Three- and Five-co-ordinate Manganese(II) in Zeolite A

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Summary Near trigonal bipyramidal and near trigonal planar co-ordination is demonstrated by Mn^{II} ions in hydrated and fully dehydrated partially Mn^{II}-exchanged zeolite A, respectively.

SINGLE crystals of zeolite A were allowed to exchange, with periodic agitation, with a large excess of 0·1M $Mn(ClO_4)_2\cdot 6H_2O$ solution at *ca.* 28°. Chemical analysis revealed 4·4 Mn^{II} ions per unit cell after 3 weeks and 4·5 Mn^{II} ions after 3 months, indicating a slowing or stopping of the initially rapid exchange. The unit cell stoicheiometry is $[Mn_{4.5}^{2+}\,Na_3^{1+}\text{-}(Si_{12}Al_{12}O_{48})^{12-}]\cdot xH_2O$, henceforth referred to as Mn[A].

X-Ray diffraction intensities for both the hydrated and dehydrated Mn[A] crystals were collected for $0° < 2\theta < 70°$

using a Syntex computer-controlled diffractometer with Mo-K_α radiation. The hydrated crystal, 65μ on an edge, was mounted on the tip of a glass fibre exposed to the atmosphere which was at 19° and at a relative humidity of 30% during data collection. The second crystal, $70\,\mu$ on an edge, was mounted in a capillary and dehydrated for 24 h at 350° and 10^{-5} Torr. The cell constants decreased from 12·268(4) Å to 12·175(3) Å upon dehydration. All unique reflections, 204 for hydrated Mn[A] and 162 for dehydrated Mn[A], for which the intensity, I, exceeded 3 times its corresponding standard deviation, σ, were used throughout.

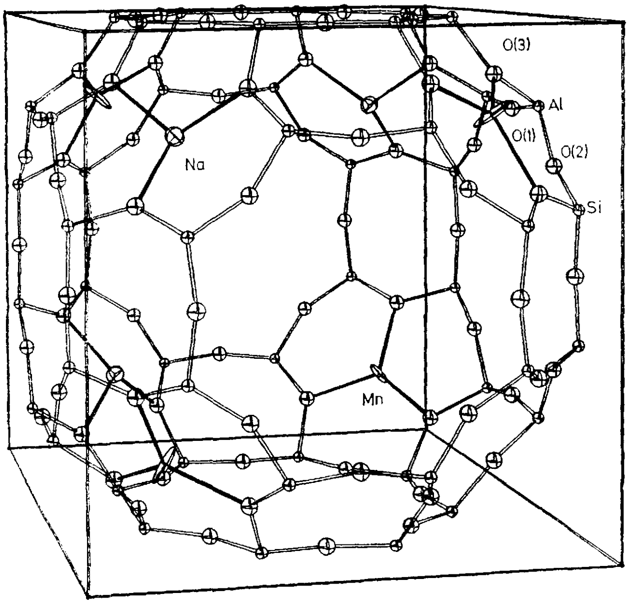

FIGURE 1. *The dehydrated* Mn[A] *unit cell is shown.*[12] *The trigonal approaches made by* Mn^{II} *and* Na^{1+} *to framework oxygen atoms are indicated by heavy lines. Ellipsoids of* 20% *probability are used.*

Both structures were determined by Fourier methods in the space group *Pm*3*m* and were refined by full-matrix least-squares to the final conventional error indices of $R = 0{\cdot}010$ for hydrated Mn[A] and 0·076 for dehydrated Mn[A]. ($R = (\Sigma|F_0\text{-}|F_c||)/\Sigma F_0$). Isotropic thermal parameters were used for all but the Na^{1+} and the Mn^{II} ions. The results indicated greater and more anisotropic thermal motion for the Mn^{II} ions in dehydrated Mn[A].

In the dehydrated Mn[A] structure, 4·5 Mn^{II} ions occupy three-fold axis sites, Wyckoff 8(*g*), near the six-oxygen windows. The Mn^{II} ions are recessed a small amount, 0·11(3) Å, into the sodalite cavity from the [111] plane formed by its closest approaches, the three equivalent O(3) atoms [Wyckoff 24(*m*)] arranged trigonally in the six-oxygen (twelve-membered) ring (see Figure 1). The three Mn^{II} to O(3) distances are all 2·11(1) Å and the O(3)–Mn^{II}–O(3) angle is 119·6(1)°, close to the trigonal planar angle, 120°. Three of the remaining six-oxygen windows are occupied by Na^{1+} ions on three-fold axes, 0·46(3) Å from the O(3) plane but in the large cavity. The three Na^{1+} to O(3) distances are 2·16(5) Å and the O(3)–Na^{1+}–O(3) angle is 115·5(7)°.

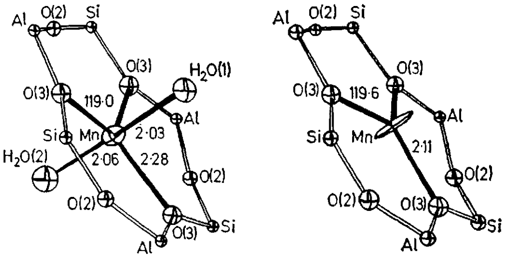

FIGURE 2. *Equivalent* Mn^{II}*-occupied six windows of dehydrated* Mn[A] (*left*) *and of the hydrated* Mn[A] *structure* (*right*) *are shown. The co-ordination about* Mn^{II} *is indicated by heavy lines. Ellipsoids of* 20% *probability are used.*

In hydrated Mn[A], Mn^{II} ions are found by similar methods at three-fold axis positions, 0·24(3) Å from the plane of the O(3) atoms, slightly into the large cavity. The Mn^{II} ions are pentaco-ordinate in a trigonal bipyramidal manner (Figure 2). The axial ligands are two non-equivalent water molecules, $H_2O(1)$ and $H_2O(2)$. The $Mn^{II}\cdot\cdot OH_2$ distances are equal: 2·03(6) Å and 2·06(7) Å for $H_2O(1)$ and $H_2O(2)$. The 3 equivalent equatorial framework O(3) atoms are 2·28(1) Å from Mn^{II}, affording the Mn^{II} ions nearly regular trigonal bipyramidal co-ordination.[5–8] The 0·24 Å deviation of Mn^{II} ions from the [111] plane at O(3), small when compared to the deviations observed for other cations (Na^{1+}, Ni^{II}, Co^{II}, and Zn^{II} of 0·52,[9] 1·53,[10] 1·65,[2] and 0·54 Å[11] respectively), indicate that Mn^{II} ions do not find near trigonal bipyramidal co-ordination unfavourable. Four other sites containing 19 water oxygen or sodium ions were located and included in the final refinements. The following angles describe Mn^{II} co-ordination: O(3)–Mn^{II}–O(3), 119·0(1)°; O(3)–Mn^{II}–$H_2O(1)$, 84(1)°; and O(3)–Mn^{II}–$H_2O(2)$, 96(1)°.

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