Dehydration Sequence of Cobalt Exchanged Synthetic A Zeolite: Evidence for 3-, 4-, 5-, and 6-Fold Co-ordination

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Summary For exchanged Na-A synthetic zeolites with cobalt contents of 1—5 atoms per unit cell the dehydration sequence is shown to be $Co^{2+}(H_2O)_6 \xrightarrow[10^{-4}\text{ Pa}]{298\text{K, } in\ vacuo}$ $Co^{2+}(H_2O)_4$ (tetrahedral) $\xrightarrow{400\text{ K, } in\ vacuo}$ $Co^{2+}(Ox)_3\cdot(H_2O)_2$ (trigonal bipyramid) $\xrightarrow{> 500\text{ K, } in\ vacuo}$ $Co^{2+}(Ox)_3$ (trigonal) (Ox refers to oxygen atoms in the 6-rings of the zeolite).

ALTHOUGH there have been several spectroscopic studies of cobalt exchanged Na-A zeolites and their dehydration,[1–3] no clear picture has emerged of the molecular events involved. We have therefore examined a series of 5 zeolites containing respectively 1, 1·7, 2·8, 3·4, and 4·9 cobalt atoms per unit cell [formula $Co_xNa_{12-2x}(AlO_2)_{12}\cdot(SiO_2)_{12}\cdot mH_2O$, where $27 < m < 40$].

The Na-A zeolite (Union Carbide Lot No. 4941040757) contained no binder and was exchanged with Co^{II} chloride solution using standard methods,[1] with careful control of the pH. Visible–u.v. spectra were recorded on a Pye-Unicam SP800 spectrometer with a diffuse reflectance attachment, using a specially constructed vacuum cell. Gravimetric measurements were performed in a vacuum apparatus (ultimate pressure *ca.* 10^{-4} Pa) using a McBain spring (sensitivity 1 mm $\equiv$ *ca.* 4 mg) with a trap cooled to 80 K situated close to the balance case.

The spectra of the hydrated zeolites will be discussed elsewhere[4] but for cobalt contents <4 atoms per unit cell closely resembled that of $Co^{2+}(H_2O)_6$, with the characteristic pale pink colour reported previously.[1] Dehydration under reduced pressure at 298 K caused a gradual colour change to bright blue; the spectrum is shown in the Figure, curve 1. This spectrum was the same for all zeolites studied. Dehydration at 400 K caused the emergence of the spectrum shown in curve 2, the sample remaining bright blue. The bands at *ca.* 16 000 and *ca.* 17 000 cm^{-1} are shifted *ca.* 300 cm^{-1} to higher frequency for lower cobalt contents. For cobalt contents <4 atoms per unit cell dehydration at $T \geqslant 500$ K caused the sample to turn pale blue, with the spectrum shown in curve 3. For $Co_{4\cdot9}$ the sample remained bright blue and the features at 13 500, 24 000,

TABLE

Zeolite	Water content, before dehydration (mol per unit cell)	Water loss during dehydration (mol per unit cell)		
		At 298 K	At 400 K	At 600 K
Na-A	24·5	16·7	4·7	3·1
Co_1	30·5	20·6	4·5	5·4
$Co_{1\cdot7}$	31·0	22·3	4·8	3·9
$Co_{2\cdot8}$	33·5	20·6	6·6	6·3
$Co_{3\cdot4}$	35·8	21·2	7·9	6·7
$Co_{4\cdot9}$	38·8	18·6	9·9	10·3

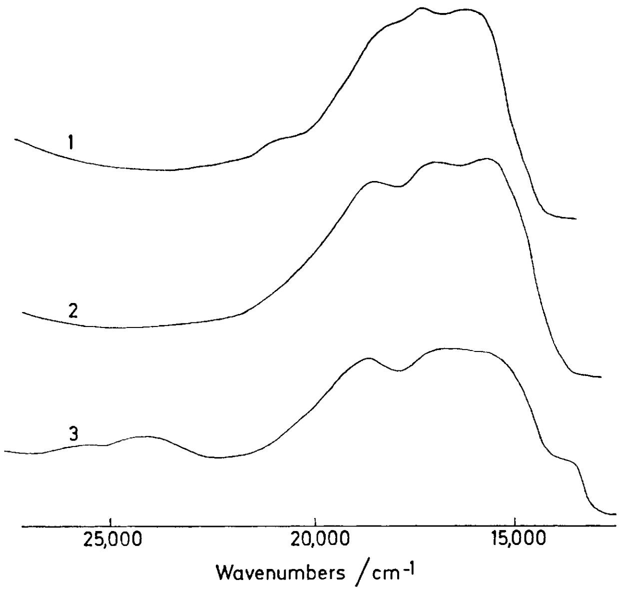

FIGURE. Diffuse reflectance spectrum of $Co_{2\cdot 8}$–A zeolite: curve 1, after dehydration *in vacuo* at 298 K; curve 2, after dehydration at 400 K; curve 3, after dehydration at 600 K. (1 cm^{-1} = 3×10^{10} Hz).

and 25 750 cm^{-1} emerged only weakly at $T \leqslant 670$ K. The Table shows the water content of the unit cells of the zeolites at each stage of dehydration, determined using the McBain spring.

The spectrum after the first stage of dehydration (curve 1) has been observed by Klier[1] on exposing fully dehydrated Co_1-A zeolite to water vapour. He noted its similarity to that of the $Co(OH)_4^{2-}$ tetrahedral complex,[5] suggesting that its structure was probably $Co^{2+}(Ox)_3{\cdot}H_2O$, although $Co^{2+}(H_2O)_4$ could not be ruled out (Ox refers to an oxygen atom in the zeolite 6-ring framework). We assign the spectrum to $Co^{2+}(H_2O)_4$ for two reasons. For $Co_{3\cdot 4}$ and $Co_{4\cdot 9}$ the water:cobalt ratio after dehydration at 290 K is *ca.* 4:1. This suggests that all the non-co-ordinated water has been removed, leaving only the $Co^{2+}(H_2O)_4$ complexes. For the other zeolites H_2O:Co always exceeds 4:1 at this stage. Also, the results show that two further dehydration stages occur, while only one stage can be envisaged for $Co^{2+}(Ox)_3{\cdot}H_2O$.

For cobalt contents <4 atoms per unit cell the final spectrum (curve 3) is identical to that reported[1] for dehydrated Co_1 zeolite. Klier assigned it to cobalt trigonally co-ordinated to oxygen atoms in the 6-ring, $[Co^{2+}(Ox)_3]$, and this was subsequently confirmed by *X*-ray diffraction.[6] The 6-ring was shown to undergo significant distortion on forming the complex.[6] For $Co_{4\cdot 9}$ the spectral transition from curve 2 to 3 is incomplete, the sample remains bright blue, and the features at 13 500, 24 000, and 25 750 cm^{-1} are weak even though the gravimetric measurements indicate complete dehydration. For cobalt contents >4 atoms per unit cell, framework oxygen atoms must be shared by two $Co^{2+}(Ox)_3$ complexes and thus cannot be distorted to the extent that occurs at lower cobalt contents.

For the intermediate stage of dehydration, at *ca.* 400 K the gravimetric results show that, at least at high cobalt contents, the stoicheiometry is $Co(H_2O)_2$. Since the cobalt ion ultimately resides in the 6-ring, we suggest that its structure at this stage is $Co^{2+}(Ox)_3(H_2O)_2$, with the trigonal bipyramid structure, one water molecule pointing into the large cavity and one into the sodalite unit. This structure is proposed for three reasons. (i) Five-co-ordinate complexes of cobalt(II) are well known with the trigonal bipyramid structure. The energy level diagram[7] predicts three broad peaks as noted here and similar features are found in the spectrum of the complex $Co[(Me_2N{-}CH_2{-}CH_2)_3N]Br$.[7] (ii) *X*-Ray diffraction[8] has established the existence of an identical 5-co-ordinate complex of manganese(II). (iii) This structure explains the comparative stability of stage II since, as shown by Seff,[8] both water molecules can form hydrogen bonds to framework oxygen atoms.

It is interesting to note that during the dehydration process the cobalt co-ordination number changes from 6 to 4 to 5 to 3.

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