Magnetic Circular Dichroism Identification of Four Distinct Species in the Dehydration of Cobalt(II) Doped Zeolite-A

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Summary M.c.d. spectra and thermogravimetry are used to reassign the species arising from dehydration of Na_4Co_4A (zeolite-A) as four distinguishable structures including a hydrated octahedral, a monohydroxo-tetrahedral, a hydroxo-dicobalt dimer, and a trigonal three-co-ordinate monomer species.

ELECTRONIC spectroscopy is important for understanding the sites of catalytically important transition metal ions in zeolite lattices. Some important structural results have been obtained from reflectance spectroscopy including, for example, the first identification of trigonally co-ordinated Co^{II} in zeolite-A.[1] However, a recent communication indicates the difficulties that arise in the interpretation of small shifts that occur in the position of absorption bands.[2] Many of the ambiguities can be reduced with the aid of magnetic circular dichroism (m.c.d.) spectroscopy because m.c.d. is associated with three band shapes (A, B, and C terms) in contrast with one and dichroism may also change sign.[3]

Akbar *et al.* have proposed that the dehydration sequence of Na_4Co_4A is as in equation (1),[2] where O designates an oxygen of the lattice, in consequence of assignment of

$$Co(OH_2)_6^{2+} \xrightarrow{298\text{ K}} Co(OH_2)_4^{2+} \xrightarrow{400\text{ K}} Co(OH_2)_2O_3 \xrightarrow{500\text{ K}} CoO_3 \qquad (1)$$

absorption spectra. The sign reversals seen in Figure 1 in m.c.d. spectra recorded at 388 and 538 K, and the fact that both spectra are distinct in number and types of bands from the spectra obtained at 613 K for a sample prepared in a manner parallel to that for preparation of the trigonal (D_{3h}) 'CoO_3' species identified by spectroscopy[1] and *X*-ray crystallography,[4] show that the interpretation of the dehydration sequence must be revised. The conclusion is confirmed by thermogravimetry.

The m.c.d. results are very helpful in indicating which temperatures are appropriate for assigning dominance of a single structure. Where sign reversals occur, the m.c.d. signal passed through zero at transitional temperatures of drying. We assign four species which are associated with the four spectra of Figure 1 using this criterion with confirmation from thermogravimetry.

Cobalt(II) doped zeolite-4A was prepared by repeated exposure of powdered zeolite to aqueous cobalt sulphate. Elemental analysis showed doping levels of 4 Co atoms per unit cell and *X*-ray diffraction powdergraphs showed retention of crystallinity[5] both after doping and at all heating stages.

The first [Figure 1(a)] and the fourth [Figure 1(d)] spectra are not controversial. The structures inferred have been the subject of an *X*-ray crystallographic examination.[4] They are the octahedral six co-ordinate and trigonal (D_{3h}) three co-ordinate species, the latter of which is located in a six face.[4] The spectra are easily rationalized by these assignments. The spectrum in Figure 1(b) is clearly that of tetrahedral Co^{II} and is essentially identical to that of $Co(OH)_4^{2-}$.[6] Thus it must be a Co^{II} tetrahedral form with oxygen atoms of an electronegativity similar to

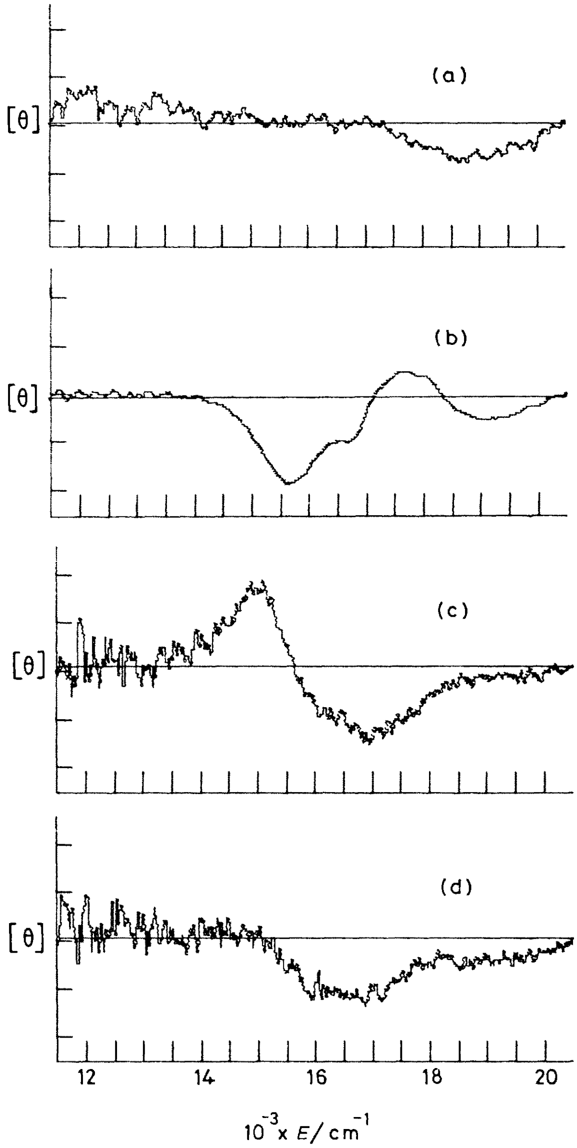

FIGURE 1. M.c.d. spectra (12,000—20,000 cm^{-1}) of cobalt doped zeolite mulls dried at (a) 25 °C, (b) 115 °C, (c) 265 °C, and (d) 340 °C. Ellipticities are arbitrary units.

that of OH^- oxygens. Thermogravimetry (H_2O:Co^{II} ratio 0·88:1) shows that these are three lattice oxygens (probably those of a six face) and one OH^- ligand.

The species which dominates at 538 K [Figure 1(c)] is more of a puzzle. It has an m.c.d. sign opposite to that of the lower temperature tetrahedral form and is quite distinct from the higher temperature trigonal form. Thermogravimetry identifies it clearly as a species with an H_2O:Co^{II} ratio of 1:2. This stoicheiometry suggests a hydroxo-bridged dimer. The sign change in the m.c.d. suggests a rotation by 90° of the axis of 3-fold quantization.[7,8] A plausible assignment which fits a model of the zeolite-A structure postulates the formation of a dimer from tetrahedral species located above neighbouring six faces by movement towards a pair of oxygen atoms at one end of the six face ring. The structure is shown in Figure 2. The three fold axis is 'requantized' from the tetrahedral form yielding a pair of five-co-ordinate chromophores derived from the 'regular trigonal hexahedron' for which the features of the present m.c.d. spectrum have been predicted.[7] Molecular models suggest that the bridging OH^- ligand lies on the $C_4{}^z$ axis of the pseudocell with a Co–OH bond length of 0·29 nm ± 10%.

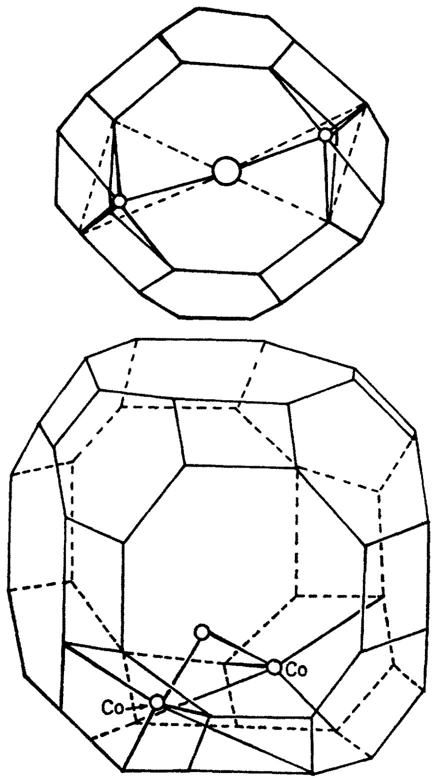

FIGURE 2. Two views of the hydroxo-bridged dimer.

The m.c.d. sign in the spectrum of the high temperature form reverts to that of the tetrahedral species. This suggests that the original axis of quantization has been restored and is consistent with the return of the Co^{II} ions to the centre of a six face on loss of the last shared OH^- ligand.

These conclusions do not confirm earlier assignments. The tetrahedral form $Co(OH_2)_4{}^{2-}$,[2] is not consistent with the oxygen electronegativity required by the spectrum. Moreover, it is without precedent in structural inorganic chemistry. If use is made of m.c.d. spectra and thermogravimetry, including results for temperatures intermediate to those reported in detail here, the recently reported absorption spectra[2] at 300 K can be consistently interpreted as a mixture of 75% octahedral and 25% tetrahedral forms. The spectrum reported at 500 K[2] is consistently assignable as a mixture of the tetrahedral and dimer forms described here. The final three-co-ordinate form is not achieved until 600 K.

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