Gas hydrate-like pentagonal dodecahedral $M_2(H_2O)_{18}$ cages (M = lanthanide or Y) in 2,5-dihydroxybenzoquinone-derived coordination polymers

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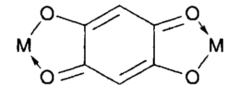
$Ce_2(dhbq)_3{\cdot}24H_2O$ ($dhbq^{2-}$ = the dianion derived from 2,5-dihydroxybenzoquinone) contains gas hydrate-like pentagonal dodecahedral $Ce_2(H_2O)_{18}$ cages which link together hexagonal grid $Ce_2(dhbq)_3$ sheets to form a three-dimensional network related to diamond and which pass through the $Ce_6(dhbq)_6$ rings of an independent, identical, interpenetrating diamond-related network.

A number of coordination polymers have been reported recently with very open framework structures akin to those of the zeolites but with entirely different chemical architectures.[1] Potential zeolite-like applications (*e.g.* in catalysis) appear not to be possible in some of these cases because the heavily solvated crystals lose their single-crystal character and presumably also their microporous structure (although this has not been proven) upon loss of channel-filling solvent. In the hope of obtaining more robust framework solids we are attempting to harness the highly potent chelate effect by investigating the coordination polymers formed by connecting ligands that can simultaneously chelate and bridge in a variety of geometrical ways. One of the simplest of such ligands is the dianion, $dhbq^{2-}$, derived from 2,5-dihydroxybenzoquinone (H_2dhbq), shown chelating and bridging two metal centres in **I**. $Dhbq^{2-}$ can be regarded as the chelating equivalent of simple linear two-connectors such as cyanide or 4,4′-bipyridine, which have proved to be prolific generators of infinite networks. An attractive feature of these 'bis-bidentate' linear two-connectors is that associated octahedral metal centres then effectively become trigonal centres giving access in principle to a range of rare three-connected three-dimensional nets.



I

Of all the three-dimensional nets available as targets to test the two-connecting and polymer-forming capacity of $dhbq^{2-}$, diamond seemed the simplest to start with. To play the role of the four-connecting tetrahedral centre of a dhbq-linked diamond net an eight-coordinate metal centre with affinity for oxygen chelators was required and for overall electrical neutrality the cation should carry a 4+ charge. Cerium(IV) appeared ideal for these purposes for it is known to form an eight-coordinate tetracatecholate complex, $[Ce(C_6H_4O_2)_4]^{4-}$.[2] Reaction of $Ce(NH_4)_4(SO_4)_4$ with 2 equiv. of H_2dhbq in water, however, gave well formed crystals of a Ce^{III} product of composition $Ce_2(dhbq)_3{\cdot}24H_2O$. Subsequently it was found that an identical crystalline product could be obtained from the reaction of cerium(III) with 1.5 equiv. of H_2dhbq in aqueous solution. The structure of $Ce_2(dhbq)_3{\cdot}24H_2O$ has been determined by single-crystal X-ray diffraction methods.†

All cerium atoms are equivalent and nine-coordinate, having three chelated dhbq ligands and three mutually *cis* water ligands. The coordination geometry is best described as tricapped trigonal prismatic, one trigonal face being defined by the $(H_2O)_3$ trio and the other trigonal face by one oxygen from each dhbq; the three rectangular faces are then 'capped' by the other oxygen of each dhbq. Each cerium is linked through dhbq

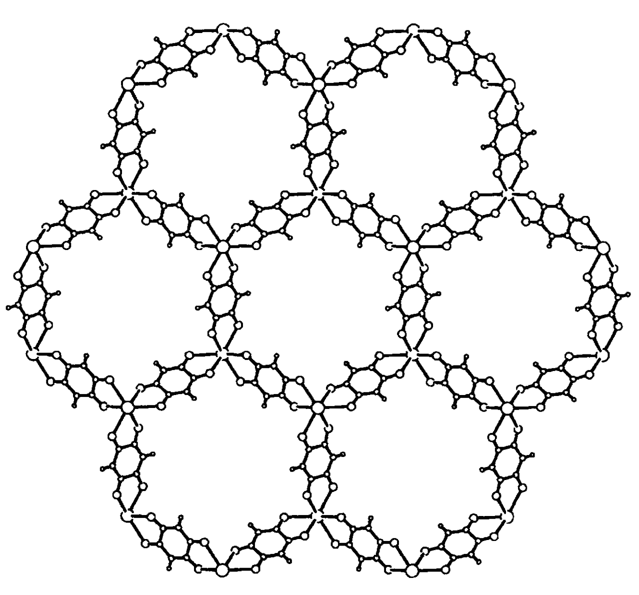


Fig. 1 Structure of a $[Ce_2(dhbq)_3]_n$ sheet. Circles in order of increasing size represent H, C, O and Ce respectively. Coordinated water molecules are omitted.

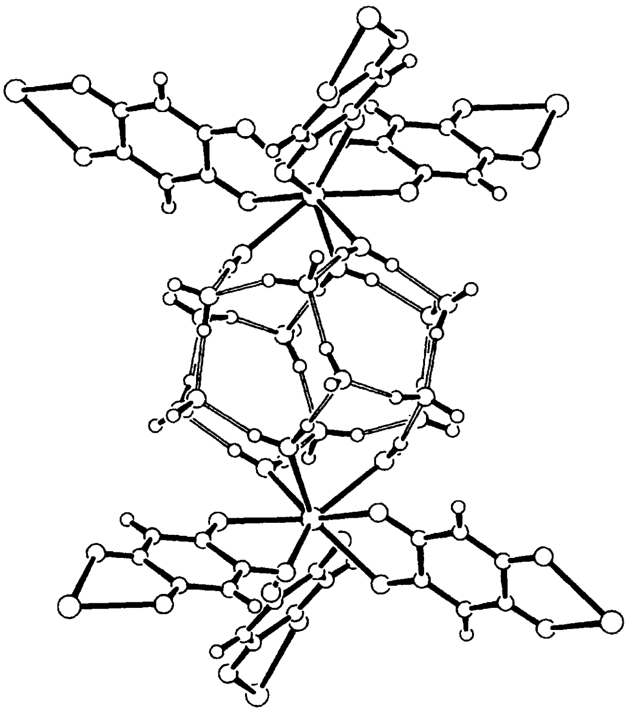


Fig. 2 A pentagonal dodecahedral $Ce_2(H_2O)_{18}$ cage. Fragments of the $[Ce_2(dhbq)_3]_n$ sheets joined together by the cage are also shown.

bridging/chelating ligands to three other metal centres generating $[Ce_2(dhbq)_3]_n$ sheets as shown in Fig. 1. The $(H_2O)_3$ groups on neighbouring ceriums within a sheet are on opposite sides of the sheet so that each $Ce_6(dhbq)_6$ ring adopts a puckered arrangement very similar to the chair form of cyclohexane. An upward-pointing $(H_2O)_3$ trio on one sheet is hydrogen-bonded *via* a group of twelve lattice water molecules to a downward-pointing $(H_2O)_3$ trio on the sheet above as shown Fig. 2. As can be seen, the two Ce atoms together with the eighteen water molecules that link them to form a pentagonal dodecahedral cage, all the atoms of which, including the H atoms, are well defined.

By coincidence the Ce···Ce separation across a cage [8.809(2) Å] is very similar to that across a dhbq connector [8.935(2) Å] so that the Ce atoms fall almost exactly on the lattice points of a diamond net. The structure in fact contains two such diamond-related networks that interpenetrate so that the $(H_2O)_{18}$ connections of one pass through the 'six-membered' rings of the other. A schematic representation of this interpenetration is shown in Fig. 3. The twelve water molecules in the central 'equatorial belt' of each $(H_2O)_{18}$ connection are hydrogen bonded, either directly or *via* six other intermediary lattice waters, to the dhbq oxygen atoms of the encompassing $Ce_6(dhbq)_6$ ring through which the connection passes, as shown in Fig. 4.

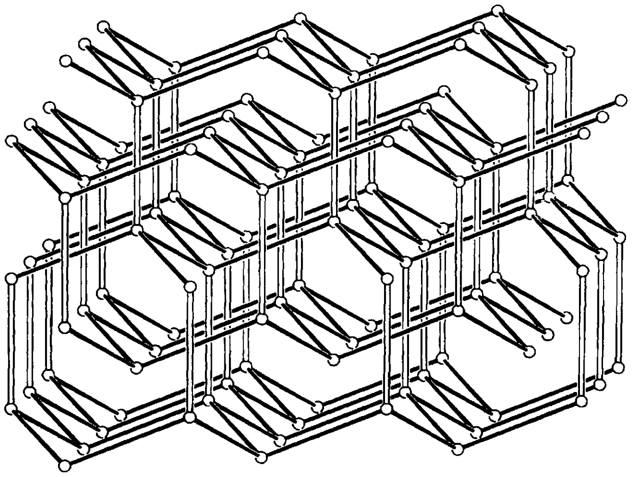


Fig. 3 Schematic representation of the two interpenetrating diamond-related nets. Circles represent Ce. 'Filled' bonds represent dhbq links; 'unfilled' bonds represent $(H_2O)_{18}$ links.

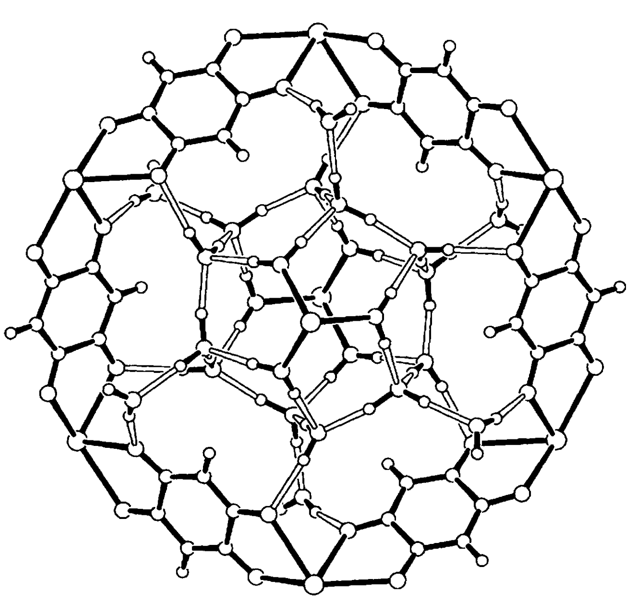


Fig. 4. Representation of a $Ce_2(H_2O)_{18}$ unit of one diamond-related framework passing through a $Ce_6(dhbq)_6$ ring of the other framework and the hydrogen-bonded links between the two

The $Ce_2(H_2O)_{18}$ pentagonal dodecahedral cages closely resemble the $(H_2O)_{20}$ cages of the same geometry found in certain of the archetypal gas hydrates. The $(H_2O)_{20}$ cages are capable of imprisoning a range of species such as rare gas atoms, O_2, N_2, Cl_2 and H_2S,[3] but preliminary attempts to observe similar inclusions in the $Ce_2(H_2O)_{18}$ cavities have thus far proved fruitless.

The compounds $M_2(dhbq)_3{\cdot}24H_2O$ (M = Ce, La, Yb, Y) are isostructural with cell parameters *a* and *c* respectively as follows (hexagonal settings of a rhombohedral cell): Ce, 14.388(4) and 18.149(5); La, 14.460(4) and 18.165(5); Yb, 14.062(4) and 18.027(5); Y, 14.114(2) and 18.084(2) Å.

The structures have been reported for dhbq coordination polymers of composition $Na_2(H_2O)_{24}[M_2(dhbq)_3]$ ($M = Mn^{2+}$, Cd^{2+}) in which M is six-coordinate and much of the associated water constitutes hydration sheaths around the two sodium atoms.[4] In these cases no cages of the type described above are present. Polymeric chloranilate compounds of composition $M_2(can)_3{\cdot}nH_2O$ ($can = C_6Cl_2O_4^{2-}$; M = La, n = 13;[5] M = Ce, n = 18;[5] M = Y, n = 12.6[6]) also have structures different from the above and contain no water cages. This difference is almost certainly a consequence of the large chlorine atoms of the chloranilates encroaching on the void space within the $M_6(can)_6$ rings so that they are unable to accommodate the $M_2(H_2O)_{18}$ pentagonal dodecahedra of the second framework.

The fact that cations as divergent in size as La^{3+} and Yb^{3+} give rise to the same structure suggests that all the lanthanide trications (and possibly non-lanthanides in addition to Y^{3+}) may do the same.

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Footnote

† $Ce(NO_3)_3{\cdot}6H_2O$ (43.4 mg) in water (25 ml) was added slowly to a solution of H_2dhbq (21 mg) in water (50 ml). Red–brown crystals of $Ce_2(dhbq)_3{\cdot}24H_2O$ suitable for single-crystal X-ray diffraction formed within a day. A sample for analysis was dried in air whereupon minor loss of water occurred. Found: C, 19.8; H, 4.5. Calc. for $Ce_2(dhbq)_3{\cdot}22H_2O$ ($C_{18}H_{50}Ce_2O_{34}$): C, 19.8; H, 4.6%.

Crystal data for $Ce_2(dhbq)_3{\cdot}24H_2O$: $C_{18}H_6Ce_2O_{36}$, $M = 1126.85$, rhombohedral, space group $R\bar{3}$ (hexagonal setting) (no. 148), $a = 14.388(4)$, $c = 18.149(5)$ Å, $U = 3254(2)$ Å^3, $F(000) = 1698$, $Z = 3$, $D_c = 1.725$ g cm^{-3}, $D_m = 1.72(1)$ g cm^{-3}, μ(Mo-Kα) = 2.177 mm^{-1}. Intensity data were collected on an Enraf-Nonius CAD4-MachS diffractometer employing the ω–2θ scan method; absorption corrections were applied. The structure was solved using heavy-atom methods (SHELXS-86) and refined using a full-matrix least-squares refinement procedure (SHELXL-93). 2112 unique reflections, 1610 observed [$I > 2\sigma(I)$, $R_1 = 0.0285$, $wR_2 = 0.0587$; 115 refined parameters], $2\theta_{max} = 60°$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546; B. F. Abrahams, B. F. Hoskins, D. M. Michail and R. Robson, *Nature*, 1994, **369**, 727.

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

3 A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, 5th ed., 1984, p. 660.

4 A. Weiss, E. Riegler and C. Robl, *Z. Naturforsch., Teil B*, 1986, **41**, 1501.

5 B. F. Abrahams, J. Coleiro, B. F. Hoskins and R. Robson, to be published.

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

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