Crystal Structure of an Ethylene Sorption Complex of Partially Cobalt(II)-Exchanged Zeolite A

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Abstract: The crystal structure of an ethylene sorption complex of a partially Co(II)-exchanged form of zeolite A, stoichiometry $Co_4Na_4Al_{12}Si_{12}O_{48}\cdot 4C_2H_4$ per unit cell, has been determined from three-dimensional X-ray diffraction data gathered by counter methods. The structure was solved and refined in the cubic space group $Pm3m$, and at 21 (1)° the unit cell constant is 12.135 (3) Å. Dehydration (or activation) of the crystal studied was achieved at 400° and 2×10^{-6} Torr in 48 hr. The crystal was then treated with 682 Torr of ethylene at ambient temperature. The Co(II) ions select sites in the large cage of the zeolite along the threefold axes of the unit cell, where they are bound to three equivalent framework oxygen atoms at distances of 2.148 (7) Å. One molecule of ethylene approaches each Co(II) ion in a symmetric, lateral fashion, so that the resultant Co(II)–C distances are equal (2.51 (6) Å). These long distances indicate that the Co(II)–C_2H_4 interaction is weak, and is probably due to the polarization of the π-electron density of the C_2H_4 molecule by the highly charged Co(II) ion. To distribute cationic charge more uniformly, the four Na^+ ions adopt similar threefold axial positions recessed somewhat into the smaller sodalite cages, at locations close to those four (remaining) triads of framework oxygen atoms which are not coordinated to Co(II) ions. No interaction between Na^+ ions and C_2H_4 molecules is indicated. Full-matrix least-squares refinement has converged to a conventional R index (on F) of 0.062 using 312 independent reflections for which $I_0 > 3\sigma(I_0)$.

Catalysis of chemical reactions by transition metal complexes continues to be a fascinating discipline of preparative chemistry. While much effort has been directed toward the development of olefinic and acetylenic hydrogenation catalytic systems,[1-4] other reactions of equal interest and importance (such as oxidative additions of H_2, N_2, O_2, acetylenes, and olefins) can be carried out over these same transition metal containing systems. According to Collman,[5] the availability of a coordination site on an activating transition metal complex (coordinative unsaturation) appears to be the most important property of such systems, for this unsaturation may encourage binding (at this site) of a substrate molecule which, in turn, may be activated.

Metals located near the ends of the transition series (notably Co, Rh, Ir, Pd, and Pt) which display variable valencies (or coordination numbers) have proved particularly useful. If undercoordinated metal species of this kind are affixed to phosphine- or sulfonate-substituted polymeric bases, the resultant heterogeneous catalytic systems demonstrate enhanced product isolation and by-product removal.[4] Furthermore, the formation of solvent channels, of particular dimensions and with particular polarities, which lead to the activating metal ions can allow passage of certain molecules to the exclusion of others, thereby exhibiting substrate selectivity.[2]

Selective catalysis of a truly wide variety of organic reactions by molecular sieve aluminosilicates, or zeolites, containing transition metal ions is well established.[6,7] The anionic aluminosilicate frameworks to some extent resemble the organic polymers described above. By sharing vertices, alumina and silica tetrahedra form infinite networks with geometrically well-defined channels and cages. The zeolitic cations located within these networks can interact with molecules whose dimensions allow them to pass through the channels. Because these inorganic polymeric catalysts (the zeolites) are crystalline, unlike the organic polymeric catalysts, their geometrical features can be readily determined by the methods of X-ray crystallography. Hence, much may be learned about the location and nature of the resulting cation–substrate complexes, some of which are likely to have structures similar to those of reaction intermediate complexes.

In our laboratory, we have been determining the crystal structures of the intrazeolitic sorption complexes formed between a variety of small molecules (C_2H_2, CO, H_2O, for example)[8-10] and some first-row transition metal ion-exchanged forms of zeolite A (nomenclature and structure of zeolite systems are discussed in ref 11) by single-crystal X-ray diffraction techniques. It has been possible to determine the geometry and symmetry of the weak complexes which form when small molecules are physically sorbed onto the inner surfaces of the zeolite. Therefore, as a part of these studies, reported herein is the crystal structure of an ethylene sorption complex of a partially Co(II)-exchanged form of zeolite A, stoichiometry $Co_4Na_4Al_{12}Si_{12}O_{48}\cdot 4C_2H_4$ per unit cell, or $Co_{0.33}Na_{0.33}[AlSiO_4]$-$\underline{A}\cdot 0.33C_2H_4$ in conventional nomenclature.

Experimental Section

Sample Preparation. Single crystals of the synthetic molecular sieve sodium zeolite 4A, stoichiometry $Na_{12}Al_{12}Si_{12}O_{48}\cdot 27H_2O$, form as colorless cubes. Crystals were grown by Charnell's[12] method which produces crystals with edge lengths as great as 0.1 mm, an acceptable size for single-crystal work. Ion exchange with 0.1 M $Co(NO_3)_2$ solution was conducted as described before[9] with crystals of zeolite 4A. After equilibrium was attained, elemental analysis indicated the stoichiometry $Co_4Na_4Al_{12}Si_{12}O_{48}\cdot xH_2O$ per unit cell, subsequently designated Co_4-A (exclusive of water).

One of the largest single crystals from this experiment, about 0.09 mm along an edge, was selected for X-ray diffraction study. It was placed in a finely drawn Pyrex capillary, attached to a vacuum system and cautiously dehydrated (activated) by gradually incrementing its temperature (*ca.* 25°/hr) at a constant pressure of 5×10^{-4} Torr. When the sample reached a temperature of 400°, the pressure was reduced again, to less than 2×10^{-6} Torr. These conditions were maintained for 48 hr.

After the crystal returned to ambient temperature (23°), it was treated with zeolitically dried ethylene (Matheson Gas Products) at a pressure of 682 Torr. Under these conditions, the crystal in its capillary was removed from the vacuum system by torch.

Microscopic examination indicated no apparent damage to the crystal, although dehydration and ethylene sorption have altered its color dramatically. In the fully hydrated form, the crystal is pink-tan; in the activated and combined (with ethylene) form, it is deep blue.

X-Ray Data Collection. It has been established that sodium zeolite 4A crystallizes in the cubic system.[13] If the alumina and silica tetrahedra are ordered and if this order can be discerned crystallographically, then an appropriate unit cell would be a face-centered one. Gramlich and Meier[14] have shown that for hydrated, unexchanged sodium zeolite 4A (Na_{12}-A) the framework tetrahedra are ordered and that the space group is *Fm*3*c*. Continuing crystallographic study of the samples used in our laboratory has provided only a marginal indication (one clear, weak superstructure reflection, and occasionally one or two more) of the existence of silica–alumina ordering and thus an F-type lattice. Accordingly, this work has been carried out using the primitive space group *Pm*3*m*.

Diffraction data were gathered as described below for a disordered, primitive unit cell. Because the resulting data set seemed to be of particularly good quality, a second data set was carefully acquired (in the same fashion as the first one (*vide infra*)) to explore again the possibility of a face-centered lattice (*i.e.*, one with a cubic cell constant twice as great as that of a primitive cell constant). Analysis of this (second) data set showed only three reflections (1,2,5, 3,5,19, and 3,7,17), possibly attributable to an *F*-type lattice, which possessed intensities significantly greater than background. Of these the most intense one (1,3,5) had an intensity only ~25% of that observed by Gramlich and Meier.[14] Furthermore, five reflections (1,1,1, 1,9,9, 3,11,11, 7,7,7, and 7,7,11) violated the extinction conditions of *Fm*3*c* at the 3σ level of significance. Hence long-range ordering of alumina and silica tetrahedra in this Co(II)-exchanged crystal is only weakly indicated, and for these reasons the "primitive cell data set" has been judged more suitable for this study.

Preliminary crystallographic experiments and subsequent data collection were performed with an automated, four-circle Syntex P$\bar{1}$ diffractometer, equipped with a graphite monochromator and a pulse-height analyzer. Molybdenum radiation was used for all experiments ($K\alpha_1$, λ 0.70926 Å; $K\alpha_2$, λ 0.71354 Å). The cubic unit cell constant at 21 (1)°, as determined by a least-squares refinement of 15 intense reflections for which $20° < 2\theta < 24°$ is 12.135 (3) Å.

Reflections from the two intensity equivalent regions of reciprocal space (hkl, $h \leq k \leq l$ and lhk, $l \leq h \leq k$) were examined analogously using the θ–2θ scan technique. Each reflection was scanned at a constant rate of 1.0° min^{-1} over a symmetric range from 1° (in 2θ) below the calculated $K\alpha_1$ peak to 1° above the $K\alpha_2$ maximum. Background intensity was counted at each end of a scan range for a time equal to half the time required to measure the reflection. The intensities of three reflections in diverse regions of reciprocal space were recorded after every 100 reflections to monitor crystal and instrument stability. Only small, random fluctuations of these check reflections were noted during the course of data collection.

For each region of reciprocal space the intensities of all lattice points for which $2\theta < 75°$ were recorded. Although few reflections were significantly greater than background for high 2θ values, this limit was selected to maximize the size of this relatively small data set.

The raw data from each region were corrected for Lorentz and polarization effects (including that due to incident beam monochromatization), the reduced intensities were merged, and the resultant estimated standard deviations were assigned for each averaged reflection by the computer program COMPARE.[15] The mean intensity for a reflection was calculated as

$$I = (I_{hkl} + I_{lhk})/2$$

where

$$I_{hkl} = [CT - 0.5(t_c/t_b)(B_1 + B_2)](\omega)$$

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, and ω is the scan rate. The standard deviation of I is

$$\sigma(I) = (\sigma^2(I_{hkl}) + \sigma^2(I_{lhk}))^{1/2}/2$$

and the standard deviation of each unmerged reflection is

$$\sigma(I_{hkl}) = [(CT + B_1 + B_2)\omega^2 + (pI_{hkl})^2]^{1/2}$$

The value of p was taken as 0.02,[16] a value found to be appropriate for the instrumentation used. No absorption correction was applied to the data; the linear absorption coefficient is 14.1 cm^{-1} and the transmission factors ranged from 0.837 to 0.855.

A reflection was used in structural analysis only when all of the following conditions were fulfilled

$$(1)\ (|I_{hkl} - I_{lhk}|/\sigma(I)) < 20.0$$

$$(2)\ (|I_{hkl} - I_{lhk}|/|I_{hkl} + I_{lhk}|) < 0.4$$

$$(3)\ (|B_1 - B_2|/|B_1 + B_2|) < 0.3$$

for each reflection before merging, and

$$(4)\ I_0 > 3.0\sigma(I_0)^{17}$$

for merged intensities. If one of a pair of equivalent reflections was not measured, then the reflection was omitted from the data set. Of the 1006 pairs of reflections examined only those 312 which fully satisfied these conditions were used in further calculations.

Structure Determination and Solution. Full-matrix least-squares refinement of the structure was initiated using framework atomic parameters ((Si, Al), O(1), O(2), and O(3)) and Co(II) and Na$^+$ parameters, which describe sites on threefold axes near triads of O(3) atoms, determined from an earlier study[18] of an acetylene sorption complex of this Co(II)-containing system. Figure 1 identifies these atoms. (Because of the indistinguishability of silica and alumina tetrahedra implicit in the choice of space group *Pm*3*m*, only the average species (Si,Al) is considered in this work.) Convergence was attained swiftly for an isotropic model, and after three cycles the discrepancy indices

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

and

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

were 0.11 and 0.10, respectively. Anisotropic refinement of this model converged with $R_1 = 0.077$ and $R_2 = 0.075$.

The quantity minimized in the least-squares treatment was $(\Sigma w(F_o - |F_c|)^2)$[15] and the weights ($w$) were the reciprocal squares of $\sigma(F_o)$, the standard deviation of each observation. Atomic scattering factors for O$^-$ and (Si,Al)$^{1.75+}$ for the zeolite framework, Na$^+$ and Co^{2+} for the exchangeable cations, and C (valence) for the C_2H_4 molecules were used.[19] The function describing (Si,Al)$^{1.75+}$ is the mean of Si^0, Si^{4+}, Al^0, and Al^{3+} functions. The scattering factors for Co^{2+} and (Si,Al)$^{1.75+}$ were modified to account for the real parts ($\Delta f'$) of the anomalous dispersion correction.[20]

The ethylenic carbon atoms (peaks with heights of 1.6 e Å^{-3}) were located on an ensuing difference Fourier synthesis at positions in the large cage on or close to diagonal mirror planes at $x = 0.28$, $y = 0.34$, and $z = 0.34$ (see Figure 2). At these positions, the ethylene molecules are only close to Co(II) ions (the Na$^+$ position is 3.6 Å away), and hence it was assumed that one C_2H_4 molecule is associated with each Co(II) ion. This description (as depicted in Figure 2) requires that in the vicinity of each Co(II) ion, one molecule of C_2H_4 be composed of two equivalent carbon atoms which lie on mirror planes, and which are disordered over three positions related by a unit cell threefold axis. Refinement of eight isotropic carbon atoms (four C_2H_4 molecules) per unit at this site converged readily but gave a short C═C bond length (1.01 Å).

However, if discrete ethylene molecules are to exist, it is probable that the carbon atoms occupy general positions, because three atomic sites (as in Figure 2) cannot except by chance describe the positions of the ethylene molecules in threefold disorder. Hence the carbon atoms were moved off the mirror planes to equivalent general positions (x,y,z). Refinement of this arrangement led to the final structure with a more satisfactory C═C bond (1.21 Å) and a slightly lower (by one standard deviation) isotropic thermal parameter for the carbon atoms. Least-squares convergence for a model with all atoms treated anisotropically except carbon which was refined isotropically was attained with $R_1 = 0.062$, $R_2 = 0.060$, and the goodness-of-fit, $(\Sigma w(F_o - |F_c|)^2/(m - s))^{1/2} = 1.50$, where m (312) is the number of observations (F_o) and s (31) is the number of variables in least-squares refinement. In the final refinement cycle, all shifts in atomic positional parameters were less than 0.9% of their corresponding estimated standard deviations and all shifts in thermal parameters were less than 2.5%. A final difference Fourier function, with an estimated standard deviation of 0.09 e Å^{-3}, showed a few small, shallow peaks of densities of *ca* 1.0 e Å^{-3} scattered about the large cage, far from established portions of the structure, which are thus not regarded as

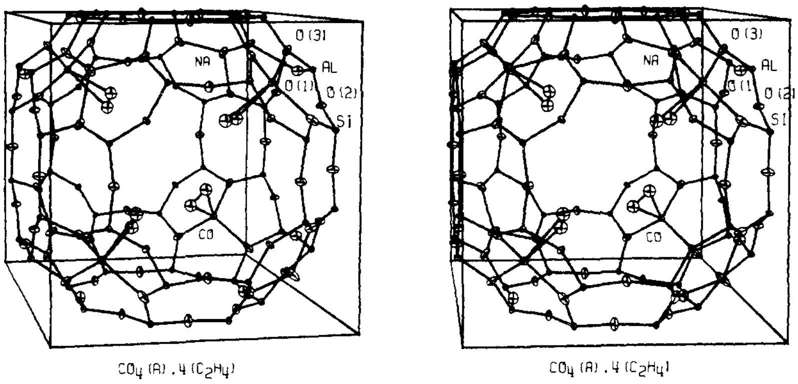


Figure 1. A stereoview of the unit cell. The approximately tetrahedral coordination about Co(II) and nearly trigonal coordination about Na^+ is indicated. Ellipsoids of 20% probability are used.

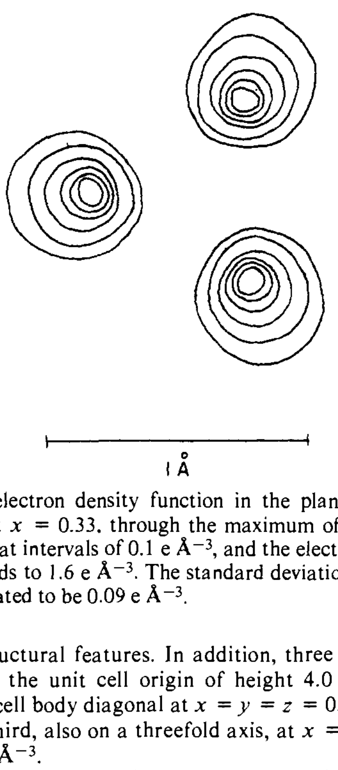


Figure 2. The electron density function in the plane normal to the threefold axis at $x = 0.33$, through the maximum of this peak. Contours are drawn at intervals of 0.1 e $Å^{-3}$, and the electron density maximum corresponds to 1.6 e $Å^{-3}$. The standard deviation of the electron density is calculated to be 0.09 e $Å^{-3}$.

meaningful structural features. In addition, three other peaks appeared: one at the unit cell origin of height 4.0 e $Å^{-3}$, another along the unit cell body diagonal at $x = y = z = 0.07$ of height 1.0 e $Å^{-3}$, and a third, also on a threefold axis, at $x = y = z = 0.245$ of height 1.8 e $Å^{-3}$.

The peaks at the origin and on the threefold axis at $x = 0.07$ are separated by 1.5 Å and have been noted in other zeolite structures.[9,10a] In its fully hydrated form,[10b] one Co(II) ion occupies the unit cell origin where it is coordinated octahedrally by water molecules. Perhaps then, these two peaks correspond to a small amount of residual hydrated Co(II) ion at the origin. Nonetheless the refined occupancies for these positions are small—for a meaningful thermal parameter there can be no more than 0.1 Co(II) per unit cell—and the great distance of the larger peak (at the origin) from well-established parts of the structure implies that both peaks probably do not represent significant features of this structure. Finally, the peak at $x = 0.245$ on the threefold axis is close to the Co(II) position, and accordingly may be due to the combined effects of residual anisotropy and Co(II) disorder.

Final positional, thermal and occupancy parameters are presented in Table I; bond lengths and bond angles are given in Table II. A listing of $10F_o$ and $10F_c$ is available.[21]

Discussion of the Structure

Dehydration (or activation) of this Co(II)-containing zeolite alters its properties and structure dramatically. In its hydrated form,[10b] the four Co(II) ions are located at two distinct crystallographic sites, where full "aquocoordination" is achieved. Hence at these positions, the Co(II) ions must be "far" (3–4 Å) from the anionic framework oxygen atoms. Removal of the zeolitic water induces migration of the Co(II) ions to locations close to the framework, where each Co(II) becomes tricoordinated by sets of equivalent oxygen O(3) atoms.[9] In this state of coordinative unsaturation, the Co(II) ions should be eager to interact with a wide variety of (sorbed) molecules, and indeed such is the case. For example, Klier[22] has demonstrated spectroscopically the formation of intrazeolitic Co(II) complexes with ammonia, cyclopropane, and nitrous oxide, and X-ray diffraction work[9] has corroborated the existence of a spectroscopically observed[23] Co(II)-carbon monoxide species.

From our crystallographic study of the carbon monoxide complex,[9] the acetylene complex[18] (see introductory section), and this ethylene complex, two conclusions may be reached: (1) the sorbed gaseous molecules interact preferentially with the Co(II) ions to the exclusion of the Na^+ ions and (2) these interactions are weak, for the resultant bonds from Co(II) ions to sorbed molecules are long, and the concomitant changes in Co(II)-framework geometries are small. That is, the strong Co(II)-framework interactions are maintained.

To bind one molecule of C_2H_4, each coordinatively unsaturated Co(II) ion moves a small distance (~0.2 Å, see

Table I. Positional, Thermal, and Occupancy Parameters for Co_4-A·$4C_2H_4$[a]

	Wyckoff position	x	y	z	β_{11} or β_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy factor
(Si,Al)	24 (k)	0	1825 (2)	3670 (2)	26 (1)	19 (1)	15 (1)	0	0	4 (2)	1[b]
O(1)	12 (h)	0	1995 (9)	1/2	90 (10)	57 (9)	31 (6)	0	0	0	1
O(2)	12 (i)	0	2994 (5)	2994 (5)	62 (7)	24 (3)	24 (3)	0	0	19 (8)	1
O(3)	24 (m)	1136 (4)	1136 (4)	3225 (6)	56 (4)	56 (4)	51 (5)	67 (8)	−44 (7)	−44 (7)	1
Co	8 (g)	2106 (2)	2106 (2)	2106 (2)	29 (2)	29 (2)	29 (2)	6 (3)	6 (3)	6 (3)	1/2
Na	8 (g)	1572 (12)	1572 (12)	1572 (12)	77 (7)	77 (7)	77 (7)	92 (20)	92 (20)	92 (20)	1/2
C	48 (n)	2886 (42)	3321 (52)	3589 (49)	6 (1)[c]						1/6

[a] Positional and anisotropic thermal parameters are given ×10^4. Numbers in parentheses are the estimated standard deviations in the last significant digits. See Figure 1 for the identities of the atoms. The anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Occupancy for (Si) = 1/2; occupancy for (Al) = 1/2. [c] Isotropic thermal parameter in units of $Å^2$.

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

Distances	
(Si,Al)–O(1)	1.627 (2)
(Si,Al)–O(2)	1.639 (3)
(Si,Al)–O(3)	1.700 (3)
Co–O(3)	2.148 (7)
Co–O(2)	2.976 (4)
Na–O(3)	2.141 (9)
Na–O(2)	3.098 (10)
Co–C	2.51 (6)
C–C'[b]	1.21 (11)
Angles	
O(1)–(Si,Al)–O(2)	112.7 (4)
O(1)–(Si,Al)–O(3)	112.2 (4)
O(2)–(Si,Al)–O(3)	105.5 (3)
O(3)–(Si,Al)–O(3)	108.4 (4)
(Si,Al)–O(1)–(Si,Al)	165.4 (3)
(Si,Al)–O(2)–(Si,Al)	150.0 (6)
(Si,Al)–O(3)–(Si,Al)	134.1 (4)
O(3)–Co–O(3)	113.1 (4)
O(3)–Co–O(2)	59.9 (3)
O(3)–Na–O(3)	113.7 (10)
O(3)–Na–O(2)	57.6 (3)
O(3)–Co–C	94.3 (14)
O(3)–Co–C'[b]	103.2 (14)
O(3)–Co–C'[b]	118.4 (14)
C–Co–C'[b]	28 (3)
C–C'–Co[b]	76 (1)

[a] Numbers in parentheses are the estimated standard deviations in the last significant digits. [b] C' is related to C by a threefold axis operation.

Table III. Deviations (Å) of Atoms from the (111) Plane at O(3)[a]

	Co_4-A·4C_2H_4	Co_4-A·4C_2H_2[b]	Co_4-A (dehydrated)[c]
Co	0.58 (2)	0.58 (2)	0.34 (5)
Na	−0.55 (3)	−0.13 (6)	−0.56 (4)
O(2)	0.34 (2)	0.31 (3)	0.29 (4)
C	3.0 (1)	3.0 (1)	

[a] A negative deviation indicates that the atom lies on the same side of the plane as the origin. Numbers in parentheses are the estimated standard deviations in the last significant digits. [b] See ref 18. [c] See ref 9.

Table III) from its triad of O(3) atoms, further into the large cage. Accordingly, the Co(II)-O(3) bonds lengthen slightly, from 2.08 (2) Å in the three-coordinate dehydrated structure to 2.148 (7) Å (see Table II) in the four-coordinate ethylene complex—a distance which differs significantly from the values noted for four-coordinate carbon monoxide (2.11 (2) Å)[9] and acetylene (2.193 (7) Å)[18] complexes. The three equivalent O(3)-Co(II)-O(3) angles have decreased responsively from the nearly planar values of 117 (1)° in the unsaturated complex[9] to 113.1 (4)° after ethylene complexation.

To balance electrostatic charge, the four Na^+ ions per unit cell recede slightly into the sodalite cages to occupy equivalent sites on threefold axes. There coordination to sets of O(3) atoms not bound to Co(II) ions is established (see Figure 1). Similar to other transition metal zeolite systems examined crystallographically, the Na^+ ions of this structure are unaffected by the transition metal-substrate interactions (Co-C_2H_4 in this instance), and in each of these structures[8,9,18] (including the dehydrated one) the Na^+ ions have selected virtually identical locations. In the dehydrated structure, the three equivalent Na^+-O(3) bonds are 2.12 (2) Å long and the (three) O(3)-Na^+-O(3) angles are 113 (1)°. Here, the Na^+-O(3) bonds are 2.141 (9) Å, and the angles at Na^+ are 114 (1)°. Correspondingly, only small changes from the framework geometry of the dehydrated structure are observed after ethylene sorption.

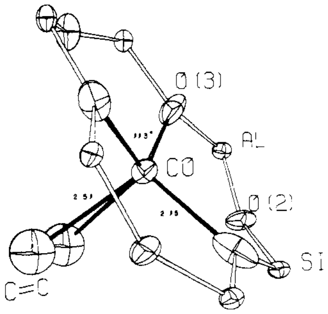


Figure 3. The approximately tetrahedral coordination of Co(II). Ellipsoids of 50% probability are used.

It should be noted that the cation to O(3) distances presented here have not taken into account the probable but unobservable (due to disorder) conformational differences between the two sets of O(3) atoms; one set is associated with the Co(II) ions and the other with the Na^+ ions. Only the average 12-membered ring of framework atoms (see Figure 3) is determined, and thus we expect that the correct Co(II)-O(3) distance is slightly shorter than that reported (in Table II), and that the correct Na^+-O(3) distance is somewhat longer. Clearly, a Na^+-O(3) distance closer to that determined in dehydrated, sodium zeolite 4A (2.32 (1) Å)[11a] might be expected.

Certainly the most interesting feature of this structure is the binding of C_2H_4 molecules by Co(II) ions. The three-dimensional electron density function generated by subtracting the contributions of framework atoms and Co(II) and Na^+ ions shows three maxima (Figure 2) in a plane normal to and related by a unit cell threefold axis, at a distance of 2.5 Å from the Co(II) position. Clearly, of the three positions only two can be occupied by the carbon atoms of an ethylene molecule. In addition, each peak is related to the other two by diagonal mirror planes (which are, of course, equivalent to one another by the operation of the threefold axis). Thus, the description which emerges is one in which a Co(II) ion holds an ethylene molecule at a site where both its carbon atoms are equivalent by mirror symmetry, but where the molecule itself is disordered by the threefold axis.

Although Figure 2 suggests that all carbon atoms are equivalent, the possibility that each ethylene molecule is composed of two nonequivalent carbons, which might allow the center of a C=C double bond to coincide with a unit cell threefold axis, was explored. The eight carbon atoms were divided equally between two general positions (x,y,z and x',y',z') and then these positions were treated by least-squares procedures. Subsequent examination of the isotropically refined thermal paramters for both carbon positions indicated that one position ($x = 0.28$, $y = 0.35$, $z = 0.35$, $B_{\text{iso}} = 3.0$ Å^2)—close to the one alluded to in the preceding paragraph (and given in Table I)—was favored over the other ($x = 0.25$, $y = 0.36$, $z = 0.38$, $B_{\text{iso}} = 17$ Å). Moreover, the resultant carbon-carbon double bonds would be too long to be correct (1.6-1.7 Å). Hence the solution offered by Figure 2 and reported in Table I is more acceptable.

With all eight carbon atoms (four molecules of C_2H_4) distributed about one equipoint (Wyckoff position 48(n)), the Co(II)-C_2H_4 interaction is symmetric. That is, each C=C bond is normal to and bisected by a plane of symmetry which contains a threefold axis (and hence a Co(II) ion), so that both carbons are equidistant from Co(II) (Co(II)-C = 2.51 (6) Å). With this particular equivalent carbon atom arrangement, a C=C bond does not intersect a unit cell threefold axis, for its (*i.e.*, C=C) center lies about 0.35 Å from it.

In this structure the ethylenic double bond length of 1.21

(11) Å (Table II) is short and imprecise and thereby reflects the combined effects of disorder and moderate thermal motion of the carbon atoms. In gaseous ethylene, a mean C=C distance of 1.344 Å is reported,[24] while in other transition metal complexes a broad range of C=C distances is displayed (1.354 (15)–1.46 (2) Å, for example).[25]

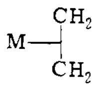
The bonding between transition metals and alkenes is usually described in terms of the Chatt–Dewar model.[26] An initial σ bond is formed between the filled π orbital of the alkene and an empty σ-acceptor orbital of the metal. Accumulated negative charge on the metal then is "back-donated" by d (or dp hybrid) π orbitals of the metal to a π-acceptor orbital of the alkene, an effect which not only strengthens the preliminary σ bond but synergically reinforces the π bond as well. Because the π-acceptor orbital of the alkene is antibonding (pπ^*), the C=C bond order may be diminished somewhat by back-donation, and such an effect may be indicated by a lengthening of the C=C bond (providing that the error in the C=C determination is small). Thus, in bis(triphenylphosphine)(ethylene)nickel ($Ni(P(C_6H_5)_3)_2(C_2H_4)$)[27] the C=C distance is very long (1.46 (2) Å), suggesting appreciable $d\pi_{Ni} \rightarrow p\pi^*_{C_2H_4}$ electron flow, but in Zeise's salt ($K[PtCl_3(C_2H_4)]H_2O$) the C=C double bond length is normal (1.354 (15) Å)[28] implying no substantial back-donation.

Usually the metals forming these π complexes are in low oxidation states, and thus their valence d orbitals are sufficiently diffuse to allow overlap with the acceptor orbital of the alkene. However, for the structure reported herein, the cobalt ion is doubly charged, and therefore its d orbitals are probably too contracted to form an effective back-bond with the ethylene molecule. The binding of C_2H_4 by Co(II) that is observed, then, is probably due solely to a σ interaction resulting from the polarization of the π-electron density of the ethylene molecule by the highly charged Co(II) ion.

The (two) equivalent Co(II)–C bonds are 2.51 (6) Å in length, a value much greater than those usually determined for first-row transition metal–ethylene π complexes, and, accordingly, this metal–alkene interaction is considered weak. Although no examples of π-bonded cobalt monoalkene structures are available in the literature,[29] Co–C distances close to those found in $Ni(P(C_6H_5)_3)_2(C_2H_4)$,[27] about 2.0 Å, would be expected for similar Co(0) complexes. For example, in the crystal structure of *trans*-di-μ-carbonyl-bis(π-2,3-*cis*-dimethylbutadienecarbonylcobalt),[30] the cobalt to butadiene carbon distances range from 2.075 (4) to 2.099 (4) Å.

Essentially the same long Co(II)–C distance (2.53 (5) Å), and the same mode of attachment, is observed in the structure of an intrazeolitic Co(II)–acetylene complex.[18] Perhaps, as suggested by Angell and Schaffer[23] from infrared studies of some intrazeolite divalent transition metal carbonyl complexes, the interaction observed may correspond to an isolation of the σ portion of what could become a σ–π synergic bond, were the metal uncharged and hence able to accumulate sufficient electronic charge for back-donation to the coordinated molecule.

From calorimetric and infrared spectroscopic work Carter, *et al.*,[31] have deduced that C_2H_4 molecules sorbed onto a variety of ion-exchange zeolite X[6] systems are held by the cations *via* a π-bonding mechanism such that the



$$M - \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}$$

moiety is of point symmetry C_2. Of the metal ions examined, the transition metal ions Ag^+ and Cd(II) were found to bind C_2H_4 most strongly. Furthermore, in every complex except that with Ag^+, the bound C_2H_4 molecules are found to rotate about the C_2 axis. These authors suggest that, although both Ag^+ and Cd(II) have filled d orbitals, the greater protrusion of the d orbitals of the larger, monovalent cation permits sufficient overlap into the pπ^* orbital of C_2H_4 to restrict its rotation; *i.e.*, relatively strong back-bonds apparently form. The bonding between Co(II) and C_2H_4 within this zeolite appears to be closely analogous to that in the Cd(II)–C_2H_4 complex, and rapid transitions of ethylene molecules among equivalent molecular sites (probably at a single Co(II)) occur.

Although the uncertainties in the carbon positions are large and the determination of the C=C distance is poor, the ethylene molecules make no significant approaches to the zeolite framework. The closest such approach is 3.4 Å to an O(3) atom. For a meaningful interaction the C–H···O distance should not exceed 3.0 Å,[32] and thus the ethylenic hydrogen atoms are far from the framework as well (see Figure 1 or 3). This apparent lack of effective nonbonded interactions, coupled with the weakness of the Co(II)–C_2H_4 binding, undoubtedly accounts for the moderate thermal vibrational parameters ascribed to the C_2H_4 molecules (Table I).

As mentioned above, because Co(II) and Na^+ ions are bound to triads of O(3) atoms in this structure, a structural difference in sets of O(3) atoms must result from the difference in cation character. If the Co(II) ions and the Na^+ ions display long-range Co_4 and Na_4 tetrahedral order, then the centric space group $Pm3m$ would be inappropriate. Hence as a test for such cation order, least-squares refinement was conducted in the acentric (cubic) space group $P\bar{4}3m$. (As with $Pm3m$, the assumption of silica and alumina disorder is maintained with $P\bar{4}3m$.) However, refinement failed to support an ordered cation arrangement. The final error indices were significantly greater for the acentric model ($R_1 = 0.087$ and $R_2 = 0.079$) than for the centric one, and the thermal ellipsoids for the Na^+ ions and for the oxygen atoms coordinated to the Co(II) ions were nonpositive definite, indicating physically impossible thermal motion for these species in space group $P\bar{4}3m$.

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Supplementary Material Available. A listing 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 JACS-75-537.

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Lanthanide-Induced Shifts in Proton Nuclear Magnetic Resonance Spectra. XI. Equilibrium Constants and Bound Shifts for Cyclohexanones and Cyclohexanols[1]

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Abstract: The results of detailed, exhaustive analyses of the concentration dependence of the lanthanide-induced shifts (LIS) induced by $Eu(fod)_3$ in CCl_4 solution at ambient nmr probe temperature (31°) are reported. The substrates employed are a variety of highly substituted cyclohexanones and cyclohexanols of high conformational purity. It was found that all these systems display both 1:1 and 1:2 (LS and LS_2) LSR–substrate complex formation. No self-association of the $Eu(fod)_3$ could be detected; assumption of this extra equilibrium step resulted in poorer fits to the data. It was found that secondary alcohols are much better binders to LSR than are ketones; these, in turn, are far superior to tertiary alcohols. Also, equatorial hydroxyls bind much more readily than do axial hydroxyls. Values for the parameters K_1, K_2, Δ_1, and Δ_2 (association equilibrium constants and bound shifts for LS and LS_2 formation, respectively) are given for all systems studied; a general discussion is given on the methods of obtaining these parameters, especially as pertains to their accuracy.

Among other areas of application of lanthanide shift reagents (LSR) to problems in structural applications of nmr spectroscopy, considerable useful progress has been made recently in delineating the various association equilibria taking place between an LSR and various organic substrates in solution.[5-8] At least for the case of $Eu(fod)_3$,[9] there is now abundant evidence for the significant involvement of *at least* two complexes: LS and LS_2, where L and S denote the shift reagent and substrate molecules, respectively. It is possible that other shift reagents may show only 1:1 complex formation.[7a,b,e] Also evidence exists that LSR's may self-associate under some circumstances to form L_2, or even L_3, aggregates.[8]

It is well-known that all complexation equilibria involved in LSR–substrate interactions are very rapid on the nmr time scale, at least at typical ambient probe temperatures.[10] Hence, the parameters needed to characterize a given complex are obtainable only through a rigorous statistical analysis of the LSR and/or substrate concentration dependence of the lanthanide-induced shifts (LIS). Such analysis gives much more detailed and specific information than can be obtained from the observation of LIS from just a single sample. In particular, one is able to obtain equilibrium constants (*e.g.*, K_1, K_2, and K_L for LS, LS_2, and L_2 formation, respectively) and "bound shifts" (Δ_1 and Δ_2 for LS and LS_2, respectively) for each species present. These quantities possess the advantage of being intensive properties of the respective complexes. Also, the bound shifts are the parameters of choice for use in any quantitative assessment of the molecular geometry of a substrate.[11] Conversely, the most rigorous test of any kind of structural assessment procedure would lie in the direct utilization of Δ_1 and Δ_2 since with these the number of extraneous degrees of freedom and hence the number of additional needed fitting parameters would be reduced to an absolute minimum.

Current practice for the fitting of molecular geometry with LIS data usually makes use of the slopes of the initial portions of a set of LSR doping curves. Even in those cases where such slopes are well-determined experimentally (by no means a universal occurrence), the slope values are a nonanalyzable function of the shifts of at least two species, LS and LS_2. The (equivocally defined) slopes are then fit to some simple form of the pseudo-contact shift equation, and the discrepancies between observed and calculated geometries are blamed on additional shifts arising from a contact mechanism. Our theses are that (a) the methods described in this paper and its precursors, as well as the work of Reuben,[6] make accessible high precision data on one or both of the two complex species generated concurrently and (b) that this provides a more exact basis for geometry fitting