Three-co-ordinate Cobalt(II). The Crystal Structure of Fully-dehydrated Partially-Co^{II}-exchanged Zeolite A

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Summary Near trigonal planar co-ordination is demonstrated by cobalt(II) ions in partially-exchanged fully-dehydrated zeolite A.

SINGLE crystals of zeolite A[1] were prepared by a modification of Charnell's method[2] which yielded clear cubes up to 0·0075 cm on an edge. Elemental analysis, and previous determinations of the structures of dehydrated zeolite 4A[3] and of the acetylene complex of zeolite 4A,[4,5] indicated that the formula per unit cell is best represented as $Na_{12}Al_{12}Si_{12}O_{48}\cdot xH_2O$. Ion-exchange was carried out in 0·1M aqueous Co^{II} nitrate solution at *ca.* 75° for three weeks. After elemental analysis, back-exchange using a measured amount of unexchanged zeolite A was conducted to give samples which contained four divalent transition-metal ions per unit cell. A single crystal, approximately 0·007 cm on a edge, was dehydrated at 10^{-5} Torr and 350 °C for 48 h. Upon dehydration, the tan crystal became deep blue in colour.

X-Ray diffraction intensities were collected for $0° < 2\theta < 70°$ using a Syntex computer-controlled diffractometer with Mo-K_α radiation. Only the 101 unique reflections (*m*) for which $I > 3\sigma$, where I is the intensity and σ is its estimated standard deviation, were used. The structure was readily determined by Fourier methods in the space group *Pm*3*m* and was refined by full-matrix least-squares to final error indices of $R_1 = R_2 = 0{\cdot}084$. [$R_1 = (\Sigma|F_0 - |F_c||)/\Sigma F_0$; $R_2 = \{\Sigma w(F_0 - |F_c|)^2/\Sigma w F_0{}^2\}^{1/2}$]. A total of 14 parameters (*s*) were varied. The weights (*w*) used in least-squares were the reciprocal squares of σ, and the "goodness of fit" $[\{\Sigma w(F_0 - |F_c|)^2/(m - s)\}^{1/2}]$ of the weighting scheme is 1·01. Isotropic thermal parameters were used for all Al, Si, and O atoms, but not for the Co^{II} ions which refined quite anisotropically to give a temperature factor of $\exp[-0{\cdot}015\,(h^2 + k^2 + l^2) - 0{\cdot}026\,(hk + hl + kl)]$.

In the zeolite structure, Co^{II} ions occupy three-fold axis sites [Wyckoff 8(*g*)] near the six-oxygen windows, but recessed by 0·16(4) Å, into the sodalite cavity (see Figure). Each Co^{II} ion is 2·06(1) Å from three equivalent O(3) atoms [Wyckoff 24(*m*)] arranged trigonally in the six-oxygen (twelve-membered) ring, and the O(3)–Co^{II}–O(3) angle is 119·4(1)°, close to the equilateral trigonal planar angle, 120°. [The distances to the other three oxygen atoms, O(2), in the ring are substantially greater, 3·04(1) Å]. The highly anisotropic ellipsoids found for the Co^{II} ions suggest that this co-ordination situation is not as energetically favourable as those usually encountered by transition-metal ions in their complexes. Trigonal planar co-ordination of Co^{II} and Ni^{II} by bulky ligands has been reported.[6]

In the hydrated material,[7] Co^{II} ions are found by similar methods at two non-equivalent sites. One Co^{II} is at the origin [Wyckoff 1(*a*) at the centre of the sodalite unit] and three are at $x = y = z = 0{\cdot}259$ on the three-fold axes [Wyckoff 8(*g*)]. Upon dehydration these ions move approximately 3·7 and 1·8 Å respectively to the single three co-ordinate site discussed above, at $x = y = z = 0{\cdot}177$. These findings are consistent with and complementary to previous spectroscopic and theoretical results.[8,9]

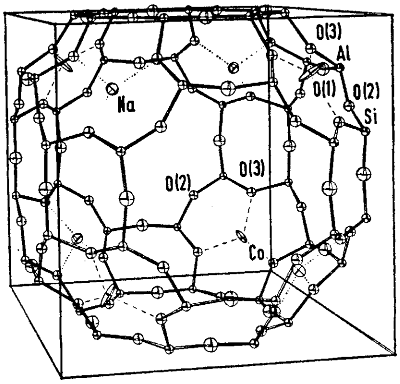

FIGURE. *The unit cell of partially* Co^{II}*-exchanged fully dehydrated zeolite A. Ellipsoids of* 20% *probability are used. The near trigonal planar co-ordination of the* Co^{II} *ions is indicated by dashed lines. Sodium ion co-ordination is indicated by dotted lines.*

The four sodium ions, whose positions [Wyckoff 8(*g*)] cannot be refined independently from those of the Co^{II} ions due to disorder, have been placed at three-fold axis positions near the centres of four six-oxygen windows. The slightly anisotropic thermal co-ordinates found in dehydrated 4A[3] were assumed. By a trial procedure, the Na^+ ion fractional co-ordinate $x = y = z = 0{\cdot}210$ was found to allow the lowest error indices to be reached after least-squares refinement of the co-ordinates of all other atoms.

The zeolite framework exhibits changes, in comparison with the dehydrated 4A structure,[3] of +23°, −16° and −11° at the three non-equivalent oxygen atoms O(1), O(2), and O(3) respectively, indicating a moderate conformational distortion. Also the average Si–O(3) and Al–O(3) distance has become 0·08 Å greater than the corresponding average distances involving O(1) and O(2), which have decreased in length relative to those in dehydrated zeolite 4A. The angle at O(3) is 135°, the smallest reported for a zeolite A structure; furthermore, the Co^{II} ions, by being displaced from the planes of their nearest neighbours [three O(3)'s], are in a better position to co-ordinate with O(3) lone-electron pairs.

We thank the U.S. Army Research Office, Durham (for support) and the University of Hawaii Computing Center.

(*Received*, 18*th September* 1972; *Com.* 1615.)

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