Crystal Structures of Dehydrated Partially Cobalt(II)-Exchanged Zeolite A and of Its Carbon Monoxide Adduct

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The crystal structures of two forms of partially Co(II)-exchanged zeolite A have been determined from three-dimensional X-ray diffraction data gathered by counter methods. Both structures were solved and refined in cubic space group $Pm3m$. At 20 (1)° the unit cell constants are 12.087 (5) Å for the fully dehydrated form, stoichiometry $Co_4Na_4Si_{12}Al_{12}O_{48}$, and 12.093 (4) Å for its carbon monoxide adduct, stoichiometry $Co_4Na_4Si_{12}Al_{12}O_{48} \cdot 4CO$, in equilibrium with CO at 716 Torr. In each structure, each Co(II) ion lies on a threefold axis so as to protrude somewhat into the large central cavity of the zeolite. At this position bonds to three equivalent zeolite framework oxygen atoms are formed. For the fully dehydrated crystal the Co(II) ions are coordinated by these three framework atoms only; the Co(II) to O distance is 2.08 (2) Å and the angle subtended at Co(II) is 117 (1)°, close to the idealized trigonal-planar value. Upon addition of carbon monoxide to this system the Co(II) ions become four-coordinate. The Co(II) to O bonds lengthen to 2.11 (2) Å and the angle at the Co-(II) ions decreases to a more tetrahedral value of 114 (1)°. One molecule of carbon monoxide is held by each Co(II) ion at a Co(II) to C distance of 2.29 (16) Å. The length of this bond implies a weak interaction which in turn suggests that the synergic bonding normally regarded as essential to transition metal–carbonyl complexation is very much diminished or absent. To distribute positive charge more uniformly, the Na+ ions of each structure, which select the remaining similar threefold axial positions, are recessed into the sodalite cavities. No interaction between CO molecules and Na+ ions is observed. Full-matrix least-squares refinement has converged to a conventional R index (on F) of 0.072 for the dehydrated structure using 101 reflections for which $I_o > 3\sigma(I_o)$ and 0.066 for its carbon monoxide adduct using 120 similarly selected observations.

Introduction

The open frameworks of crystalline molecular sieve zeolites allow ready exchange of numerous cations and the sorption of a variety of small molecules. For example, such chemically diverse ions as Na+, Tl(I), Ag+, Ca2+, Pb(II), Hg-(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(I), and Cu(II) have been studied intrazeolitically in conjunction with sorbed molecules of equally broad chemical variation (elemental iodine, phosphorus, sulfur, and tellurium; CO, CO_2, NO, N_2O, NH_3, and H_2O; cyclopropane, acetylene, methyl isocyanide, and pyridine).[1-15] The breadth of these studies is apparently limited by metal ion charge (for example, trivalent cations tend to destroy some zeolite frameworks) and the bulk or size of sorbed molecules. Because zeolites often crystallize in cubic systems and because the aluminosilicate frameworks are anionic, the exchangeable cations usually occupy sites of high symmetry (threefold axes, mirror planes) close to the oxygen atoms of the framework. Upon sorption, competition between the framework and sorbed molecules for cation coordination sites often results in appreciably distorted or unusual coordination geometries.

For example, in the hydrated form of partially Mn(II)-exchanged zeolite 4A (ref 16 and 17 offer a discussion of zeolite nomenclature), X-ray diffractions studies[5] have shown that the Mn(II) ions are located at the centers of distorted trigonal bipyramids, formed by three symmetry-related framework oxygen atoms in a plane and two water molecules, not related by crystallographic symmetry, at axial positions. Following dehydration, the Mn(II) ions are three-coordinate[5]—bound solely in the triangular planes of oxygen atoms.

From electronic reflectance spectroscopic studies, Klier and Ralek have shown that Ni(II) or Co(II) ions exchanged (incompletely) into zeolite 4A are coordinated to three, four, or six ligands, as the content of the zeolite is altered.[7,11] As with the Mn(II) species mentioned above, complete dehydration of the sieve produces metastable, three-coordinate Ni-(II) or Co(II) ions, possessing near D_{3h} symmetry. The introduction of certain gaseous molecules, notably N_2O, NH_3, and H_2O, readily produces complexes with distinct C_{3v} symmetry. Thus, these systems are amenable to the formation of a variety of intrazeolitic metal complexes with applications in the areas of structural chemistry, sorption, and catalysis. In addition, some insight into the nature of the binding and activation of small molecules (N_2, O_2, CO, and S_2, for example) by metal ions in biological and geological systems may be acquired.

With a view toward these objectives we wish to report the crystal structures of two forms of partially cobalt(II)-exchanged zeolite A: the empty or fully dehydrated species, Co_4-$Na_4Si_{12}Al_{12}O_{48}$, $Co_{0.33}Na_{0.33}[AlSiO_4]$-A in suggested notation;[18] and its carbon monoxide addition complex, $Co_{0.33}$-$Na_{0.33}[AlSiO_4] \cdot 0.33CO$-A, whose unit cell composition is $Co_4Na_4Si_{12}Al_{12}O_{48} \cdot 4CO$. A preliminary account of the dehydrated structure has been published.[8]

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Experimental Section

Sample Preparation. Single crystals of sodium zeolite 4A were prepared by a modification of Charnell's method,[19] which included a second crystallization using seed crystals from the first synthesis. Ion exchange with 0.1 M aqueous solutions of $Co(NO_3)_2$ at 75° for 3 weeks yielded pink to tan cubic crystals. Elemental analysis, followed by a small back-exchange step of −0.5 Co(II) ion/unit cell, yielded a material with stoichiometry $Co_4Na_2Si_{12}Al_{12}O_{48} \cdot xH_2O$, or $Co_4[A] \cdot xH_2O$.

A crystal, 0.065 mm along an edge, was placed in a finely drawn Pyrex capillary, attached to a vacuum system, and cautiously dehydrated by incrementing the temperature of the capillary by *ca.* 25°/hr, to 350°. This temperature was maintained for 48 hr at a pressure of 1 × 10⁻⁵ Torr. After the system had returned to ambient temperature, the crystal in its evacuated capillary was sealed off by torch.

Another crystal of similar size was dehydrated in an analogous fashion at a pressure of 1 × 10⁻⁶ Torr. Upon return to room temperature, the specimen was treated with chemically pure and zeolitically dried carbon monoxide (Matheson Co., Inc.) at a pressure of 716 Torr. To promote (possibly) sorption of the gas, the capillary temperature was slowly raised to 200° where it was maintained for 24 hr. After the system had returned to room temperature, the crystal was removed from the vacuum line as before. Microscopic examination showed each crystal to be intensely blue.

X-Ray Data Collection. As determined in earlier efforts,[2,14] *Pm3m* (no systematic absences) is a suitable space group and was accordingly used. (Justification for this selection as opposed to another cubic space group (*Fm3c*, for example) is available.[17])

Diffraction experiments were performed similarly for each crystal using an automated, four-circle Syntex $P\bar{1}$ diffractometer equipped with a graphite monochromator and a pulse height analyzer. In each study Mo Kα radiation was used (Kα₁, λ 0.70926 Å; Kα₂, λ 0.71354 Å). Cubic unit cell constants at 20 (1)°, as determined by a least-squares refinement of 15 intense reflections for which 20° < 2θ < 24° (in each case), are 12.087 (5) Å for the dehydrated material and 12.093 (4) Å for the carbon monoxide complex.

Data were gathered by the θ–2θ technique employing a scan speed which varied in 2θ from 0.5° min⁻¹ for the weakest reflections to 24.0° min⁻¹ for the most intense. Nearly all data were measured at the slowest scan rate. A symmetric scan range, from 1° (in 2θ) below the calculated Kα₁ position to 1° above the Kα₂ position, was used for each reflection. Background counts were recorded at each end of the scan range for a time equal to half the time necessary to examine the reflection. Three reflections in different regions of reciprocal space, measured after every 100 reflections as a check on crystal and instrument stability, showed no significant trends in intensity for either crystal.

All unique reciprocal lattice points for which 2θ < 70° were examined. This high upper limit of 2θ was selected to maximize the rather small data sets, limited by crystal size, although few reflections were significantly greater than background for large 2θ values.

Standard deviations were assigned in accordance with the expression

$$\sigma(I) = [\omega^2 \{CT + 0.25(t_c/t_b)^2(B_1 + B_2)\} + (pI)^2]^{1/2}$$

where CT is the total integrated count obtained in a scan time t_c, B_1 and B_2 are the background counts each measured in time t_b. ω is the scan rate, and $I = \omega[CT - 0.5(t_c/t_b)(B_1 + B_2)]$. A value of 0.02 for *p* has been determined as suitable for our instrumentation.[2,20] The net counts were then corrected for Lorentz and polarization effects; no absorption correction to the data was required. The linear absorption coefficients (μ) are 13.1 and 13.2 cm⁻¹ for the dehydrated and carbonyl species, respectively; and in the same order, the transmission factors varied from 0.900 to 0.888 and 0.898 to 0.886. Only those reflections which exceeded their assigned standard deviations by a factor of 3 were judged significantly greater than background and only these[21] were utilized in subsequent structural analysis. Of the 849 reflections examined for the dehydrated crystal, only 102 met this criterion. Similarly, for the CO adduct, 121 reflections from a total of 849 measured were regarded as observed. Near the conclusion of the refinement of each structure an examination of the data revealed that one reflection per data set had apparently been erroneously measured. These were discarded, resulting in final data sets totaling 101 and 120 reflections.

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Structure Determination and Solution of $Co_4[A]$

Using the zeolite framework atomic parameters (Si,Al), O(1), O(2), and O(3) (see Figure 1 for the identity of the atoms) obtained from our study of the fully hydrated form of this system,[22] full-matrix least-squares refinement of an isotropic model was commenced. (Because of the indistinguishability of silica and alumina tetrahedra implicit in the choice of space group, only the average species, (Si,Al), is considered.) Convergence was attained in two cycles of refinement at values of 0.24 and 0.23 for the discrepancy indices R_1 and R_2.

$$R_1 = \Sigma |F_o - |F_c||/\Sigma F_o$$

$$R_2 = (\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2)^{1/2}$$

A difference Fourier function prepared from these refined framework positions indicated two peaks (see Figure 2) with densities of 4.0 and 2.9 e Å⁻³ on the unit cell threefold axis (Wyckoff position 8 (g) at $x = y = z = 0.207$ and $x = y = z = 0.156$, respectively. These sites correspond to positions on opposite sides of an oxygen "six-window." (Figures 1, 3, and 4 depict these "six-windows," which are composed of six alternating (Si,Al) atoms and six oxygens atoms joined so as to form twelve-membered aluminosilicate rings.) Although separated (virtually) by only 1 Å (see Figure 2), these peaks were judged the most structurally significant of this map. Accordingly, the larger peak was attributed to the four Co(II) ions and the smaller peak to the four Na⁺ ions; hence each Wyckoff site 8 (g) is 50% occupied. Also, placing four Co(II) ions in the large cage and four Na⁺ ions in the small cage (see Figure 1) seems reasonable, because such an arrangement maximizes the separation between the more highly charged Co(II) ions.

Including these cation positions in isotropic least-squares refinement yielded convergence at $R_1 = 0.086$ and $R_2 = 0.082$. Full anisotropic refinement converged at $R_1 = 0.072$ and $R_2 = 0.065$. The goodness of fit, $(\Sigma w(F_o - |F_c|)^2/(m - s))^{1/2}$, is 0.86, where m is the number of observations (101) and s is the number of variables (27) in the least-squares treatment. (Reflection (003) appeared to be erroneously measured, so it was excluded from final calculations.) In the final cycle of least-squares refinement no parameter shifted by more than 0.5% of its estimated standard deviation.

A subsequent difference Fourier function was featureless except for a peak at the origin of density 2.8 e Å⁻³ and a small peak of height 0.8 e Å⁻³ at $x = y = z = 0.09$. The estimated standard deviation of the electron density was calculated as 0.1 e Å⁻³. The quantity minimized in the least-squares treatment[23] was $(\Sigma w(F_o - |F_c|)^2)$ and the weights (w) were the reciprocal squares of $\sigma(F_o)$, the standard deviation of each observation. Atomic scattering factors for O⁰ and C (valence) for CO, O⁻, and (Si,Al)¹·⁷⁵⁺ for the zeolite framework (half formal charges) and Na⁺ and Co(II) for the exchangeable cations were used.[24] The function describing (Si,Al)¹·⁷⁵⁺ is the mean of the Si⁰, Si⁴⁺, Al⁰, and Al³⁺ functions. The scattering factors for Co(II) and (Si,Al)¹·⁷⁵⁺ were modified to account for the real parts ($\Delta f'$) of the anomalous dispersion correction.[25]

The peak at the origin is difficult to comprehend, although from our study of the hydrated form of this system,[22] it has been discovered that one fully hydrated Co(II) occupies this site. Inclusion of this position with its refined occupancy of 0.13 (4) Co(II) ion/unit cell reduced the error functions appreciably ($R_1 = 0.066$ and $R_2 = 0.061$) but required a thermal parameter of 1.1 Å², after alternate refinement of occupancy and thermal parameters. The other significant peak on the final difference function is 2.0 Å from the central position and could represent the appropriate fractional octahedral coordination sphere of water molecules. These possible low-occupancy positions were excluded from calculations leading to the structure reported herein.

Final positional, thermal, and occupancy parameters are pre-

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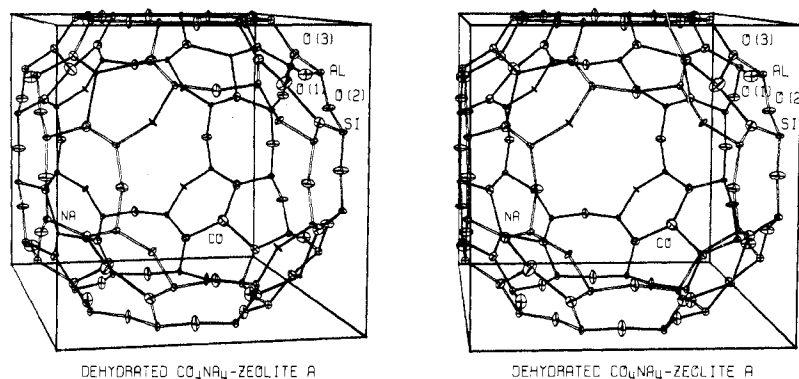
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Figure 1. A stereoview of the dehydrated $Co_4[A]$ unit cell. The trigonal approaches made by Co(II) ions to framework oxygen atoms are indicated by solid lines. Ellipsoids of 20% probability are used. To produce a physically meaningful drawing, the thermal parameter β_{23} for atom O(2) is reduced by 0.5σ.
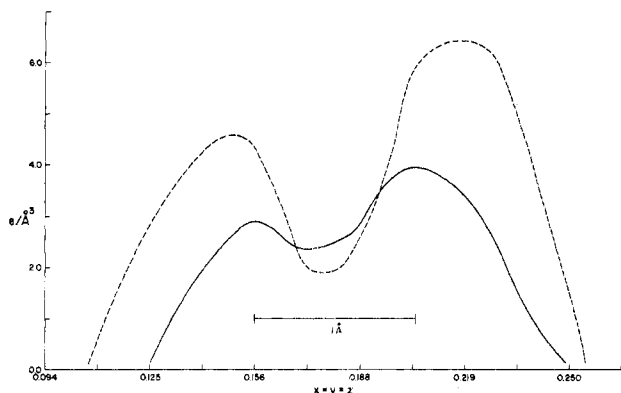

Figure 2. A plot of electron density in e Å^{-3} *vs.* fractional coordinate along the unit cell threefold axis for $Co_4[A]$ (solid line) and $Co_4[A]\cdot4CO$ (broken line). It was from these curves that the cation positions were initially assigned.

located in the large cavity along the threefold axis. Inclusion of only the two most significant peaks as Na^+ and Co(II) ions in isotropic least-squares refinement yielded convergence with R indices of 0.099. From a difference Fourier function, the position of bound carbon monoxide was better determined ($x = y = z = 0.305$ and $x = y = z = 0.367$), at a reasonable distance (2.0 Å) from the Co(II) ions. Isotropic least-squares refinement of all species, treating the peak closer to the Co(II) ions as carbon and the remaining peak as oxygen, reduced R_1 and R_2 to 0.092 and 0.087, respectively. Full anisotropic refinement was then carried out to convergence yielding the final structure with $R_1 = 0.066$ and $R_2 = 0.056$ and a goodness of fit of 0.68 for 120 reflections and 33 parameters. (As before, one reflection (369) appeared to be incorrectly measured and was excluded from the final calculations.) In the last cycle of least-squares refinement, no parameter shifted by more than 0.7% of its estimated standard deviation. A final difference Fourier function showed only a peak of 1.5 e Å^{-3} at the origin. (The estimated standard deviation of the electron density was calculated to be 0.1 e Å^{-3}.) When the origin position was included in least-squares refinement with an occupancy equal to that determined in the dehydrated structure (0.13 (4) Co(II) ion/unit cell), R_1 and R_2 decreased to 0.062 and 0.054,
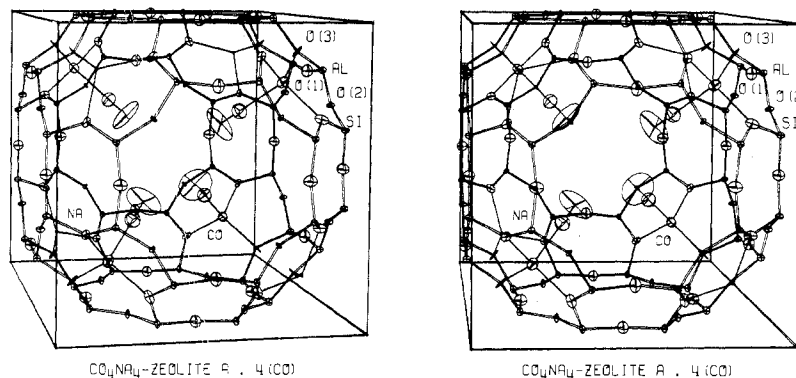

Figure 3. The unit cell of the carbon monoxide adduct of dehydrated $Co_4[A]$ shown in stereoview. The coordination of Co(II) by framework oxygen atoms and carbon monoxide is indicated by solid lines. Ellipsoids of 20% probability are used. To produce a physically meaningful drawing, the thermal parameters β_{12} for atom O(4) and ion Na^+ are reduced by 0.5σ and 1.0σ, respectively.

sented in Table I. Bond lengths and bond angles are given in Table II. A listing of $10F_o$ and $10F_c$ is available.[26]

Structure Determination and Solution of $Co_4[A]\cdot4CO$

Least-squares refinement of $Co_4[A]\cdot4CO$ commenced using atomic framework parameters learned from a study of a partially dehydrated form of this system.[27] Convergence was reached quickly with $R_1 = 0.28$ and $R_2 = 0.27$. An examination of a difference Fourier map revealed two large peaks, as before, along the threefold axis on opposite sides of the six-windows (see Figure 2) with heights of 4.5 e Å^{-3} at $x = y = z = 0.154$ and 6.4 e Å^{-3} at $x = y = z = 0.207$. In addition, two smaller peaks (possibly carbon monoxide) with heights of 1.2 and 2.0 e Å^{-3}, which were separated by *ca.* 1 Å, were

(26) See paragraph at end of paper regarding supplementary material.

(27) P. E. Riley and K. Seff, unpublished results.

respectively, as the isotropic thermal parameter refined to 5.5 Å^2. As before, a peak at this special position may correspond to a small concentration of hydrated Co(II), but, as before, it was not included in the final structure.

In order to increase the size of the data set and to improve it (possibly), 53 additional reflections, those for which $2\sigma(I_o) < I_o < 3\sigma(I_o)$, were added and included in the calculations. No new features appeared on Fourier functions, and no significant structural changes were observed upon least-squares convergence. Both R_1 and R_2 increased greatly to 0.093 and 0.083, respectively, and the standard deviations of all parameters increased markedly. These additional reflections were then deleted; the structure reported is based only on the smaller more reliable data set.

Bond lengths and bond angles are given in Table II; the final positional, thermal, and occupancy parameters, in Table III. Observed and calculated structure factors are available.[26]

The thermal parameters determined for the Co(II) and Na^+ ions of each structure (see Tables I and III) seem anomalous. That is, the

Table I. Positional, Thermal (×10⁴), and Occupancy Parameters for Co₄[A]ᵃ

	Wyckoff position	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy factor
(Si,Al)	24(k)	0	0.183 (1)	0.367 (1)	35 (6)	26 (6)	15 (5)	0	0	12 (9)	1
O(1)	12(h)	0	0.201 (3)	¹/₂	136 (44)	73 (31)	28 (19)	0	0	0	1
O(2)	12(i)	0	0.298 (2)	0.298 (2)	107 (32)	25 (14)	25 (14)	0	0	65 (33)	1
O(3)	24(m)	0.115 (1)	0.115 (1)	0.323 (1)	47 (10)	47 (10)	56 (16)	28 (25)	−3 (23)	−3 (23)	1
Co	8(g)	0.200 (2)	0.200 (2)	0.200 (2)	103 (12)	103 (12)	103 (12)	69 (29)	69 (29)	69 (29)	¹/₂
Na	8(g)	0.158 (2)	0.158 (2)	0.158 (2)	8 (13)	8 (13)	8 (13)	−2 (19)	−2 (19)	−2 (19)	¹/₂

ᵃ Standard deviations are in the units of the least significant digit given for the corresponding parameter. See Figure 1 for the identities of the atoms. The anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.
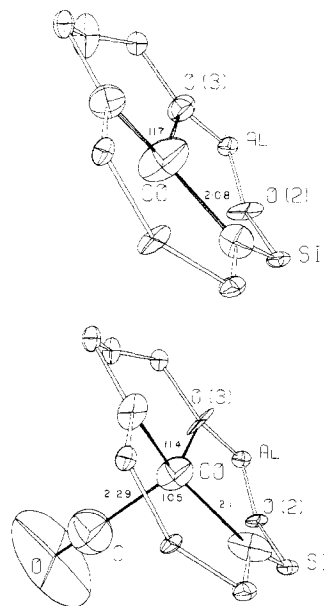

Figure 4. A six-oxygen window from each structure, showing the environment of the Co(II) ions. Ellipsoids of 50% probability are used. The same modifications required to prepare Figures 1 and 3 (see their figure captions) are used in these drawings.

large thermal motion of the Co(II) ions and the small thermal motion of the Na⁺ ions may indicate a level of Co(II) exchange that differs significantly from the 4 Co(II)–4 Na⁺ model determined by elemental analysis. Least-squares refinement of the occupancy parameters of the cations indicated that the fully dehydrated structure possesses 3.5 (2) Co(II) ions and 4.4 (2) Na⁺ ions per unit cell at the positions given in Table I. Similarly, least-squares treatment of the CO adduct indicated 3.7 (1) Co(II) ions and 4.5 (2) Na⁺ ions per unit cell at the sites found in Table III. Due to the virtual positional proximity of Na⁺ and Co(II) ions and to the large least-squares correlations between occupancy and thermal parameters, it is acknowledged that crystallographic conclusions regarding the accurate chemical composition of the two crystals actually studied are somewhat tenuous. Furthermore, the imprecision of the agreement between these refined occupancy parameters and those based on chemical analyses performed on bulk samples composed of crystals of widely varying size, and perhaps composition, provides a weak basis for the revision of the cationic composition of the zeolite from integral values. Accordingly the composition 4 Co(II)–4 Na⁺ was used throughout.

Discussion of the Structures

Dehydrated Co₄[A]. Dehydration removes a large portion of the structure, including members of the coordination spheres of the exchangeable cations. In order to satisfy their charge and coordination requirements, as well as those of the anionic framework, the cations move closer to the framework. It can be expected that the transition metal ions would be more affected than the weakly coordinating Na⁺ ions because the Co(II) ions have departed from a stable state of high aquo coordination[22] (not well-defined at present) to one of relative instability—nearly trigonal-planar coordina-

Table II. Interatomic Distances (Å) and Angles (deg)ᵃ

	Co₄[A]	Co₄[A]·4CO
	Distances	
(Si,Al)–O(1)	1.624 (8)	1.611 (6)
(Si,Al)–O(2)	1.622 (12)	1.634 (8)
(Si,Al)–O(3)	1.699 (9)	1.701 (8)
Co–O(3)	2.077 (18)	2.113 (15)
Co–O(2)	2.941 (20)	2.948 (18)
Na–O(3)	2.124 (20)	2.126 (15)
Na–O(2)	3.063 (21)	3.081 (16)
Co–C		2.29 (16)
C–O(4)		1.07 (16)
	Angles	
O(1)–(Si,Al)–O(2)	113.2 (13)	114.7 (8)
O(1)–(Si,Al)–O(3)	112.1 (14)	112.7 (12)
O(2)–(Si,Al)–O(3)	104.4 (9)	104.2 (8)
O(3)–(Si,Al)–O(3)	109.9 (12)	107.6 (9)
(Si,Al)–O(1)–(Si,Al)	164.3 (11)	167.2 (9)
(Si,Al)–O(2)–(Si,Al)	152.2 (21)	152.2 (12)
(Si,Al)–O(3)–(Si,Al)	133.5 (12)	132.4 (9)
O(3)–Co–O(3)	117.4 (12)	113.9 (11)
O(3)–Na–O(3)	113.4 (13)	112.8 (13)
O(3)–Co–C		104.6 (33)
Co–C–O(4)		180

ᵃ Standard deviations are in the units of the least significant digit given for the corresponding parameter.

tion. This appears to be the second example of trigonal coordination of Co(II). In the crystal structure of Co[N-(Si(CH₃)₃)₂]₂P(C₆H₅)₃,[28] three-coordinate Co(II) is observed; there, however, the great bulk of the ligands so inhibits coordination of the Co(II) ion at a fourth position, that trigonal coordination is stabilized.

The shifts of the framework atoms from their positions in hydrated Co₄[A] are substantial. The framework bond lengths of the hydrated system, which can be compared to the corresponding bonds of Table II are (Si,Al)–O(1) = 1.656 Å, (Si,Al)–O(2) = 1.659 Å, and (Si,Al)–O(3) = 1.661 Å; the largest concomitant changes in framework bond angles are 23, −5, and −14° at O(1), O(2), and O(3), respectively. Estimated standard deviations in these bond lengths and bond angles for the hydrated structure do not exceed 0.004 Å or 0.8°.

In the dehydrated Co₄[A] structure, the four Co(II) ions (probably arranged tetrahedrally with respect to one another) lie on the unit cell threefold axes, recessed into the large cavity (see Figure 1). Each Co(II) ion is bound to the three equivalent O(3) oxygen atoms related by these triads, at a distance of 2.08 (2) Å (Table II). This may be compared to the following distances: distorted octahedral Co(II) to oxygen bonds in tris(octamethylpyrophosphoramide)cobalt-(II) perchlorate (2.084 (3) Å),[29] trigonal-prismatic Co(II) to oxygen bonds in the trinuclear cation [Co(Co(OCH₂CH₂-

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Table III. Positional, Thermal ($\times 10^4$), and Occupancy Parameters for $Co_4[A]\cdot 4CO^a$

	Wyck-off posi-tion	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occu-pancy factor
(Si,Al)	24(k)	0	0.182 (1)	0.368 (1)	33 (5)	23 (4)	15 (4)	0	0	5 (7)	1
O(1)	12(h)	0	0.197 (3)	$^1/_2$	71 (21)	96 (24)	58 (16)	0	0	0	1
O(2)	12(i)	0	0.298 (1)	0.298 (1)	44 (15)	14 (8)	14 (8)	0	0	18 (22)	1
O(3)	24(m)	0.114 (1)	0.114 (1)	0.321 (1)	57 (10)	57 (10)	44 (11)	113 (23)	−17 (17)	−17 (17)	1
Co	8(g)	0.208 (1)	0.208 (1)	0.208 (1)	68 (5)	68 (5)	68 (5)	23 (13)	23 (13)	23 (13)	$^1/_2$
C	8(g)	0.317 (8)	0.317 (8)	0.317 (8)	129 (54)	129 (54)	129 (54)	−17 (116)	−17 (116)	−17 (116)	$^1/_2$
O(4)	8(g)	0.368 (2)	0.368 (2)	0.368 (2)	543 (182)	543 (182)	543 (182)	−633 (192)	−633 (192)	−633 (192)	$^1/_2$
Na	8(g)	0.155 (1)	0.155 (1)	0.155 (1)	4 (6)	4 (6)	4 (6)	19 (15)	19 (15)	19 (15)	$^1/_2$

^{a} Standard deviations are in the units of the least significant digit given for the corresponding parameter. See Figure 3 for the identities of the atoms. The anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

$NH_2)_3)_2]^{2+}$ (2.03 (2)–2.05 (2) Å),[30] and the Co(II) to oxygen bonds in Co_3O_4 (1.97 Å, calcd).[31] The angle subtended at the Co(II) ions is 117 (1)°—near the idealized trigonal-planar angle (120°); accordingly, each Co(II) lies somewhat "above" (by 0.34 (5) Å; see Table IV) its plane of O(3) atoms.

To distribute positive charge more uniformly so as to minimize cation–cation interactions as well as to neutralize the negative charge of the zeolite framework, the four sodium ions adopt sites on the threefold axes recessed slightly into the small cages (sodalite units). Here, each Na^+ ion is coordinated to one of the remaining four triads of O(3) atoms, *i.e.*, those not bound to a Co(II) ion. The Na^+ to O(3) distance is 2.12 (2) Å, about 0.20 Å shorter than the corresponding distance in the dehydrated form of sodium A (2.32 (1) Å).[17] The bond angle at the Na^+ ions is 113 (1)°, and the Na^+ ions are displaced 0.56 (4) Å "below" the O(3) planes.

The cation to O(3) distances presented here have not taken into account the probable but unobservable (due to disorder) conformational differences between the Co(II)-centered and the Na^+-centered six-windows; only the average six-window is determined. It is reasonable to expect the true Co(II)–O(3) distance to be slightly less than that reported here and the true Na^+–O(3) bond length to be moderately greater.

$Co_4[A]\cdot 4CO$. When carbon monoxide is introduced into the dehydrated sieve, the Co(II) ions, but not the Na^+ ions, interact with the gaseous molecules. Hence, as illustrated by a comparison of Figures 1 and 3 and Tables II and IV, the Na^+ ions exhibit similar trigonal coordination in both crystal structures. Changes in the coordination geometry about the Co(II) ions are, however, apparent when Figures 1 and 3 are considered.

Although the carbon monoxide content of the zeolite crystal was not determined gravimetrically, consideration of the sorption isotherm[32] for carbon monoxide onto Na_{12}-[A] indicates that few, if any, CO molecules are associated with Na^+ ions. Approximately two CO molecules are sorbed by $Na_{12}[A]$ at 20°, probably by interaction with Na^+ ions at positions[33] unoccupied in $Co_4[A]$.

To bind carbon monoxide, each Co(II) ion has moved 0.19 Å along its threefold axis toward the center of the large zeolite cage. Here coordination of one CO molecule by each Co(II) ion is achieved at a cobalt to carbon distance of 2.29 (16) Å. Accompanying this cation migration is, of course, a small (and perhaps insignificant) elongation of the

Table IV. Deviations (A) of Atoms from the [111] Plane at at $O(3)^a$ in $Co_4[A]$

	Dehydrated	CO adduct
Co	0.34 (5)	0.53 (4)
Na	−0.56 (4)	−0.58 (4)
O(2)	0.29 (4)	0.33 (3)

^{a} A negative deviation indicates that the atom lies on the same side of the plane as the origin.

three equivalent Co(II)–O(3) bonds, from 2.08 (2) Å in the dehydrated structure to 2.11 (2) Å in this complex. A correspondingly small decrease in O(3)–Co(II)–O(3) angle from 117 (1)° to a more tetrahedral value of 114 (1)° is noted also.

The CO triple bond length of 1.07 (16) Å is close to the value normally observed in carbonyl complexes. (The high thermal motion of the oxygen atom is undoubtedly contributing to the foreshortening of this bond in this structure.) In the crystal structure of $Co_5(CO)_{15}C_3H$,[34] the 15 C–O distances average 1.17 (2) Å; in gaseous carbon monoxide this distance is 1.1282 Å.[35]

The cobalt to carbon distance (2.29 (16) Å) is much longer than previously reported bond lengths in other cobalt complexes. For example, in the structure of $Co_5(CO)_{15}C_3H$ the Co–C distances range from 1.75 (1) to 1.79 (2) Å.[34] However, in this zeolite system a weaker metal to CO interaction might be expected, since the cobalt ions are doubly charged rather than essentially uncharged as metals are in most carbon monoxide complexes. As a consequence of this high charge the Co(II) d orbitals are probably so contracted that the synergic bonding[36] normally attributed to metal-carbonyl complexes (*i.e.*, donation of electron density from a σ orbital of carbon monoxide into a σ-acceptor orbital of the metal and "back-donation" of accumulated charge on the metal to a π-acceptor orbital of carbon monoxide through a metal d or dp hybrid π orbital) is severely inhibited. Accordingly, the Co–C bond in this structure is unusually long.

From infrared studies Angell and Schaffer[37] have reported that when carbon monoxide is sorbed by divalent transition metal exchanged X- and Y-type zeolites the C–O stretching frequency shifts to values (which vary with cation) that are higher than the frequency observed for gaseous carbon monoxide. To account for this increase in C–O bond strength these authors have proposed the following model. The electrostatic field of a Co(II) ion accentuates the small dipole moment of a CO molecule so that electron density

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(34) R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson, and J. L. Spencer, *Inorg. Chem.*, 9, 2197 (1970).
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(36) See, for example, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972, p 684.
(37) C. L. Angell and P. C. Schaffer, *J. Phys. Chem.*, 70, 1413 (1966).

can be donated from a σ orbital of (presumably) carbon to a σ-acceptor orbital of the metal. This creates a charge deficiency on the carbon atom which in turn induces a transfer of electron density from oxygen toward carbon, thereby strengthening the C–O bond. As these workers suggest, what may be observed is an isolation of the σ portion of a potentially σ–π synergic bonding system, *i.e.*, a metal to CO bond with no metal d-orbital participation.

Calculations have shown,[38] however, that because the cations interact strongly with the anionic zeolite framework, their (the cations') effective charges are somewhat reduced. Conceivably then, some contribution of the Co(II) d orbitals in binding CO might be possible.

Because the bonding between the metal and carbon monoxide is unusual in this structure and because the thermal motion of the CO molecules, more particularly the oxygen atoms, is large, an alternative structure was considered—one in which CO is coordinated to Co(II) through its oxygen atom. Interchanging the positions of C and O in least-squares refinement had little effect upon R_1 and R_2, although both indices did increase slightly. Further (weak) support is provided by a comparison of the ORTEP[23] drawings made with the refined anisotropic parameters for each arrangement. It would be expected that for the Co–O≡C model the central atom thermal parameter would be larger and the end atom's thermal parameter smaller than those in Co–C≡O; only the first effect was observed. Also, despite high standard deviations, the lengths of the two bonds made by these three atoms favor the conventional mode of metal-carbon monoxide bonding; Co–C≡O. For these two alternative structures, the interatomic distances are Co(II)–C = 2.29 Å and C–O = 1.07 Å for the Co–C≡O model; Co(II)–O = 2.45 Å and O–C = 0.92 Å for Co–O≡C. (The estimated standard deviations for these four bonds do not exceed 0.18 Å.) Thus, the most satisfactory description of this structure is one in which CO molecules are held to Co(II) ions at the carbon atoms.

Because the thermal motion for the oxygen atoms (O(4)) of the coordinated CO groups is so large, the influence of these atoms upon the structure was evaluated by omitting these atoms from least-squares refinement. Both R indices increased (R_1 from 0.066 to 0.073 and R_2 from 0.056 to 0.063) and the carbon atoms moved 0.17 Å along the threefold axes away from the Co(II) ions. Hence, despite their large thermal motion, the four oxygen atoms are clearly indicated. Indeed, large thermal motion is very much to be expected since *no other atom* is within a van der Waals distance—the closest approach is 4.5 Å to three other carbon monoxide oxygen atoms. Only the linear coordination of

the CO molecule directs the position of the O(4) atom, whose very oblate thermal ellipsoid indicates a "riding" motion of the oxygen atom on the carbon. No correction for this effect was made to the C–O bond.

As stated initially, the constraints imposed upon the exchangeable cations (charge neutralization at sites of high crystallographic symmetry) by the anionic zeolite framework (a very large, rigid ligand) afford an opportunity to examine some unusual metal complexes. In this work, for example, determination of the positions of the Co(II) ions (relative to framework atomic positions) allows direct comparison of the coordination geometry of "uncomplexed" Co(II) (in the fully dehydrated structure) to that of "complexed" Co(II) (in the CO adduct). From this, a number of revealing observations can be made. To begin with, upon dehydration the Co(II) ions adopt nearly trigonal-planar coordination, a coordination geometry that is somewhat unfavorable but which is stabilized by the aluminosilicate framework. When carbon monoxide is introduced, the Co(II) ions, but not the Na$^+$ ions (see Table IV), react with the gaseous molecules to give four-coordinate complexes of C_{3v} symmetry. Thus in this form of zeolite A the Co(II) ions are responsible for sorption of CO; and the sorption sites (which may be sites of catalytic activity as well) are ones along axes of threefold symmetry. Although the Co(II) ions do bind CO, the binding is presumably weak because the Co(II) to C distance is long and because the concomitant Co(II) to framework bond lengthening is not substantial. Finally, the formation of this unusual complex between a highly charged Co(II) ion and a weakly basic CO molecule demonstrates the unique coordination possibilities offered by a zeolite system. Characterization of other novel intrazeolitic metal ion complexes is continuing.

Registry No. Dehydrated Co_4Na_4-zeolite A, 50940-66-4; Co_4Na_4-zeolite A·4CO, 50940-67-5.

Supplementary Material Available. Listings of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1355.

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