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$Cs(Me_4N)_2(OH)_3 \cdot 14H_2O$: A Metal Ion in a Clathrate Hydrate Polyhedral Cage[1,2]

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Clathrate hydrates are solid inclusion compounds with a three-dimensional host structure of space-filling polyhedral cages formed by hydrogen-bonded four-connected water molecules and accommodating a large variety of possible guest molecules.[3] A group of compounds with analogous structural principles are some hydrates of tetramethylammonium hydroxide.[4,5] The guest is the cation, of an appropriate size and shape to fit again into certain polyhedral cages of a water host structure. This is now anionic or proton-deficient, since it contains also the hydroxide ion. Nevertheless, the various host structures of the highest hydrates of Me_4NOH are fully four-connected, i.e., with a hydrogen bond along every polyhedron edge.[6]

The host structure of the stable form[4] of $Me_4NOH \cdot 7.5H_2O$ is composed of eight $[5^{12}6^3]$ and four smaller $[4^25^8]$ polyhedra per unit cell.[5] The Me_4N^+ occupies the larger cage; the smaller cage is empty. A closely related crystal structure has now been observed for the new hydrated *ternary* hydroxide $Cs(Me_4N)_2(OH)_3 \cdot 14H_2O$, where one H_2O of twice the formula unit of the metal-free compound is substituted by another OH^-, while the additional Cs^+ occupies the smaller cage. This appears to be the first instance in which a metal ion is found as a guest—largely inert and even facultative—in a clathrate hydrate polyhedral cage.

Crystals of the new compound were grown from their melt in thin-walled glass capillaries using a miniature zone-melting technique.[7] The melting point is 57 °C, as compared to 4 °C for the cesium-free analogue.[4] The X-ray analysis[8] yielded the same space group with very similar unit cell dimensions and comparable coordinates for most of the atoms. The cages, together with the enclosed cations, are shown in Figure 1. Besides the additional atomic site for the Cs^+ in the smaller cage, there is a change in the larger one involving a disorder[11] of the Me_4N^+. The polyhedral packing[5] is shown in Figure 2.

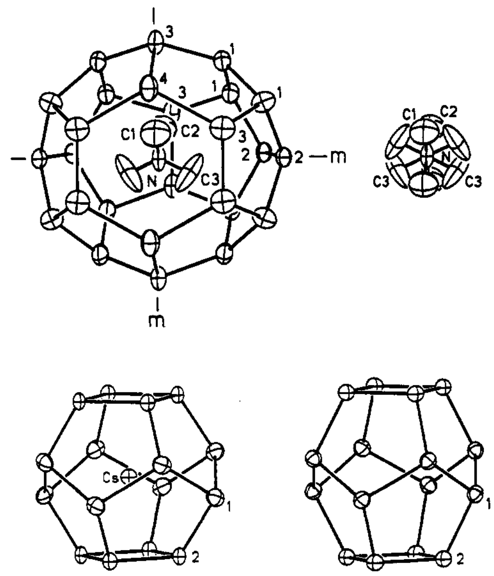

Figure 1. Top: The larger polyhedron (26 vertices, 12 pentagonal and three hexagonal faces, *mm* symmetry) enclosing the Me_4N^+ ion, of which a 2-fold orientational disorder[11] is shown separately. Bottom: The smaller polyhedron (16 vertices, two square and eight pentagonal faces, 422 symmetry) with the enclosed Cs^+ ion (O···O distances along edges between 2.64 and 3.11 Å, average 2.77 Å) and empty in the isostructural cesium-free compound[5] (2.72–2.84, average 2.75 Å).

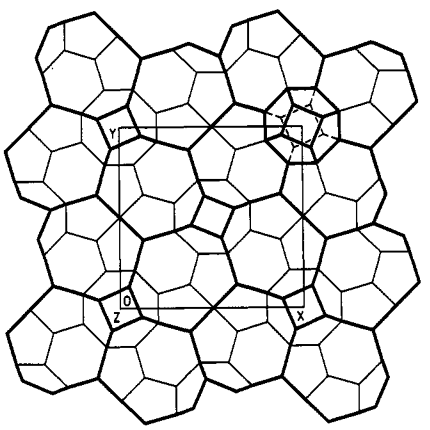

Figure 2. Face linking of the larger polyhedra into a tetragonal layer with quadratic holes, these being common faces of the smaller polyhedra in protruding columns.

The Cs^+ ion with its low charge is a good candidate for the observed phenomenon, since its size is appropriate. The quite uniform Cs···O distances within the smaller cage of 3.428(5) and 3.527(3) Å to eight O1 and O2 atoms each[12] are evidence for a good fit. This is seen from recent studies of the chemically related *non*-clathrate hydrates $CsOH \cdot 2H_2O$ and $CsOH \cdot 3H_2O$[13] as well as undeuterated[14] and perdeuterated[15] (neutron diffraction) $CsNa_2(OH)_3 \cdot 6H_2O$, which yielded an average Cs···O of 3.47 Å.

Encagement of the Cs^+ ion by polyhedra of hydrogen-bonded water molecules in the *gas* phase was recently deduced from the observation of magic numbers for $Cs^+(H_2O)_n$ clusters in mass spectra.[16] With values of *n* equal to 18 and 20, the smallest

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[1] Dedicated to Professor Reinhard Schmutzler on his 60th birthday.

[2] This is paper 10 of the series Hydrates of Weak and Strong Bases, from the Dissertation of Stäben, D., Zur Kristallchemie von Hydraten des Tetramethylammoniumhydroxids und strukturverwandter Substanzen, Universität Düsseldorf, 1993. For paper 9, see ref 15.

[3] For a comprehensive insight into structural principles and representatives of the clathrate hydrates and other hydrate inclusion compounds, the reader is referred to the following: Jeffrey, G. A. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 1, pp 135–190.

[4] Mootz, D.; Stäben, D. *Z. Naturforsch.* **1992**, *47b*, 263–274.

[5] Mootz, D.; Seidel, R. *J. Inclusion Phenom.* **1990**, *8*, 139–157.

[6] Concluded from the observed O···O distances of 2.57 to 3.25 Å. The H atoms in structures of this kind are usually disordered and cannot be located unambiguously from X-ray diffraction data.

[7] Brodalla, D.; Mootz, D.; Boese, R.; Osswald, W. *J. Appl. Crystallogr.* **1985**, *18*, 316–319.

[8] Space group *I*4/*mcm*, $a = 15.242(8)$ Å, $c = 11.819(6)$ Å, $V = 2746(2)$ Å^3 at −50 °C, $Z = 4$, d(calcd) = 1.41 mg mm^{-3}; diffractometer Siemens-Stoe AED 2, graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å), $\mu = 1.41$ mm^{-1}, $2\theta(\max) = 60°$, 784 independent reflections with $|F_o| \geq 4\sigma_F$; direct methods, 58 refined parameters, weighting by $w = 1/(\sigma_F{}^2 + 0.0003|F_o|^2)$, final $R(F) = 0.064$; computer programs DIFABS[9] for absorption correction and SHELXTL-PLUS.[10]

[9] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158–166.

[10] *SHELXTL-PLUS, Structure Determination System*, Revision 4.11; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1990.

[11] In addition to the 2-fold orientational disorder of the Me_4N^+ ion, there is a 4-fold positional one of the atom O4 around its averaged site of $\bar{4}2m$ symmetry shown in Figure 1. The two kinds of disorder are coupled through a prohibitively short distance of 2.27(5) Å between atoms C1 and O4 in certain of their disordered sites. A single disordered O4 is only three-connected, so that the the disorder may be a consequence of the increased relative proton deficit of the host structure as compared to the cesium-free compound.

[12] For the empty cage of the isostructural cesium-free compound,[5] which is also shown in Figure 1, the analogous distances from the midpoint of 3.261–3.657 Å reveal a somewhat less spherical shape.

[13] Mootz, D.; Rütter, H. *Z. Anorg. Allg. Chem.* **1992**, *608*, 123–130.

[14] Mootz, D.; Rütter, H. *Angew. Chem.* **1990**, *102*, 949–950; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 904–905.

[15] Mootz, D.; Rütter, H.; Heger, G. *Z. Anorg. Allg. Chem.*, in press.

[16] Selinger, A.; Castleman, A. W., Jr. *J. Phys. Chem.* **1991**, *95*, 8442–8444.

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isolated polyhedra identified in that way are larger than that stabilized in the title compound as part of a three-dimensional solid.

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Supplementary Material Available: Tables of atomic parameters and interatomic distances and angles for the title compound (2 pages); listing of observed and calculated structure factors for the title compound (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.