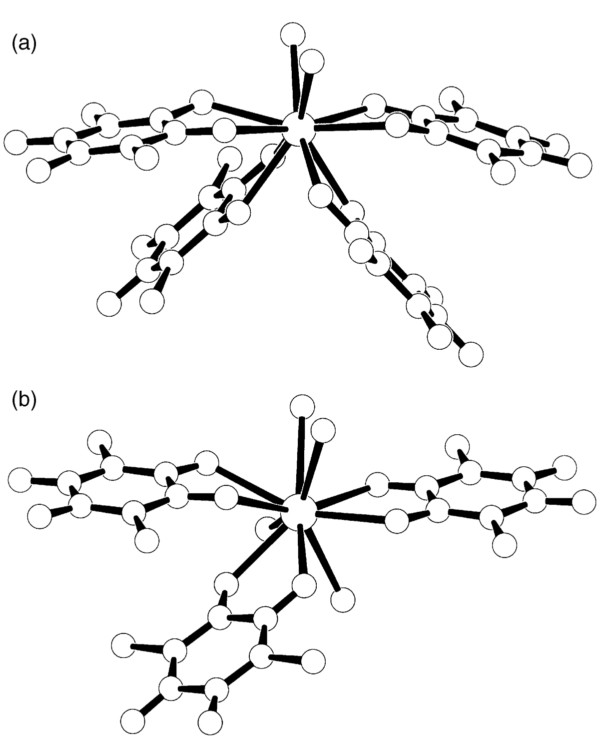


Fig. 15 The coordination environment of (a) the thorium atom in $Thcan_2\cdot6H_2O$ and (b) the lanthanum atom in $La_2can_3\cdot13H_2O$.

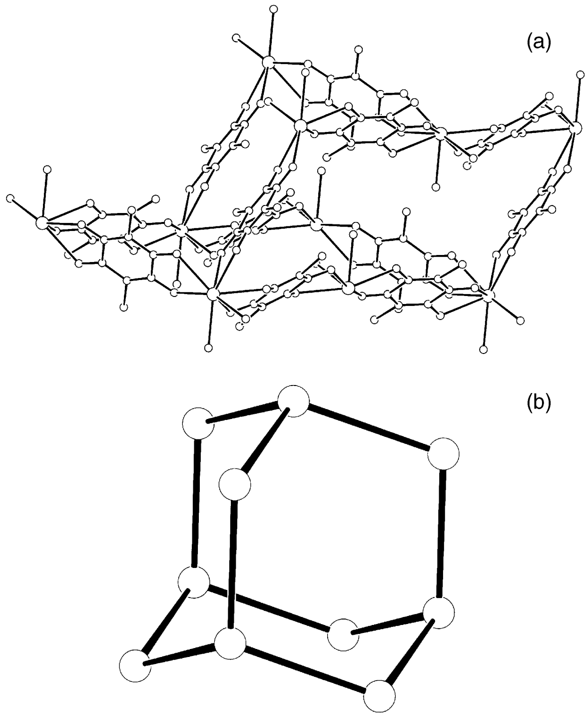


Fig. 16 (a) The highly distorted adamantane-type unit in the diamond-like structure of $Thcan_2\cdot6H_2O$. (b) The adamantane-type unit in diamond.

Syntheses

$Ln_2can_3\cdot xH_2O$. $Ce_2can_3\cdot18H_2O$ was prepared by dissolving 63 mg of $canH_2$ in 20 mL of water by gentle heating on a steam bath and mixing this solution with a 10 mL aqueous solution containing 87 mg of $Ce(NO_3)\cdot6H_2O$. Crystals of $Ce_2can_3\cdot18H_2O$ slowly appeared over a period of a few days. Yield 100 mg. Aquachloranilate complexes involving Sc, Y, La, Nd, Eu, Gd, Tb, Yb and Lu were prepared in a similar manner. Analysis is provided for one member of each isostructural series. Calc. for $Sc_2can_3\cdot13.5H_2O$ ($C_{18}H_{25}Cl_6O_{24.5}Sc_2$): C, 23.1; H, 2.7. Found: C, 23.1; H, 2.6%. Calc. for $La_2can_3\cdot13H_2O$ ($C_{18}H_{26}Cl_6La_2O_{25}$): C, 19.08; H, 2.3. Found: C, 19.2; H, 1.9%. Calc. for $Tb_2can_3\cdot18H_2O$ ($C_{18}H_{36}Cl_6O_{30}Tb_2$): C, 17.1; H, 2.9; Cl, 16.8. Found: C, 17.3; H, 2.5; Cl, 16.7%. Calc. for $Gd_2can_3\cdot16H_2O$ ($C_{18}H_{32}Cl_6Gd_2O_{28}$): C, 17.7; H, 2.6; Cl, 17.4. Found: C, 17.5; H, 2.3; Cl, 17.0%. Calc. for $Lu_2can_3\cdot8H_2O$ ($C_{18}H_{16}Cl_6Lu_2O_{20}$): C, 19.4; H, 1.5. Found: C, 19.4; H, 2.1%.

$Ycan_2\cdot H_3O\cdot8CH_3OH$. A buffer zone of a solution of methanol–1,1,2,2-tetrachloroethane (4 : 1 by volume) was layered carefully on top of a solution of methanol–chloroform (1 : 1) containing chloranilic acid (41.8 mg) and triethylamine (100 mg). A methanol solution of $Y(NO_3)_3\cdot6H_2O$ (38.3 mg) was layered on top of the buffer zone. Over a period of days the intense purple colour of the basic chloranilic acid solution

Table 2 Crystal data and refinement details

Compound	$La_2dhbq_3\cdot 24H_2O$	$Ce_2dhbq_3\cdot 24H_2O$[a]	$Gd_2dhbq_3\cdot 24H_2O$	$Yb_2dhbq_3\cdot 24H_2O$	$Lu_2dhbq_3\cdot 24H_2O$	$Y_2dhbq_3\cdot 24H_2O$	$La_2can_3\cdot 13H_2O$	$Ce_2can_3\cdot\approx 18H_2O$	$Pr_2can_3\cdot\approx 18H_2O$	$Nd_2can_3\cdot\approx 18H_2O$[b]
Formula	$C_{18}H_{54}La_2O_{36}$	$C_{18}H_{54}Ce_2O_{36}$	$C_{18}H_{54}Gd_2O_{36}$	$C_{18}H_{54}Yb_2O_{36}$	$C_{18}H_{54}Lu_2O_{36}$	$C_{18}H_{54}Y_2O_{36}$	$C_{18}H_{26}Cl_6La_2O_{25}$	$C_{18}H_{36}Ce_2Cl_6O_{30}$	$C_{18}H_{36}Cl_6O_{30}Pr_2$	$C_{18}H_{36}Cl_6Nd_2O_{30}$
M	1124.43	1126.85	1161.11	1192.69	1196.55	1024.43	1132.91	1225.41	1226.99	1233.68
T/K	293(2)	150(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Trigonal	Trigonal	Trigonal	Trigonal	Trigonal	Trigonal	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	14.460(4)	14.388(4)	14.202(2)	14.062(1)	14.026(1)	14.113(3)	8.425(2)	9.9480(8)	9.899(3)	9.892(2)
b/Å	14.460(4)	14.388(4)	14.202(2)	14.062(1)	14.026(1)	14.113(3)	8.999(3)	10.0430(7)	9.998(2)	9.983(2)
c/Å	18.165(5)	18.149(5)	18.106(2)	18.027(1)	18.044(1)	18.091(4)	12.447(3)	11.1940(6)	11.141(4)	11.139(2)
α/°	90	90	90	90	90	90	72.14(2)	88.914(5)	89.07(2)	89.12(2)
β/°	90	90	90	90	90	90	71.60(2)	85.035(6)	84.37(3)	84.49(2)
γ/°	120	120	120	120	120	120	84.59(2)	67.714(6)	67.93(3)	68.01(2)
V/Å^3	3289(2)	3254(2)	3162.7(7)	3087.1(4)	3074.2(4)	3120.6(12)	852.3(4)	1030.83(12)	1016.6(5)	1015.0(4)
μ/mm^{-1}	2.026	2.177	3.226	9.193	4.900	4.730	3.039	2.665	2.860	
Unique reflections	2136	2112	1238	1305	1572	1300	3907	4732	4648	
R(int.)	0.0767	0.0984	0.0254	0.0368	0.0126	0.0635	0.0207	0.0215	0.0521	
$wR2$ (on F^2, all data)	0.1261	0.0587	0.0602	0.0888	0.0364	0.1185	0.1056	0.0918	0.2677	
$R1$ ($I > 2\sigma(I)$)	0.0623	0.0285	0.0270	0.0330	0.0150	0.0623	0.0398	0.0368	0.0842	

Compound	$Tb_2can_3\cdot\approx 18H_2O$	$Ce_2can_3\cdot\approx 18H_2O$	$Y_2can_3\cdot\approx 16H_2O$	$Gd_2can_3\cdot\approx 16H_2O$	$Eu_2can_3\cdot\approx 16H_2O$[b]	$Lu_2can_3\cdot\approx 12H_2O$	$Yb_2can\cdot\approx 12H_2O$[b]	$Sc_2can_3\cdot\approx 16H_2O$	$[Ycan_2]H_3O\cdot 8CH_3OH$	$Thcan_2\cdot 6H_2O$
Formula	$C_{18}H_{36}Cl_6O_{30}Tb_2$	$C_{18}H_{36}Ce_2Cl_6O_{30}$	$C_{18}H_{32}Cl_6O_{28}Y_2$	$C_{18}H_{32}Cl_6Gd_2O_{28}$	$C_{18}H_{32}Cl_6Eu_2O_{28}$	$C_{18}H_{24}Cl_6Lu_2O_{24}$	$C_{18}H_{24}Cl_6O_{24}Yb_2$	$C_{18}H_{32}Cl_6O_{28}Sc_2$	$C_{20}H_{35}Cl_4O_{17}Y$	$C_{12}H_{12}Cl_4O_{14}Th$
M	1263.01	1225.41	1086.96	1223.65	1213.09	1187.01	1183.19	999.06	778.20	754.06
T/K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Tetragonal	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/m$	$C2/m$	Cc	$I4_1/a$	$C2/c$
a/Å	9.796(1)	11.376(2)	9.324(2)	9.381(1)	9.400(3)	18.956(8)	18.949(3)	9.056(1)	11.578(1)	13.884(1)
b/Å	9.905(1)	16.598(3)	9.882(2)	9.941(1)	9.957(1)	16.680(5)	16.696(2)	19.258(2)	11.578(1)	11.522(1)
c/Å	11.028(2)	11.224(2)	11.238(2)	11.311(1)	11.330(2)	10.970(4)	10.950(3)	21.842(3)	25.391(4)	12.720(1)
α/°	89.75(1)	90	76.91(2)	76.90(1)	76.95(1)	90	90	90	90	90
β/°	83.48(1)	92.83(2)	77.51(2)	77.15(1)	77.10(2)	110.97(3)	111.08(2)	96.750(9)	90	96.231(8)
γ/°	68.40(1)	90	75.08(2)	74.79(1)	74.71(2)	90	90	90	90	90
V/Å^3	987.7(2)	2116.7(7)	960.7(3)	976.4(2)	981.2(3)	3239(2)	3232(1)	3782.9(8)	3403.7(7)	2022.8
μ/mm^{-1}	4.057	2.596	3.519	3.872		6.653		0.880	5.905	7.972
Unique reflections	3471	2513	4393	3567		2915		2711	1258	1781
R(int.)	0.0420	0.0155	0.0215	0.0185		0.0782		0.0426	0.0978	0.0442
$wR2$ (on F^2, all data)	0.1024	0.0939	0.0893	0.0586		0.2303		0.1443	0.2721	0.0962
$R1$ ($I > 2\sigma(I)$)	0.0482	0.0340	0.0396	0.0235		0.0859		0.0560	0.0808	0.0485

[a] Reported originally in ref. 8. [b] Unit cell data only.

faded and small, highly reflective, black, octahedral crystals appeared on the vessel walls at the ligand solution/metal solution interface. After 10 days no colour was left in solution. A considerable amount of dark precipitate lay at the bottom of the vessel. A comparison of the infra-red spectra of the precipitate and the crystals which grew on the side of the vessel walls revealed they were identical. The infra-red spectrum also indicated the absence of 1,1,2,2-tetrachloroethane, triethylamine and the triethylammonium ion. Microanalysis was performed on a sample that had been allowed to equilibrate with the air. Calc. for $Y(C_6O_4Cl_2)_2 \cdot H_3O \cdot 8H_2O \cdot 1.5CH_3OH$: Cl, 19.84; C, 22.71; H, 3.56. Found: Cl, 19.75; C, 22.91; H, 3.38%.

Thcan$_2$·6H$_2$O. An aqueous solution containing 28 mg of $Th(NO_3)_4 \cdot 4H_2O$ was layered on top of 10 mL of a chloroform solution containing 21 mg of H_2can. Small dark crystals (elongated octahedra) formed at the interface of the two solutions.

Crystallography

Structures were solved using SHELXS-86[15] or SHELX-97[16] and refined using SHELXL-93[17] or SHELX-97.[16] Absorption corrections were applied using SHELX-76.[18] Crystal data and structure refinement details are summarised in Table 2.

CCDC reference numbers 100527, 175597–175610 and 175612.

See http://www.rsc.org/suppdata/dt/b1/b109296k/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We are grateful to the Australian Research Council for supporting this research. S. D. O. gratefully acknowledges the Royal Society for a Post-doctoral Fellowship.

References

1 *Comprehensive Supramolecular Chemistry*, Exec. Eds. J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vogtle, Eds. D. D. MacNicol, F. Toda and R. Bishop, Elsevier Science Ltd., Oxford, vol. 6, 1996; P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2639; B. Moultan and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.

2 S. Kawata, S. Kitagawa, H. Kumagai, T. Ishiyama, K. Honda, H. Tobita, K. Adachi and M. Katada, *Chem. Mater.*, 1998, **10**, 3902; S. Kawata, S. Kitagawa, H. Kumagai, C. Kudo, H. Kamesaki, T. Ishiyama, R. Suzuki, M. Kondo and M. Katada, *Inorg. Chem.*, 1996, **35**, 4449; S. Cueto, H.-P. Straumann, P. Rhys, W. Petter, V. Gramlich and F. S. Rys, *Acta Crystallogr., Sect. C*, 1992, **48**, 458; S. Decurtains, H. W. Schmalle, H. R. Oswald, A. Linden, J. Ensling, P. Gutlich and A. Hauser, *Inorg. Chim. Acta*, 1994, **216**, 65; H. O. Stumpf, L. Ouahab, Y. Pei, P. Bergerat and O. Kahn, *J. Am. Chem. Soc.*, 1994, **116**, 3866; A. Bouayad, J.-C. Trombe and A. Gleizes, *Inorg. Chim. Acta*, 1995, **230**, 1; M. R. Sundberg, R. Kivekas and J. K. Koskimies, *J. Chem. Soc., Chem. Commun.*, 1991, 526; F. D. Rochon, R. Melanson and M. Andruh, *Inorg. Chem.*, 1996, **35**, 6086; R. P. Farrell, T. W. Hambley and P. A. Lay, *Inorg. Chem.*, 1995, **34**, 757; A. Weiss, R. Reigler and C. Robl, *Z. Naturforsch., Teil B*, 1986, **41**, 1501.

3 C. Robl, *Mater. Res. Bull.*, 1987, **22**, 1483.

4 P. E. Riley, S. F. Haddad and K. N. Raymond, *Inorg. Chem.*, 1983, **22**, 3090.

5 H. Steinfink and G. D. Brunton, *Inorg. Chem.*, 1970, **9**, 2112; R. R. Ryan and R. A. Penneman, *Inorg. Chem.*, 1971, **10**, 2637.

6 R. B. English and D. J. Eve, *Inorg. Chim. Acta*, 1993, **203**, 219; N. Bulc, L. Golic and J. Siftar, *Acta Crystallogr., Sect. C*, 1983, **39**, 176.

7 S. R. Sofen, S. R. Cooper and K. N. Raymond, *Inorg. Chem.*, 1979, **18**, 1611.

8 B. F. Abrahams, J. Coleiro, B. F. Hoskins and R. Robson, *Chem. Commun.*, 1996, 603.

9 PLATON, A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34.

10 T. C. W. Mak and R. K. McMullan, *J. Chem. Phys.*, 1965, **42**, 2732.

11 T. Miyanaga and S. Sudoh, *Polyhedron*, 1999, **18**, 3433.

12 B. F. Abrahams, B. F. Hoskins and R. Robson, *Acta Crystallogr., Sect. C*, 1996, **52**, 2766.

13 G. D. Brunton and C. K. Johnson, *J. Chem. Phys.*, 1975, **62**, 3797.

14 R. Robson, *J. Chem. Soc., Dalton Trans.*, 2000, 3735.

15 SHELXS-86, Program for Crystal Structure Solution, G. M. Sheldrick, Institut fur Anorganische Chemie der Universitat, Tammanstrasse 4, D-3400, Göttingen, Germany, 1986.

16 G. M. Sheldrick, SHELX-97, Program for Crystal Structure Analysis, Universitat of Göttingen, 1997.

17 G. M. Sheldrick, SHELXL-93, Program for the Refinement of Crystal Structures, Universitat of Göttingen, 1993.

18 G. M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, Cambridge, UK, 1976.

19 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.