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The Structure of a Carbon Monoxide Adduct of Cobalt-Exchanged Zeolite A ($Co_{5.25}Na_{1.5}$–A · 1.5CO) by Neutron Profile Refinement

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The structure of a carbon monoxide adduct of cobalt-exchanged zeolite A, $CO_{5.25}Na_{1.5}$–A · 1.5CO, has been determined by Rietveld neutron profile refinement. The space group used was $Fm\bar{3}c$ with a = 24.1557(14) Å; the final R_{pw} was 13.8%. All exchangeable cations are located in sites adjacent to the 6-rings; 3.75 of the cobalt cations sit 0.4 Å inside the β-cage (Co(2)) and are arranged tetrahedrally about the eight 6-ring sites in the β-cage. The sodium cations (Na(1)) reside just inside the α-cage in sites similar to those found previously for zeolites 3A, 4A, and 5A. The remaining 1.5 cobalt cations (Co(1)) are located in sites similar to those for sodium, but they are also coordinated to the carbon monoxide molecules, which lie on, or close-to, the threefold axis which passes through the 6-ring. Inside the β-cage there is a tetrahedral aluminum complex of AlO_4 type, the oxygen atoms (O*) of which point toward six rings not occupied by cobalt cations, Co(2). Each of the oxygen atoms of this complex is involved in a hydrogen bond (2.83 Å) to the 6-ring oxygen O(3). Approximately 2/3 of these bonds are of type O*–H· · ·O(3) and 1/3 of type O*· · ·H–O(3).

Introduction

Riley and Seff (*1*) studied the structure of a dehydrated partially cobalt-exchanged zeolite A (Co_4Na_4–A) and its carbon monoxide sorption complex using single-crystal X-ray diffraction data. The structure determinations were carried out in space group $Pm\bar{3}m$ (a = 12.3 Å), which is a first approximation to the true structure. Two exchangeable cation positions were located. Both Co(1) and Na(1) were found to be trigonally coordinated to the O(3) atoms of the 6-rings with Co(1) projecting slightly into the α-cage (large cavity) while Na(1) projected into the β-cage (sodalite unit). It was suggested that inter-cobalt ion interactions would be minimized if the Co^{2+} ions were distributed tetrahedrally over the 8 possible 6-ring sites in each α-cage. The carbon monoxide molecule was found to interact with Co^{2+}, but not Na^+, and lie along the $\bar{3}$ axis. The observed Co(1)–C(1) bond length was 2.29(16) Å, while sorption of the gas caused Co(1)–O(3) to increase from 2.077(18) to 2.113(13) Å. The C(1)–O(4) bond length of the carbon monoxide molecule was 1.07(16) Å compared to ~1.15 Å usually found in cobalt carbonyls (*2*) and 1.128 Å in gaseous CO. In the dehydrated structure Riley and Seff (*1*) noted small electron density peaks at the center of the β-cage and at positions ~2 Å away along [111] at $x = y = z = 0.09$. In the sorption complex only the origin peak was observed. These small peaks were not included in the model, but Riley and Seff (*1*) concluded that they were due to a

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small amount of hydrated Co^{2+} in an octahedral arrangement, trapped in the β-cage.

It was decided to reinvestigate the structure of the carbon monoxide adduct of Co–A using Rietveld profile refinement methods in space group $Fm\bar{3}c$ for several reasons. First, as a test of the profile refinement method itself. This adduct is somewhat more complicated than the dehydrated ion-exchanged samples of zeolite A studied to date (*3–7*). Second, previous refinements of zeolite A samples using $Pm\bar{3}m$ have on occasion given results which have been shown to be spurious when refinements in $Fm\bar{3}c$ have been performed (see, e.g. (*8, 9*)). Now, although $Fm\bar{3}c$ is only an approximation to the correct space group—it is the group of the aluminosilicate framework undistorted by exchangeable cations and guest species—it is known to be a rather better approximation than $Pm\bar{3}m$ (*10*). Third, it was considered that neutron diffraction might help elucidate the nature of the species found inside the β-cage. X-Ray studies by Pluth and Smith on Ca–A and Sr–A (*11, 12*) have suggested "AlO_4"-type materials, but whether the O is present as O^{2-}, OH^-, or OH_2, or indeed as a mixture of these could not be determined from the X-ray data. Finally, in our previous studies on 3A, 4A, and 5A zeolites (*3–5*) the Na^+ cations bonded to the 6-ring were found just inside the α-cage, rather than the β-cage. We hoped to clear up this discrepancy between our previous studies and those of Riley and Seff (*1*). A preliminary structural study was made on the cobalt-exchanged zeolite itself—$Co_{5.25}Na_{1.5}$–A. This showed two scattering density maxima along the $\bar{3}$ axis near the 6-ring. The peak inside the β-cage was much larger than that inside the α-cage, suggesting strongly that the Co^{2+} ions were the species present inside the β-cage, with the Na^+ cations inside the α-cage ($5.25 \times b_{Co} = 1.47$, $1.5 \times b_{Na} = 0.52$).

Experimental

The sample used in this study was derived from a commercially available 4A zeolite manufactured by Union Carbide (Linde). Ten grams of the zeolite was ion-exchanged using 5 dm^3 of 0.02 mole dm^{-3} cobalt(II) nitrate solution for 23 hr at 82°C with constant stirring. The pH of the solution was ~5.8 when measured at room temperature. The resultant purple solid was washed twice with 5 dm^3 of deionized water to remove excess exchanging salt. Subsequent drying in a vacuum desiccator yielded a blue powder which turned pink on exposure to moist air. Silicon and aluminum were determined by gravimetric procedures (*3*) and residual sodium was analized by atomic absorption spectrometry. The cobalt content of the zeolite was measured by atomic absorption, EDTA titration, and colorimetry using the red complex formed with nitroso-R salt (sodium 1-nitroso-2-hydroxynaphthalene-3,6-disulfonate). Water was determined using thermogravimetric analysis. The Si/Al ration was found to be 1.02 ± 0.02 and therefore the framework of the zeolite was stoichiometric within the analysis limit (*14*). The final composition was $Co_{42}Na_{12}Si_{96}Al_{96}O_{384} \cdot 36H_2O$.

The neutron powder diffraction data were collected on the high-resolution diffractometer D1A at the Institut Laue-Langevin, Grenoble (*15*). Five grams of the zeolite powder were loaded into a 16-mm-diameter vanadium sample can and dehydrated in the D1A vacuum furnace at 320 ± 2°C and 5×10^{-4} Torr for 18 hr. The sample was then allowed to cool under vacuum to ~250°C. At this temperature the carbon monoxide gas was introduced into the furnace at ~1140 Torr. The sample was equilibrated with the gas in the cylinder for 2 hr while cooling to room temperature occurred. The furnace and sample were then sealed before data collection commenced.

Because the sample was prepared *in situ* no independent determination of the carbon monoxide content of the sample was made. The diffraction data were collected from 6.04 to 158.04° (2θ) for 22 hr at a neutron wavelength of 1.909 Å. The background was estimated by linear interpolation from regions where no Bragg scattering occurred. The peak intensities were found to be less than the statistical scatter of the data points beyond 131° (2θ) and the data set was therefore truncated at this value ($0.03 < \sin\theta/\lambda < 0.476$). Peaks which occurred below 20° (2θ) were found to suffer from slight asymmetry and this portion of the diffraction trace was omitted from the refinement, as was found necessary in previous studies (*3–5*).

Structure refinement was carried out using the Rietveld technique (*16, 17*) with the programs of Hewat (*18, 19*). The scattering lengths used were taken from the "International Tables for X-Ray Crystallography" (*20*). A total of 377 reflexions contributed to the profile intensity between 20 and 131° (2θ) when using a 24.6-Å cell.

Structure Refinement

A preliminary refinement was carried out in space group $Pm\bar{3}m$ using the framework coordinates of Riley and Seff (*1*) as a starting model. Refinement of all the atom coordinates and isotropic thermal parameters gave $R_{pw} = 24.6\%$ and introduction of anisotropic thermal parameters lowered this to 21.3%.

After transforming the coordinates, refinement was begun in space group $Fm\bar{3}c$ (with $a = 24.6$ Å). Refinement of all the coordinates and isotropic thermal parameters gave $R_{pw} = 26.5\%$. A difference Fourier map calculated at this stage revealed three peaks of scattering density on the $\bar{3}$ axis at $x = y = z$ values of ~0.08, 0.11, and 0.16 (Fig. 1). These peaks were interpreted as being due to Co(2), Co(1)/Na(1), and C(1) (of the carbon monoxide molecule), respectively. The oxygen atom of the carbon monoxide molecule was not resolved in this difference plot either on, or just adjacent to, the $\bar{3}$ axis. A suitable position for this oxygen atom O(4) was calculated 1.07 Å along the $\bar{3}$ axis from C(1) (see Ref. (*1*)). Introduction of atoms at all of these sites (except Na(1)) reduced R_{pw} to 21.0%. Inclusion of Na(1) at a site equivalent to that found previously for Linde 4A ($x = y = z = 0.10102$) and a refinement with anisotropic thermal parameters for the framework atoms reduced R_{pw} to 17%. A second difference Fourier map showed peaks inside the β-cage at the origin and at $x = y = z = 0.041$, i.e., the central atom appeared to be surrounded in cubic fashion by eight equivalent species. These peaks were considered to derive from two disordered tetrahedral entities of AlO_4 type, each accounting for half of the central peak intensity and four of the eight peaks lying on the $\bar{3}$ axes. This type of arrangement has been found previously by Pluth and Smith in dehydrated Ca–A (*11*) and Sr–A (*12*). Refinements were carried out with increasing amount of aluminum (Al*) and oxygen (O*) until a positive isotropic thermal parameter was obtained for Al*. It appeared that ~3/4 of the β-cages were occupied by the "AlO_4" ions; R_{pw} decreased to 14.4%.

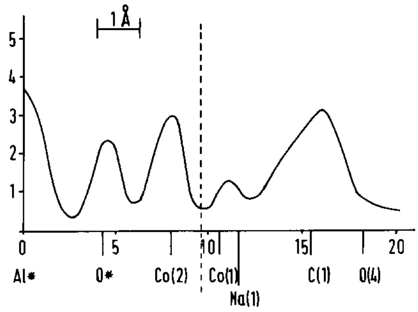

FIG. 1. F_0 projection of the scattering density along [111]. The dashed line indicates the intersection of [111] with the plane of the 6-ring.

In the next stage of refinement, the occupancies of Co(1) and Co(2) were adjusted so that their thermal parameters were approximately equal; this yielded 12 Co(1) and 30 Co(2) cations per unit cell. The site occupancies of C(1) and O(4) were constrained to be equal to that of Co(1).

Since the exact identity of the "AlO$_4$" species in the β-cage had not previously been established, a further Fourier difference map was calculated and searched in the region of the oxygen atoms. Minima indicative of hydrogen atom positions were located along the line from O* to the framework oxygen O(3). Figure 2 shows a one-dimensional F_{obs} trace along O*–O(3). There are two minima, approximately 1 Å from O* and O(3), respectively. Since rotation around the $\bar{3}$ axis gives only three lines on which there are hydrogen atoms (O*–O(3), O(3^{i}), O(3^{ii})), the possibility that the oxygen atoms O* are constituent parts of water molecules can be ruled out. The O* atoms must, on the whole, be part of OH groups, although the possibility of a small percentage of O^{2-} ions cannot be dismissed.

A totally free refinement of all atomic species present at this stage proved impossible, so Al*–O* was fixed at 1.80 Å—the distance found in the hydroxide (*12*). In addition, Na(1)–O(3) was constrained to the bond length found in our previous refinement of Linde 4A, while C(1)–O(4) was constrained at 1.17 Å, the value found in $Co_5(CO)_{15}C_3H$ (*21*). Hydrogen atoms were added to the refinement, H*(1) bonded to O* and H*(2) bonded to O(3). Both atoms were constrained to be 1.0 Å from their oxygen neighbor and their site occupancies were adjusted until the thermal parameters for these sites had similar values. The final R_{pw} obtained with this model was 13.8% with R_p = 15.8%, which is as close to the expected R-factor based on counting statistics (11.4%) as is usually found in this type of refinement.

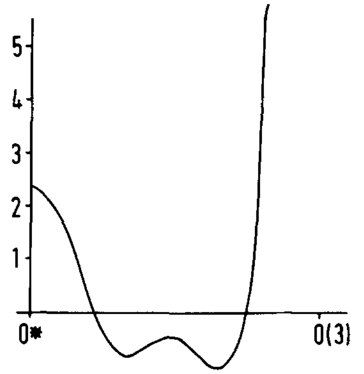

FIG. 2. One-dimensional F_{obs} projection along the line between O* and O(3). The two minima correspond to hydrogen atom positions.

Final atomic parameters are given in Table I; the bond distance and angle formation appears in Table II. The observed and calculated diffraction profiles are given in Fig. 3.

It was noteworthy that examination of the separated F_{obs} and F_{calc} values at the end of the refinement showed that many reflexions of type (odd, odd, odd) had significant intensities, e.g., 531, 731, 973 and 11, 7, 5. This suggests that the choice of space group $Fm\bar{3}c$ was indeed more appropriate than $Pm\bar{3}m$.

Discussion

In addition to the usual complexities found in dehydrated zeolite structures, such as incomplete cation exchange, this sorption complex contained carbon monoxide and the aluminum complex found in the β-cages. Since totally free refinements proved impossible, it was necessary to constrain some of the bond lengths to fixed values. As a result, there were only three more refineable parameters than were used in the refinement of the 4A structure (*3*). The relatively high value of the expected R-factor (11.4%) is due, first, to some framework damage resulting from hydrolysis during the ion-exchange procedure, and second, to the presence of some hydrogen atoms in the structure. Both of these factors create high

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS FOR $Co_{5.25}Na_{1.5}$–A CARBON MONOXIDE COMPLEX IN $Fm\bar{3}c$

Site	Position	Population	x	y	z	β or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si(1)	96(i)	96	0	0.0927(5)	0.1836(6)	42(4)	1(2)	19(3)	0	0	−4(2)
Al(1)	96(i)	96	0	0.1828(6)	0.0906(7)	7(2)	9(3)	33(4)	0	0	20(3)
Co(1)	64(g)	12	0.1067(6)	0.1067(6)	0.1067(6)	16(10)	16(10)	16(10)	−23(6)	−23(6)	−23(6)
Co(2)	64(g)	30	0.0804(7)	0.0804(7)	0.0804(7)	18(3)	18(3)	18(3)	5(3)	5(3)	5(3)
Na(1)	64(g)	12	0.1172	0.1172	0.1172	91(45)	91(45)	91(45)	89(46)	89(46)	89(46)
O(1)	96(i)	96	0	0.0959(3)	0.2490(5)	35(2)	33(2)	15(1)	0	0	20(3)
O(2)	96(i)	96	0	0.1489(5)	0.1499(5)	35(1)	21(3)	9(2)	0	0	10(1)
O(3)	192(j)	192	0.0543(3)	0.0573(3)	0.1589(2)	24(2)	22(2)	33(2)	14(1)	− 2(2)	−11(2)
C(1)	64(g)	12	0.1552(10)	0.552(10)	0.1552(10)	28(4)	28(4)	28(4)	21(6)	21(6)	21(6)
O(4)	64(g)	12	0.1832(10)	0.1832(10)	0.1832(10)	72(3)					
Al*	8(b)	6	0	0	0	6.5(10)					
O*	64(g)	24	0.0430	0.0430	0.0430	16(1)					
H*(1)	192(j)	16	0.0470	0.0480	0.0839	5(2)					
H*(2)	192(j)	8	0.0503	0.0502	0.1178	3(4)					

Note. Anisotropic displacement factor given by $10^4 \exp(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} = 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$; $R_p = 100\Sigma|y(\text{obs}) - (1/c)y(\text{calc})|/\Sigma|y(\text{obs})|$, $R_{pw} = 100[\Sigma w(y(\text{obs}) - (1/c)y(\text{calc}))^2/\Sigma(y(\text{obs}))^2]^{1/2}$, where w is the weight at each 2θ step and y(obs) and y(calc) are the observed and calculated intensities at that point: c is the scale factor.

TABLE II

BOND DISTANCES (Å) AND ANGLES (°) FOR $Co_{5.25}Na_{1.5}$–A CARBON MONOXIDE COMPLEX IN $Fm\bar{3}c$[a]

Si(1)–O(2)	1.582(16)	O(1)–Si(1) –O(2)	118.0(9)
Si(1)–O(1)	1.582(19)	O(1)–Si(1) –O(3)	112.5(6)
Si(1)–O(3), O(3^{iv})	1.677(11)	O(2)–Si(1) –O(3)	104.8(6)
Al(1)–O(2)	1.653(19)	O(3)–Si(1) –O(3^{iv})	102.9(7)
Al(1)–O(1^{ix})	1.654(19)	O(1^{ix})–Al(1) –O(2)	115.1(10)
Al(1)–O(3^{ii}), O(3^{v})	1.735(12)	O(1^{ix})–Al(1) –O(3^{ii})	111.9(6)
Co(1)–O(3), O(3^{i}), O(3^{ii})	2.147(17)	O(2)–Al(1) –O(3^{ii})	105.8(7)
Co(1)–O(2), O(2^{i}), O(2^{ii})	2.963(17)	O(3^{ii})–Al(1) –O(3^{v})	105.6(9)
Co(2)–O(3), O(3^{i}), O(3^{ii})	2.072(17)	Si(1)–O(1) –Al(1^{viii})	172.6(8)
Co(2)–O(2), O(2^{i}), O(2^{ii})	3.055(17)	Si(1)–O(2) –Al(1)	150.5(10)
Na(1)–O(3), O(3^{i}), O(3^{ii})	2.327	Si(1)–O(3) –Al(1^{i})	132.9(7)
Na(1)–O(2), O(2^{i}), O(2^{ii})	3.038	O(3)–Na(1)–O(3^{i})	98.3
Co(1)–C(1)	2.03(3)	O(3)–Co(1)–O(3^{i})	110.0(7)
C(1)–O(4)	1.17	O(3)–Co(2)–O(3^{ii})	116.3(8)
Al*–O*, O*^{iii}, O*^{vi}, O*^{vii}	1.80	O(3)–Co(1)–C(1)	108.9(10)
O*–H*(1), H*(1^{i}), H*(1^{ii})	1.00	O*–Al* –O*^{iii}	109.5
O*–O(3), O(3^{i}), O(3^{ii})	2.83	Al*–O* –H*(1)	134.1
O*–H*(2), H*(2^{i}), H*(2^{ii})	1.83	O*–H*(1)–O(3)	180.0
O(3)–H*(1)	1.83	O(3)–H*(2)–O*	180.0
O(3)–H*(2)	1.00		

Symmetry code

(i) z, x, y
(ii) y, z, x
(iii) $x, -y, -z$
(iv) $-x, y, z$
(v) $-y, z, x$
(vi) $-x, y, -z$
(vii) $-x, -y, z$
(viii) $-x, z, \frac{1}{2} - y$
(ix) $x, \frac{1}{2} - z, y$

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[a] The e.s.d's in the last figure are given in parentheses.

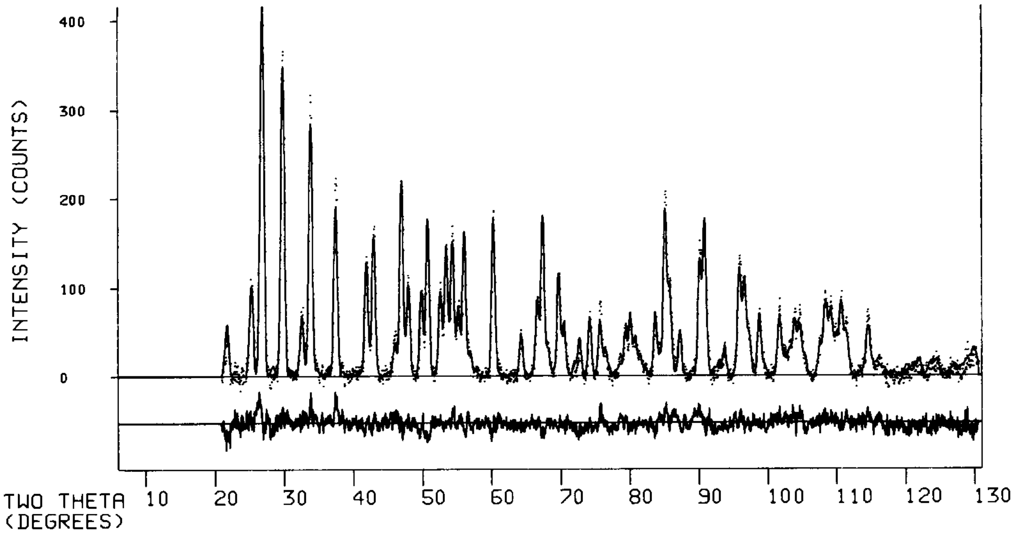

FIG. 3. Cobalt 4A C–O complex at 300 K on the high-resolution diffractometer D1A. Observed (···) and calculated (—) neutron diffraction patterns, together with difference plot, for the title compound.

backgrounds, with relatively poor counting statistics.

Framework Structure

The mean Si–O and Al–O bond length show the bimodal distribution expected of alternation of Si and Al tetrahedra. However, the mean bond lengths (1.63 and 1.70 Å) are just significantly different from those expected for "pure" Si–O and Al–O bonds (1.60 and 1.74 Å, respectively). Moreover, the tetrahedra are rather distorted, for reasons which are not totally clear, but may be connected with the low scattering power of Si, Al for neutrons and the consequent large e.s.d.'s for the positions of these atoms. Significantly, perhaps, the average (Si, Al)–O bond lengths obtained by Riley and Seff (*1*) (Table III) show the same trend as that found here with (Si, Al)–O(1), O(2) shorter, and (Si, Al)–O(3), longer than expected. If we compare the distances from the centroid of the 6-ring (denoted CEN) to the O(2) and O(3) framework oxygen sites in this structure and those of zeolites 4A(3) and 3A(4) we observe a decrease in CEN–O(3) and increase in CEN–O(2) with decreasing ionic radius and increasing ionic charge.

Aluminum Complex

The complex at the center of the β-cage could have formed in one of three ways. First, it could be due to occluded sodium aluminate trapped in the framework during synthesis of the parent 4A zeolite. Second, it could be a remnant $[Co(H_2O)_x]^{2+}$ species trapped during ion-exchange as suggested by Riley and Seff (*1*), and third, it could be hydrated or hydroxylated aluminosilicate

TABLE III

BOND DISTANCES (Å) FOR Co_4Na_4—A · 4CO (RILEY AND SEFF (*1*)) IN $Pm\bar{3}m$

(Si, Al)–O(1)	1.611(6)
(Si, Al)–O(2)	1.634(8)
(Si, Al)–O(3)	1.701(8)
Co(1)–O(3)	2.113(15)
Co(1)–O(2)	2.948(18)
Na(1)–O(3)	2.126(15)
Na(1)–O(2)	3.081(16)
Co(1)–C(1)	2.29(16)
C(1)–O(4)	1.07(16)

species formed during the ion-exchange procedure.

Occluded aluminate can be ruled out since the sample used here was prepared from a batch of Linde 4A whose structure has been determined (*3*) and does not contain any complex in the β-cage. A hydrated cobalt species is also unlikely since such a complex would have been destroyed on dehydration. The third possibility therefore seems the most likely. Pluth and Smith have previously suggested species such as $(Al_xSi_{1-x})O_4^{-x}$ or $(Al_xSi_{1-x})O_4H_x$ as the entities found in the β-cages in Ca–A and Sr–A samples (*11, 12*). Since there is considerable evidence that aluminum is more readily extracted from zeolite frameworks than silicon (*22*) and forms mobile species at low levels of hydrolysis, we have assumed the metal ion in the complex to be Al. Moreover, since the oxygen atoms of the complex lie along the $\bar{3}$ axes, the environment around Al is cubic: we have interpreted this in the same way as Pluth and Smith (*11, 12*) as being due to a tetrahedral ion which has two possible orientations. The identity of the oxygen species of this complex has not previously been determined, but could be O^{2-}, OH^-, OH_2, or a mixture of these. If O^{2-} were present there would be no evidence of hydrogen atoms nearby, whereas (since the oxygen lies on a threefold axis) if OH^- were present there should be three hydrogen positions, each ~1 Å from O* and lying along the O*–O(3) direction since this bond has a typical hydrogen-bonding distance of ~2.8 Å. If water molecules were present, six hydrogen positions would be likely to be found on rotation about the [111] direction.

From the difference Fourier maps it was found that OH^- were the species present. However, the site occupancies for the hydrogen atoms showed ~2/3 of a hydrogen atom per O* oxygen bonded to O* (i.e., H*(1)) with ~1/3 of a hydrogen atom per O* oxygen atom bonded to O(3) (i.e., H*(2)). For ~2/3 of the O* oxygen species, then, we have OH^- and ~1/3 of the time O* is O^{2-} which is hydrogen-bonded to hydrogen atom attached to O(3) (Fig. 4).

Exchangeable Cation Positions

All of the exchangeable cations have been located in 6-ring sites and no evidence of scattering density in the 8-ring was observed.

The scattering density along the $\bar{3}$ axis, near the plane of the 6-ring, consists of two separate peaks (Fig. 1) of which the larger lies on the β-cage side and the smaller on the α-cage side of the 6-ring. Three cation positions have been proposed to model the observed scattering density based on the following criteria. First, in the preliminary refinement of our sample of dehydrated Co–A the majority of the cobalt cations were located on the β-cage side of the 6-

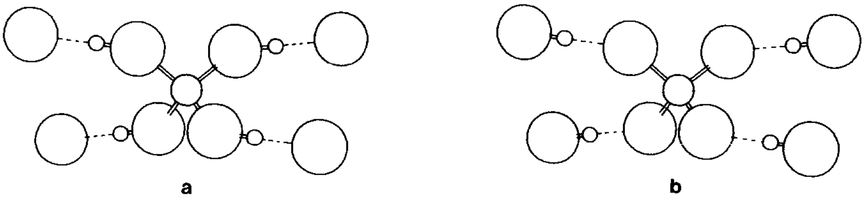

FIG. 4. (a) $Al(OH)_4$ complex and (b) Al(O)· · ·H complex. Hydrogen-bonding arrangement around the Al complex found in the β-cage. Two extremes are shown. Of the two alternative hydrogen positions, that bonded to the Al–O fragment has an occupancy of ~2/3 of that of the oxygen to which it is bonded while the occupancy of the other is ~1/3, i.e., for any particular bond, ~2/3 of the time there is Al(OH)· · ·O(3) and ~1/3 of the time there is Al(O)· · ·HO(3).

ring and scattering density at this same site was confirmed early in the refinement of the present structure. Second, in our previous studies on zeolites 3A(4), 4A(3), and 5A(5) we have found sodium cations located in the 6-ring α-cage site, while none have been found in the β-cage site. Moreover, this situation also exists in the dehydrated Co–A structure. Third, it was not considered likely that there would be any strong interaction between sodium ions and CO molecules. This suggests that upon exposure to CO gas, some Co ions previously just on the β-cage side of the 6-ring might move through the ring to α-cage sites in order to bond to the CO molecules. Various constraints exist upon atom populations in these sites. The total number of sodium ions is known as is the total number of cobalt ions. Moreover, the number of cobalt ions in the α-cage site must be equal to the number of CO molecules. These considerations result in describing the scattering density peak on the α-cage site by two cations positions (one sodium, one cobalt). These positions are highly correlated and, for this reason, the position of Na(1) was constrained.

Co(2) lies just on the β-cage side of the 6-ring: it projects 0.14 Å into the β-cage and is in near-trigonal planar coordination to O(3). Because of the presence of the Al complex in the β-cage these cobalt ions are constrained to take up a tetrahedral distribution over the 6-ring β-cage sites, occupying 6-rings which do not have O* atoms pointing toward them, otherwise Co(2)–O* would only be 1.56 Å. Occupancy of alternate 6-rings by Co(2) and O* results in a Co(2)–O* distance of 3.24 Å.

Co(1) lies on the α-cage 6-ring site in near tetrahedral coordination to O(3), $O(3^{i})$, $O(3^{ii})$, and C(1). The Co(1)–C(1) distance of 2.03 Å is larger than that usually found in cobalt carbonyls (1.75–1.79 Å). The reasons for this are described by Riley and Seff (*1*), but basically arise from coordination of CO to Co^{2+} rather than Co^0. Co^{2+} is a d^7 ion and the ligand field stabilization energies disfavor the tetrahedral configuration over the octahedral one to a lesser extent than other *d*-electron arrangements. Co(1) is in a stable environment, especially compared with the trigonal planar arrangement of Co(2).

Carbon Monoxide

The relative lack of scattering density from O(4) in Fourier maps indicates that this oxygen atoms is either undergoing a high degree of thermal motion, or is positionally disordered, or both. The large thermal motion might be expected since the nearest neighbor (apart from C(1)) is O(4) on an adjacent CO molecule 4.5 Å away (Fig. 5). Moreover, the Co^{2+}–C–O bond could well be bent: M–C–O angles are commonly found between 165 and 179° (*23*). Since the molecule lies along a threefold axis, any deviation of O(4) away from this axis would generate three equally probable positions for O(4).

The (C1)–O(4) distance was fixed at the value observed in $Co_5(CO)_{15}C_3H$ (*21*). However, it should be noted that Angell and Schaffer (*24*) have studied CO sorbed on X and Y zeolites and found an increase in the C–O stretching frequency of ~60 cm^{-1} which implies some shortening of the bond from that found for CO bonded to neutral atoms.

Protons Derived from Hydrolysis of Zeolite Framework during Ion Exchange

We have found no evidence of H^+ in this structure, apart from that associated with the "AlO_4" complex found in the β-cage. Six of these complexes exist per 24-Å cell and resonance occurs between situations corresponding to $[Al(OH)_4^- \; . \; . \; . \; O\lhd]$ and $[Al(OH)_3 \; . \; . \; . \; HO^+\lhd]$. It should be born in mind, however, that crystallographic studies would only find evidence of free protons if these positions were ordered over many unit cells.

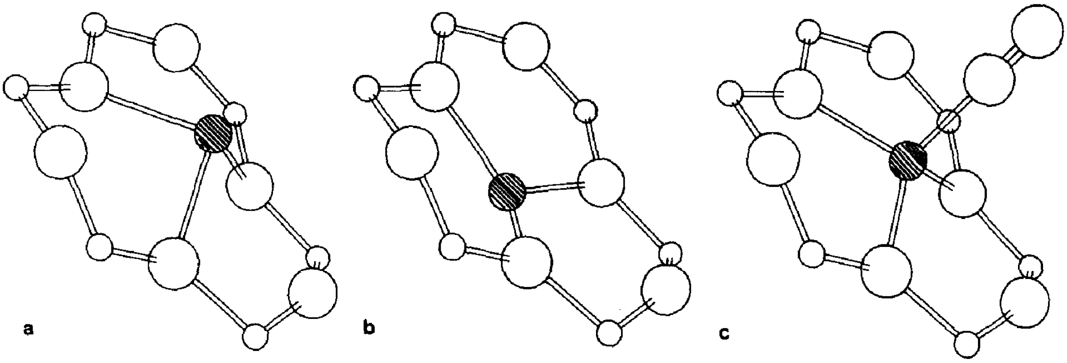

FIG. 5. Plot of nearest neighbor atoms for the exchangeable cations (shaded). Sites in cobalt C–O complex: (a) Na(1); (b) Co(2); (c) Co(1). The oxygen atoms to which these cations are bonded are O(3), O(3^{i}), O(3^{ii}).

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