Preparation and Structure of Fully Caesium Exchanged Zeolite A and of the Linear $(Cs_4)^{3+}$ Cation

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Fully dehydrated, fully Cs^+-exchanged zeolite A has been prepared by reducing the Na^+ ions in dehydrated zeolite 4A with caesium vapour at 623 K, to give Cs_{12}–A·1/2Cs which contains $(Cs_4)^{3+}$, followed by baking the occluded caesium atoms out at 1273 K to give Cs_{12}–A; both structures were determined by single crystal *X*-ray diffraction methods.

A series of attempts spanning a decade to prepare fully Cs^+-exchanged zeolite A have led to gradual increases in the maximum extent of exchange, from 7/12 to 11/12.[1—3] Fully dehydrated, fully Cs^+-exchanged zeolite A would be a remarkably ionically crowded material. It is to avoid this crowding, presumably, that the zeolite does not easily accept twelve large Cs^+ ions per 12.3 Å unit cell as the result of conventional ion-exchange procedures.[2,3] This most ionically crowded zeolite, Cs_{12}–A, has now been synthesized by utilizing the difference in reduction potential between Na and Cs, together with excess caesium vapour, as driving forces for complete Cs^+ exchange.

The reaction between a single crystal of dehydrated Na_{12}–A and 0.1 Torr of caesium vapour went to completion at 623 K to give Cs_{12}–A·1/2Cs. Even after evacuation at 723 K for 4 days to remove all metal from its surface, the product crystal remained black. Attempts to bake the extra caesium atoms of Cs_{12}–A·1/2Cs out at 923 or 1123 K produced crystals which were colourless and transparent on the outside but black within.[4] A colourless crystal of Cs_{12}–A was obtained, however, by heating *in vacuo* at 1273 K. The structures of Cs_{12}–A·1/2Cs and Cs_{12}–A have been determined by single crystal *X*-ray diffraction methods with relatively large data sets in the cubic space group *Pm*3*m*. Refinements in *Fm*3*c* yielded no additional insights.†

In each crystal structure, Cs^+ ions are distributed over four crystallographically distinct sites. They are found on fourfold axes at the centres of 8-rings as seen previously,[2,3] on threefold axes both on the sodalite- and large-cavity sides of 6-rings,[2,3] and finally on twofold axes opposite 4-rings in the large cavity[3] (see Table 1).

Table 1. Distribution of Cs^+ ions in fully Cs^+-exchanged zeolite A.

Crystal (components)	In 8-rings	No. of Cs^+ ions Opposite 6-rings		Opposite 4-rings	Total
		α-cage	β-cage		
Cs_{12}–A	3	6 + 1[a]	1 + 1[a]	0	12
Cs_{12}–A·1/2Cs	3	7	2	0.5	12.5
(Cs_{12}–A)	3	6	2	1	12
(Cs_{13}–A)	3	8	2	0	13

[a] One 6-ring is occupied on both sides by Cs^+ ions. These two ions have refined to positions somewhat different from those of the remaining 6-ring Cs^+ ions.

In Cs_{12}–A, three Cs^+ ions per unit cell lie at the centres of 8-rings. Two Cs^+ ions, 4.04 Å apart, lie on a single threefold axis within each sodalite cavity. One of these Cs^+ ions shares its 6-ring with a large-cavity Cs^+ ion, and the remaining six 6-rings are occupied only by such large-cavity Cs^+ ions. A large-cavity view of Cs_{12}–A is shown in Figure 1.

Cs_{12}–A·1/2Cs may be viewed as an equimolar mixture of Cs_{12}–A and Cs_{13}–A. Together with three Cs^+ ions at the centres of 8-rings and six in the large cavity, this Cs_{12}–A unit cell contains two Cs^+ ions in each sodalite unit and one Cs^+ ion opposite a 4-ring in the large cavity, this 4-ring being the one between the two 6-rings occupied by sodalite Cs^+ ions. Cs_{13}–A differs by having eight Cs^+ ions opposite 6-rings in the large cavity with no Cs^+ ion opposite a 4-ring. The short intercaesium distances of 3.98(2) Å within the sodalite unit and 3.87(1) Å through two opposite 6-rings indicate that the extra caesium atom in the Cs_{13}–A unit cell has added to form a linear cationic cluster $(Cs_4)^{3+}$, unlike the tetrahedral clusters of $(Na_4)^{3+}$ and $(K_4)^{3+}$ observed in zeolite Y by e.s.r.

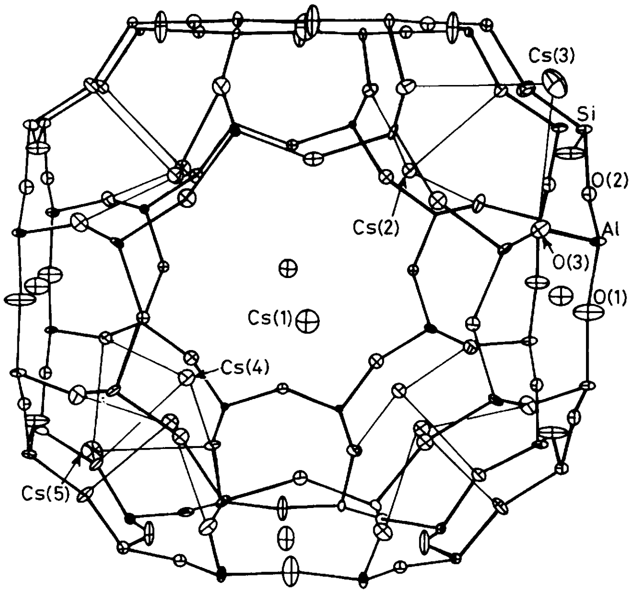

Figure 1. A large-cavity view of Cs_{12}–A. The zeolite A framework is drawn with heavy bonds between tetrahedrally co-ordinated (Si, Al) and oxygen atoms. Cs^+ ion co-ordination by framework oxygens is indicated by fine lines. Three Cs^+ ions are located at the centres of 8-rings at Cs(1), seven are in the large cavity (α-cage) at Cs(2) and Cs(4), and two are in the sodalite unit (β-cage) at Cs(3) and Cs(5). Two Cs^+ ions at Cs(4) and Cs(5) share a unique 6-ring. Ellipsoids of 20% probability are shown.

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† *Crystal data:* Cs_{12}–A [Cs_{12}–A·1/2 Cs]: each cubic, space group *Pm*3*m*, a = 12.258 [12.279] Å; Syntex diffractometer, Mo radiation ($K_{\alpha1}$, λ = 0.70930; $K_{\alpha2}$, λ = 0.71359 Å), θ–2θ scan; 205 [360] reflections with $I > 3\sigma(I)$; absorption corrections judged unnecessary; full-matrix least-squares refinement; anisotropic thermal parameters; R = 0.073 [0.053], R_w = 0.079 [0.041].

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.

spectroscopy.[5] $(Cs_4)^{3+}$ appears to be stable even *in vacuo* at 1123 K.[4]

The excess electrons in Cs_{12}–A·1/2Cs might have formed a metallic continuum of electron density encompassing the entire single crystal; a three-dimensional array of Cs^+ ions with intercaesium distances comparable to those in caesium metal exists.[6] However, a test for metallic character using a metal detector on an evacuated macroscopic sample was negative.

Cs_{12}–A showed little indication of crystal damage after preparation at 1273 K, and therefore has remarkable thermal stability. Na_{12}–A, K_{12}–A, and $Ca_{5.8}$–A decompose in air at about 1025, 1100, and 1100 K, respectively.[7] Cs_{12}–A has a relatively relaxed framework, like that of hydrated Na_{12}–A and very unlike those of dehydrated K_{12}–A and $Rb_{11}Ba_{0.5}$–A.[8] This may be partly responsible for its high thermal stability.

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