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Crystal Structures of Cyclopropane Complexes of Cobalt(II) and Manganese(II) in Partially Exchanged Zeolite A

Wyona V. Cruz, Peter C. W. Leung, and Karl Seff*

Contribution from the Chemistry Department, University of Hawaii, Honolulu, Hawaii 96822. Received March 27, 1978

Abstract: The crystal structures of the cyclopropane sorption complexes of partially Co(II)-exchanged and partially Mn(II)-exchanged zeolite A have been determined using X-ray diffraction data collected by counter methods. Both structures were solved and refined in the cubic space group $Pm\bar{3}m$; at 26 (1)°, the unit cell constants are 12.147 (2) Å for $\text{Co}_4\text{Na}_4\text{Si}_{12}\text{Al}_{12}\text{O}_{48}\cdot 4\text{C}_3\text{H}_6$ (unit cell stoichiometry) and 12.146 (4) Å for $\text{Mn}_4\text{Na}_4\text{Si}_{12}\text{Al}_{12}\text{O}_{48}\cdot 4\text{C}_3\text{H}_6$. Both complexes were prepared by dehydration at 350 °C and 1×10^{-5} Torr for 48 h, followed by exposure to cyclopropane gas at approximately atmospheric pressure. In each structure, the transition metal cations are located on threefold axes inside the large cavity, close to three trigonally arranged framework oxide ions on alternate 6-oxygen rings. The metal to oxygen distances are Co(II)-O = 2.174 (7) Å and Mn(II)-O = 2.122 (8) Å. Each of the four cyclopropane molecules in each structure is found to complex to a transition metal ion with Co(II)-C = 2.81 (7) Å and Mn(II)-C = 3.09 (6) Å. The threefold axes of the zeolite and of the sorbed molecules coincide, so that all carbon atoms in each cyclopropane molecule are equivalent and equidistant from the transition metal cation with which they are associated. In both cases, the cyclopropane molecules are loosely bound to the metal ions by a π ion to induced dipole interaction, a conclusion based on the long metal to carbon approach distances and the large anisotropic carbon thermal parameters. No interaction between Na^+ ions and cyclopropane molecules is observed. Full-matrix least-squares refinement converged to weighted R indices of 0.065 for the Co(II) complex and 0.083 for the Mn(II) complex, using the 373 and 331 reflections, respectively, for which $I_0 > 3\sigma(I_0)$.

Introduction

Transition metal ions which have been ion exchanged into zeolites are generally unusually coordinated or coordinately unsaturated. As a result, they have unusual chemical properties. The zeolite framework, in contrast to conventional complexing ligands, does not conform to the geometrical requirements of the metal ions to form stable complexes. Rather, the metal ions must situate themselves in the most suitable of the various unsuitable sites available, using water or guest molecules if available, to achieve a relatively stable coordination environment. Upon dehydration, coordinative unsaturation appears or is very much enhanced.

For example, in hydrated partially Mn(II)-exchanged zeolite A, all Mn(II) ions are found to have nearly regular trigonal-bipyramidal coordination, with water molecules in the axial positions and three equivalent framework oxygen atoms arranged equatorially.¹ Upon dehydration, the Mn(II) ions are found to be three coordinate, with a near trigonal-planar geometry.¹ Co(II) ions have nearly the same trigonal-planar coordination² in dehydrated partially Co(II)-exchanged zeolite A.

Three-coordinate transition metal ions are unusual, and should tend to increase their coordination numbers by forming complexes with a large variety of ligand molecules, including some which are very poor Lewis bases indeed and are not commonly thought of as ligands at all. By vacuum methods and by using a zeolite, it is possible to study these ions without the interference of competing ligands from a solvent or from the atmosphere.

In order to characterize the activity of transition metal ions in the zeolitic environment, several structural studies of sorption complexes of zeolite A have been carried out by diffraction methods. The structures of the complex of Mn(II) with C_2H_2 ,³ and those of Co(II) with CO, C_2H_2 , C_2H_4 , NO, NO_2 , and Cl_2 , have been determined.²⁻⁶ Similarly, the complexes of Ag(I) with N_3H_3 ,⁷ N_3H_5 ,⁷ C_2H_4 ,⁸ Cl_2 ,⁹ and Br_2 ¹⁰ have been reported. The structures of the sorption complexes of Cl_2 and O_2 with dehydrated Eu(II)-exchanged zeolite A have also been determined;^{11,12} these show that oxidative addition has occurred to give Eu(IV), a new oxidation state for this element.

As a continuation of this work, cyclopropane was sorbed into dehydrated partially Co(II)- or Mn(II)-exchanged zeolite A. Nuclear quadrupole resonance¹³ studies of C_3H_6 indicate that all of the carbon atoms in the cyclopropane molecules are sp^2 hybridized. This is further evidenced by the marked resemblance between cyclopropane and olefinic bond reactions.¹⁴ Hence cyclopropane has some π character by which it might interact with transition metal cations. It has been found that cyclopropane sorbed by partially Ni(II)-exchanged zeolite A complexes with Ni(II) ions.¹⁵ It is reasonable, therefore, to expect that similar complexes would form in the Co(II) and Mn(II) systems. The work was initiated to learn the detailed geometry of the cyclopropane complexes.

Experimental Section

Single crystals of the synthetic molecular sieve sodium zeolite 4A, stoichiometry $\text{Na}_{12}\text{Si}_{12}\text{Al}_{12}\text{O}_{48}\cdot 27\text{H}_2\text{O}$, were prepared by Charnell's

Table I. Positional, Thermal, and Occupancy Parameters^a

	Wyck-off position	x	y	z	β_{11}^b	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	occupancy factor
a. Co ₄ Na ₄ -A·4C ₃ H ₆											
(Si,Al)	24(k)	0	1820(2)	3667(2)	21(2)	15(1)	84(2)	0	0	3(3)	1 ^c
O(1)	12(h)	0	1993(8)	1/2	77(10)	35(8)	23(7)	0	0	0	1
O(2)	12(i)	0	2983(5)	2983(5)	58(8)	19(4)	19(4)	0	0	19(11)	1
O(3)	24(m)	1133(4)	1133(4)	3238(5)	58(4)	58(4)	36(5)	71(10)	-32(8)	-32(8)	1
Co	8(g)	2124(3)	2124(3)	2124(3)	28(2)	28(2)	28(2)	12(4)	12(4)	12(4)	1/2
Na	8(g)	1791(21)	1791(21)	1791(21)	217(30)	217(30)	217(30)	378(65)	378(65)	378(65)	1/2
C	24(m)	3005(59)	3638(38)	3638(38)	128(52)	582(111)	582(111)	-198(122)	-198(122)	-372(167)	1/2
b. Mn ₄ Na ₄ -A·4C ₃ H ₆											
(Si,Al)	24(k)	0	1819(3)	3671(2)	26(3)	24(2)	17(2)	0	0	8(4)	1 ^c
O(1)	12(h)	0	1962(10)	1/2	64(12)	64(12)	39(10)	0	0	0	1
O(2)	12(i)	0	2986(7)	2986(7)	52(11)	33(6)	33(6)	0	0	54(15)	1
O(3)	24(m)	1131(4)	1131(4)	3222(6)	42(4)	42(4)	48(7)	20(11)	-14(9)	-14(9)	1
Mn	8(g)	2041(5)	2041(5)	2041(5)	63(3)	63(3)	63(3)	42(9)	42(9)	42(9)	1/2
Na	8(g)	1541(8)	1541(8)	1541(8)	16(4)	16(4)	16(4)	7(11)	7(11)	7(11)	1/2
C	24(m)	3053(60)	3696(38)	3696(38)	127(60)	548(112)	548(112)	-44(112)	-44(112)	-372(190)	1/2

^a Positional and isotropic thermal parameters are given $\times 10^4$; standard deviations are in units of the least significant digit given for the corresponding parameter. The anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^b Rms displacements can be calculated from β_{ii} values using the formula $\mu_i = 0.225a(\beta_{ii})^{1/2}$, where a is the cell constant. ^c Occupancy factor for (Si) = 1/2; occupancy factor for (Al) = 1/2.

method¹⁶ using seed crystals from a previous synthesis. The ion exchange of crystals of zeolite 4A with 0.1 M Co^{II}(NO₃)₂ or Mn^{II}(ClO₄)₂ solutions was conducted as described before.^{1,2} These exchanges yielded materials whose approximate stoichiometries were Co₄Na₄Si₁₂Al₁₂O₄₈·xH₂O and Mn₄Na₄Si₁₂Al₁₂O₄₈·yH₂O per unit cell, subsequently to be referred to as Co₄Na₄-A and Mn₄Na₄-A, exclusive of water molecules. A single crystal from each ion-exchange experiment, cubes approximately 0.08 and 0.10 mm on an edge for Co₄Na₄-A and Mn₄Na₄-A, respectively, were selected for X-ray diffraction study. Each crystal was placed in a finely drawn Pyrex capillary, attached to a vacuum system, and then dehydrated (activated) by gradually increasing its temperature (ca. 25 °C/h) to 350 °C at a constant pressure of 1×10^{-5} Torr. Finally, the system was maintained at this state for 48 h.

After the crystals were returned to ambient temperature (23 °C), each was treated with zeolitically dried cyclopropane (Matheson Gas Products), at pressures of 677 and 703 Torr for Co₄Na₄-A and Mn₄Na₄-A, respectively. Under these conditions, each crystal in its capillary was removed from the vacuum system by torch.

Microscopic examination indicated that neither crystal had been damaged. In an earlier study,² it was observed that upon dehydration, the color of the Co₄Na₄-A crystal changed from pink to deep blue, and, in this case, the deep blue color was retained after the sorption of cyclopropane gas. The dehydration of Mn₄Na₄-A caused the color to change from pinkish tan to tan (perhaps a component of this color is due to a trace of MnO₂), and no additional change in color was observed upon the sorption of cyclopropane.

X-ray Data Collection

The space group *Pm3m* (no systematic absences) was used throughout this work for reasons discussed previously.^{17,18} Preliminary crystallographic experiments and subsequent data collection were performed with an automated, four-circle Syntex PI diffractometer, equipped with a graphite monochromator and a pulse-height analyzer. Molybdenum radiation was used for all experiments ($K\alpha_1$, $\lambda = 0.709$ 30 Å; $K\alpha_2$, $\lambda = 0.713$ 59 Å). The cubic unit cell constants, as determined by a least squares refinement of 15 intense reflections for which $20^\circ < 2\theta < 24^\circ$, are 12.147 (2) Å for Co₄Na₄-A and 12.146 (4) Å for Mn₄Na₄-A, both at 26 °C.

For each crystal, reflections from the two intensity-equivalent regions of reciprocal space (hkl , $h \leq k \leq l$, and lkh , $l \leq h \leq k$) were examined using the θ - 2θ scan technique, for $2\theta < 70^\circ$. Each reflection was scanned at a constant rate of 1.0 deg 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.

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 to each averaged reflection by the computer program COMPARE.¹⁹ The mean intensity for a reflection was calculated as $I = (I_{hkl} + I_{lkh})/2$, 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

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

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 0.02,²⁰ a value found to be appropriate for the instrumentation used. No absorption correction was applied to the data; the linear absorption coefficients are 14.1 and 12.7 cm⁻¹, and the transmission factors range from 0.879 to 0.885, and 0.871 to 0.877, for Co₄Na₄-A and Mn₄Na₄-A, respectively. Of the 854 pairs of reflections examined for the Co₄Na₄-A complex, and 852 for that of Mn₄Na₄-A, only the 373 and 331, respectively, whose net counts exceeded three times their corresponding esd's were used in structure solution and refinement. Other details of the data reduction are as have been discussed before.⁴

Structure Determination

Co₄Na₄-A·4C₃H₆. Full-matrix least-squares refinement of the structure was initiated using the atomic parameters of the framework ions ((Si,Al), O(1), O(2), and O(3)) and of Co(1) which had previously been determined for an ethylene complex of Co₄Na₄-A.⁴ An isotropic refinement of these ions converged quickly to an R_1 index, $(\sum |F_o - |F_c|| / \sum F_o)$, of 0.092 and a corresponding weighted R_2 index, $(\sum w(F_o - |F_c|)^2 / \sum wF_o^2)^{1/2}$, of 0.134. (Refer to Table Ia and Figure 1 to identify these positions.)

A subsequent difference Fourier synthesis revealed a possible position for the Na⁺ ions in the sodalite cage on the threefold axis ($x = 0.16$; density = 3.7 (1) e Å⁻³), and a probable carbon position for the cyclopropane molecules inside the large cavity on the diagonal mirror plane ($x = 0.28$; $y = z = 0.34$; density = 1.2 (1) e Å⁻³). Isotropic refinement of the parameters for Na⁺ converged to the error indices,

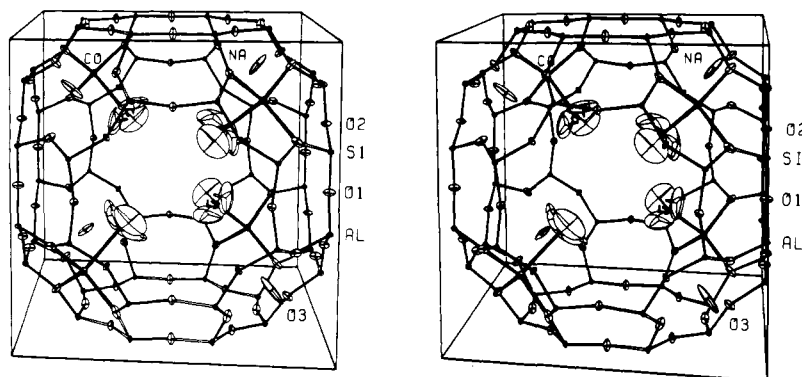


Figure 1. A stereoview of the $\text{Co}_4\text{Na}_4\text{-A}\cdot 4\text{C}_3\text{H}_6$ unit cell. Heavy bonds indicate the approximate tetrahedral coordination about Co(II). The root mean square displacements of the carbon atoms due to thermal motion average about 0.65 \AA in the plane of the cyclopropane molecule. This drawing, which appears to be of a structure in the space group $P43m$, represents only a necessary local ordering of cations and molecules consistent with the calculations presented, which were done exclusively in the space group $Pm3m$. Ellipsoids of 20% probability are used.

Table II. Interatomic Distances (\AA) and Angles (deg)^a

	$\text{Co}_4\text{Na}_4\text{-A}\cdot 4\text{C}_3\text{H}_6$	$\text{Mn}_4\text{Na}_4\text{-A}\cdot 4\text{C}_3\text{H}_6$
(Si,Al)-O(1)	1.633(3)	1.624(3)
(Si,Al)-O(2)	1.639(3)	1.643(5)
(Si,Al)-O(3)	1.692(3)	1.698(4)
M-O(3) ^b	2.174(7)	2.122(8)
M-O(2) ^b	2.972(4)	2.963(6)
Na-O(3)	2.089(7)	2.160(9)
Na-O(2)	2.987(8)	3.109(11)
M-C ^b	2.813(66)	3.088(65)
C-C ^c	1.10(12)	1.10(12)
O(1)-(Si,Al)-O(2)	113.1(5)	114.3(6)
O(1)-(Si,Al)-O(3)	111.7(3)	111.8(4)
O(2)-(Si,Al)-O(3)	105.6(4)	105.2(2)
O(3)-(Si,Al)-O(3)	108.9(4)	108.0(5)
(Si,Al)-O(1)-(Si,Al)	165.2(7)	167.7(9)
(Si,Al)-O(2)-(Si,Al)	150.9(6)	150.9(8)
(Si,Al)-O(3)-(Si,Al)	135.0(4)	133.9(5)
O(3)-M-O(3) ^b	112.5(4)	115.7(6)
O(3)-Na-O(3)	120(2)	112.5(6)
O(3)-M-C ^b	99(1)	96(1)

^a Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter. ^b "M" REPRESENTS Mn(II) or Co(II). ^c The coordinates of a primed atom are related to those given in Table Ia or Ib by a threefold-axis operation. These distances are severely foreshortened owing to high thermal motion, as is discussed in the text.

$R_1 = 0.093$ and $R_2 = 0.132$. The carbon positions were close to the Co(II) ions only and not close to Na^+ positions. Therefore, a correspondence of one cyclopropane molecule per Co(II) was assumed at this stage. Inclusion in least-squares refinement of 12 carbon atoms with isotropic thermal parameters at this position lowered the error indices at convergence to 0.066 and 0.074, respectively. Anisotropic least-squares refinement of Na^+ led to $R_1 = 0.062$ and $R_2 = 0.068$.

At this point, simultaneous positional and thermal parameter refinement of all cations, and occupancy refinement of Co(II), Na^+ , and C, further reduced the error indices to 0.055 and 0.050, respectively. However, this reduction was also accompanied by unreasonable occupancy values (Co = 4.2; Na = 2.1; and C = 24 atoms per unit cell) and a high carbon thermal parameter (51 \AA^2). This carbon occupancy corresponds to eight cyclopropane molecules per unit cell, and requires an unacceptably short intermolecular carbon-carbon contact distance of 3.01 \AA . Because the Co(II) ions are equivalent, there cannot be fewer than four C_3H_6 molecules per unit cell. Therefore, the original assumption of an occupancy of four cyclopropane molecules (12 carbon atoms) per unit cell is retained.

In subsequent cycles of least-squares refinement, the occupancy factors were fixed at the values shown in Table Ia while positional and anisotropic thermal parameters were allowed to vary. The final R_1 and R_2 indices are 0.062 and 0.065, respectively.

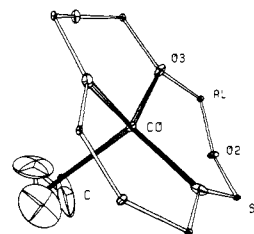


Figure 2. The coordination environment of the Co(II) ion. Ellipsoids of 10% probability are used.

The goodness of fit, $(\sum w(F_o - |F_c|)^2 / (m - s))^{1/2}$, is 3.23; m (373) is the number of observations, and s (33) is the number of independent variables in least squares. All shifts in the last cycle of refinement were less than 5% of their respective standard deviations, except those of some carbon parameters.

The final difference Fourier function, whose estimated standard deviation at a general position was $0.08 e \text{ \AA}^{-3}$, revealed two peaks on the threefold axis: one $2(4) e \text{ \AA}^{-321}$ in height at $x = 0$ and the other $1.2(5) e \text{ \AA}^{-321}$ at $x = 0.16$. The peak at the origin was discarded as was discussed previously.² The second peak is too close to the Na^+ ions on the threefold axis at $x = 0.179$ and may be attributed to residual density at that position.

The final structural parameters are presented in Table Ia. Interatomic distances and angles are given in Table II. A listing of observed and calculated structure factors is available; see paragraph at end of paper regarding supplementary material. The proposed atomic arrangement in a particular unit cell is shown in Figure 1, and the coordination environment of Co(II) can be seen in Figure 2.

$\text{Mn}_4\text{Na}_4\text{-A}\cdot 4\text{C}_3\text{H}_6$. Initial full-matrix least-squares refinement of the framework and Mn parameters taken from the acetylene complex of $\text{Mn}_4\text{Na}_4\text{-A}^3$ converged quickly to the error indices $R_1 = 0.16$ and $R_2 = 0.18$. A subsequent difference electron density function (esd at a general position = $0.16 e \text{ \AA}^{-3}$) contained a peak $5.9 e \text{ \AA}^{-3}$ in height on the unit cell threefold axis at $x = 0.16$. Previous results³ indicated that this was a Na^+ position. Its approach distance to O(3), 2.13 \AA , was comparable to the Na-O(3) distance of $2.19(1) \text{ \AA}$ in the acetylene complex.³ Least-squares refinement of this position as three isotropic Na^+ ions reduced the error indices to 0.14 and 0.16, respectively. However, anisotropic refinement of the Na^+ position led to a non-positive-definite thermal ellipsoid. Because the positional parameter was well behaved and no other possible positions for the Na^+ ions were located in the difference Fourier function, this position was retained.

A second difference function, generated to locate the carbon atoms, revealed a possible position at (0.28, 0.34, 0.34). With an estimated occupancy of 12 carbons per unit cell, corresponding to four cyclopropane molecules, least-squares refinement led to the error indices $R_1 = 0.094$ and $R_2 = 0.092$. However, the isotropic thermal parameter of Na^+ became negative. Alternate least-squares refinement of the occupancy and isotropic thermal parameters of the Mn(II) and Na^+ positions led to the occupancy ratio of approximately 1:1. To give a

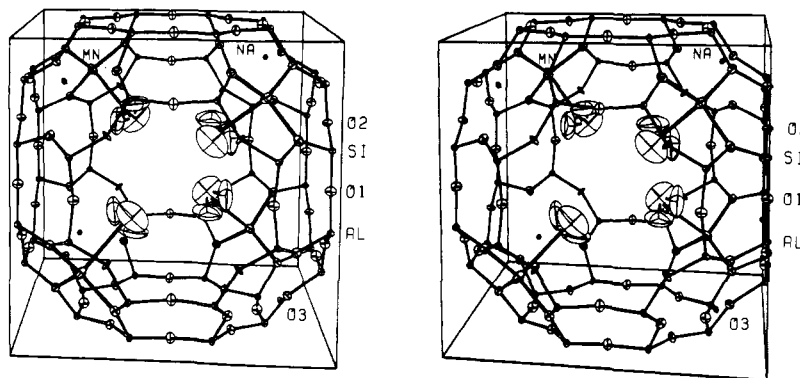


Figure 3. A stereoview of the $\text{Mn}_4\text{Na}_4\text{-A}\cdot 4\text{C}_3\text{H}_6$ unit cell. All other comments in the caption to Figure 1 are applicable here as well.

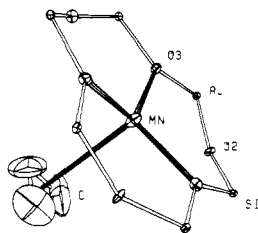


Figure 4. The coordination environment of the Mn(II) ion. Ellipsoids of 10% probability are used.

total cationic charge per unit cell of +12, the occupancies were fixed at four Mn(II) and four Na^+ ions at their respective positions.

Least-squares refinement of the carbon occupancy led to a value of 23 carbons per unit cell with an isotropic thermal parameter of 43 \AA^2 , an unrealistic result as discussed above for $\text{Co}_4\text{Na}_4\text{-A}$. Further, the presence of 23 carbons per unit cell (approximately 8 cyclopropane molecules) would require one molecule of cyclopropane in the vicinity of each oxygen 6-ring, and a too-close intermolecular carbon-carbon distance of 2.93 \AA . (The van der Waals radius of carbon is $1.65^{22-1.7}$.²³ In fact, a consideration of the hydrogen atoms would require this "radius" to be substantially longer.) Furthermore, to be consistent with the occupancy of Mn, only four molecules of cyclopropane can exist at these positions, one bound to each Mn(II) ion. Therefore, although the 23-carbon model has lower error indices ($R_1 = 0.072$ and $R_2 = 0.071$) it was rejected in favor of the 12-carbon model.

The Na^+ position could now be refined successfully along with its anisotropic thermal parameters; this lowered the error indices to 0.078 and 0.084, respectively. A similar anisotropic refinement of the carbon position was also successful. Simultaneous occupancy and thermal parameter refinement of the Mn(II) and Na^+ positions indicated 3.09 ± 0.18 Mn(II) ions and 5.98 ± 0.43 Na^+ ions per unit cell with $R_1 = 0.068$ and $R_2 = 0.078$. It should be noted, however, that those occupancies are both about 4σ from the proposed occupancies of four Mn(II) ions and four Na^+ ions per unit cell.

The final model contains 4 Mn(II), 4 Na^+ ions, and 12 carbon atoms as a reasonable compromise of the refined occupancies. The final R_1 and R_2 indices are 0.077 and 0.083, respectively. The goodness of fit is 4.11. The number of observations is 331, and the number of parameters is 33. Except for some carbon parameters, all shifts in the final cycle of least-squares refinement were less than 6% of their respective standard deviations. The final difference Fourier function (esd at a general position = $0.084 e \text{ \AA}^{-3}$) was mostly featureless except for two peaks of height 5 (4) $e \text{ \AA}^{-321}$ at (0, 0, 0) and 1.1 (5) $e \text{ \AA}^{-321}$ at (0.17, 0.17, 0.17), neither of which was significant.

The final structural parameters are presented in Table Ib. Interatomic distances and angles are given in Table II. See paragraph at end of paper regarding supplementary material. The probable atomic arrangement in a particular unit cell is illustrated in Figures 3 and 4.

The full-matrix least-squares program used¹⁹ in all structure determinations minimized $\sum w(\Delta|F|)^2$; the weight (w) of an observation was the reciprocal square of σ , its standard deviation. Atomic scattering factors^{24,25} for Na^+ , Co^{2+} , Mn^{2+} , C (valence), O^- , and

(Si,Al)^{1.75+} were used. The function describing (Si,Al)^{1.75+} is the mean of the Si^0 , Si^{4+} , Al^0 , and Al^{3+} functions. The scattering factors for (Si,Al)^{1.75+}, Co^{2+} , and Mn^{2+} were modified to account for the real components ($\Delta f'$) of the anomalous dispersion correction.^{26,27}

Discussion

$\text{Co}_4\text{Na}_4\text{-A}\cdot 4\text{C}_3\text{H}_6$. Each Co(II) ion, which is more polarizing and a better Lewis acid than Na^+ , has increased its coordination number to a more usual value by coordinating to a cyclopropane guest molecule. Each Co(II) ion is 2.74 \AA from the plane defined by the three carbon atoms of a cyclopropane molecule, too long a distance for the interaction to be very strong. Since the hydrogen atoms were not located in structure determination, their role in complexation has not been observed. However, assuming that the hydrogens are in the same relative positions with respect to the carbons as those in free cyclopropane (C-H = 1.08 \AA and H-C-H = 118° , symmetry D_{3h}),²⁸ a Co(II) to hydrogen approach of 2.17 \AA can be calculated. The hydrogens, then, act to prevent a closer Co(II)-carbon approach.

The positions of the Co(II) ions have changed upon coordination. The three-coordinate Co(II) ions in dehydrated $\text{Co}_4\text{Na}_4\text{-A}$ are 0.34 \AA^2 from the O(3) plane of the nearest 6-rings. However, four-coordinate Co(II) in the ethylene,⁴ acetylene,³ carbon monoxide,² and chlorine⁶ complexes of $\text{Co}_4\text{Na}_4\text{-A}$ deviate by more than 0.50 \AA from the same plane. With cyclopropane, the corresponding deviation is 0.61 \AA , indicating by this alone that Co(II) is complexed by a sorbed ligand. There appears to be a relationship between the deviation of Co(II) from the O(3) plane and the strength of its complex with the fourth ligand.

As a consequence of the movement of the Co(II) ion into the large cavity upon complexation, the Co(II)-O(3) bonds lengthen somewhat, from 2.08 \AA in the dehydrated structure to $2.174 (7) \text{ \AA}$ (see Table III), a distance comparable to that of other four-coordinate Co(II) ions in zeolite A.²⁻⁴ Also the O(3)-Co-O(3) bond angle changes from a near trigonal planar value of $117.5 (1)^\circ$ in dehydrated $\text{Co}_4\text{Na}_4\text{-A}$ to $112.5 (4)^\circ$ in the cyclopropane complex, a value closer to tetrahedral. Figure 2 illustrates the coordination environment of the Co(II) ion.

The Na^+ ions are inside the sodalite unit near the oxygen 6-ring in this complex. The Na^+ to O(3) distance is $2.089 (7) \text{ \AA}$, significantly shorter than the corresponding ionic radii ($r(\text{Na}^+) + r(\text{O}^{2-}) = 0.97 + 1.32 = 2.29 \text{ \AA}$).²⁹ This distance could be virtual, an artifact of the "averaging" of the atomic positions of the variously occupied (by Co(II) or Na^+) oxygen 6-rings. The doubly charged Co(II) ion with its considerably smaller radius can cause the 6-ring O(3)'s to buckle inward toward the center, while a singly charged Na^+ ion should cause a much smaller ring deformation. Thus, the actual Co(II)-O(3) distance should be somewhat shorter than that observed, and the Na^+ -O(3) distance longer.

Table III. Deviation of Ions from Six-Ring Planes and Selected Interatomic Distances (Å)^a and Angles (deg) in M₄Na₄-A^b and Their Sorption Complexes

zeolite	deviations ^c from the (111) plane at O(3), Å		M(II)-O(3), Å	O(3)-(Si,Al), Å	Si-O(3)-Al	ref
	M(II)	Na ⁺				
Co ₄ Na ₄ -A, dehydrated	0.34	-0.56	2.077(18)	1.699(9)	133.5(12)	2
Co ₄ Na ₄ -A·4CO	0.53	-0.58	2.113(15)	1.701(8)	132.4(9)	2
Co ₄ Na ₄ -A·4C ₂ H ₂	0.58	-0.13	2.193(7)	1.687(3)	136.0(4)	3
Co ₄ Na ₄ -A·4C ₂ H ₄	0.58	-0.55	2.148(7)	1.700(3)	134.1(4)	4
Co ₄ Na ₄ -A·4Cl ₂ at 24 (1) °C	0.73	<i>d</i>	2.244(6)			6
Co ₄ Na ₄ -A·4Cl ₂ at -165 (3) °C	0.78	<i>d</i>	2.26(1)			6
Co ₄ Na ₄ -A·4C ₃ H ₆	0.61	-0.09	2.174(7)	1.692(3)	135.0(4)	this work
Mn _{4.5} Na ₃ -A, dehydrated	-0.11	0.46	2.11(1)	1.70(1)	135.7(9)	1
Mn ₄ Na ₄ -A·4C ₃ H ₆	0.45	-0.61	2.122(8)	1.698(4)	133.9(5)	this work
Mn _{4.5} Na ₃ -A·4.5C ₂ H ₂	0.50	-0.55	2.177(10)	1.692(4)	135.5(6)	3

^a Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding value. ^b "M" represents Mn(II) or Co(II). ^c A negative deviation indicates that the ion lies on the same side of the plane as the origin, that is, inside the sodalite unit. ^d These ions are located at qualitatively different sites within the zeolite lattice.

The intramolecular carbon-carbon distances are observed to be short, 1.10 (12) Å, as compared to 1.51 Å in free C₃H₆ molecules.²⁸ These observed C-C bond lengths are severely foreshortened, an effect of thermal motion, by an amount which can be estimated to be a few tenths of an angstrom. Accordingly, the C-C bonds have not been shown by this work to be shortened by complexation.

For packing reasons (as discussed in the Structure Determination section), the four cyclopropane molecules in a unit cell must be arranged tetrahedrally in the large cavity, close to alternate oxygen 6-rings. Since it has been concluded that each C₃H₆ is associated with a Co(II) cation, these four ions must also be arranged tetrahedrally as shown in Figure 1. Furthermore, if a Co(II) and a Na⁺ ion were to occupy a 6-ring simultaneously, the Co(II)-Na⁺ distance would be 0.70 Å. Hence the four Na⁺ ions must occupy the remaining four 6-rings. As discussed in earlier work, if long-range ordering of the Co(II) and Na⁺ ions exists, then the centric space group *Pm3m* would be incorrect. It has been shown,⁴ however, that the alternative, *P43m*, is not appropriate to these systems, leading to the conclusion that this long-range ordering does not exist. Indeed, since the cation compositions are not expected to be precisely stoichiometric, long-range order was not anticipated. Thus the space group *Pm3m* remains appropriate, and the Co(II) and Na⁺ ions can be treated as disordered.

A more detailed presentation of the previously discussed π character of cyclopropane is possible. Miller,³⁰ using Hellmann-Feynman arguments and ring bending strain energies, calculated a "negative pole" in cyclopropane to be 0.288 e⁻. This negative pole or π cloud would be polarized by the field of the Co(II) ion to form the bond between cyclopropane and Co(II).

In a Ni(II) complex of triphenylcyclopropene,³¹ Ni(II) was found to be bonded to the center of the ring with an ion to ring-plane distance of 1.76 (1) Å. The bonding involves a π interaction from cyclopropane to Ni(II) with back-donation of electrons from the metal to ligand. Since the Co(II) to cyclopropane distance in this report is 2.74 Å, the synergic effect can be expected to be absent in this complex.

Attempts were made to estimate the relative strengths of complexation of sorbed molecules in partially Co(II)- and Mn(II)-exchanged zeolite A. When the coordination number of the transition metal cation in dehydrated zeolite A is increased, the metal to framework interaction is inevitably weakened. This is manifested by the lengthening of the metal-O(3) bonds (see Table III). Furthermore, the weak-

ening of the metal-O(3) interaction can lead to the strengthening of the O(3)-(Si,Al) bond and a shortened bond length. Also, the extent of the deformation of the oxygen 6-rings, manifested by the Si-O(3)-Al bond angle, decreases as the metal-O(3) interaction is weakened. By such considerations, the relative strength (and hence the sorption selectivity) of complexation of these ligands in Co₄Na₄-A can be estimated as Cl₂ > C₂H₂ > C₃H₆ > C₂H₄ > CO.

Mn₄Na₄-A·4C₃H₆. To complex with the C₃H₆ molecules, the Mn(II) ions shift to a position 0.45 Å from the plane defined by the three O(3)'s of the corresponding 6-rings (see Figure 3). This shift is quite large; in the dehydrated structure, the Mn(II) ions are located on the other side of the 6-ring just inside the sodalite cage¹ (see Table III). Also, the bond angle O(3)-Mn-O(3) changes significantly from a near trigonal-planar value of 119.6 (1)° to a more tetrahedral value of 115.7 (6)°. However, each Mn(II) ion retains a strong interaction with the 6-ring O(3)'s; no significant change in Mn(II) to O(3) distance is observed between this (2.122 (8) Å) and the dehydrated structure (2.11 (1) Å). The observed Mn(II)-C distance, 3.09 (6) Å, is long, consistent with that in Co₄Na₄-A·4C₃H₆. Altogether, this indicates that the C₃H₆ interaction with Mn(II) must be weaker than that with Co(II), as the larger ionic radius²⁹ of Mn(II) would indicate. However, it is sufficiently strong to modify the Mn(II) position and to hold the C₃H₆ molecules in ordered positions in the unit cell (see Figure 3).

As in Co₄Na₄-A, each carbon atom of a cyclopropane molecule approaches a Mn(II) ion equivalently. These carbon atoms are related by a unit cell threefold axis, and are chemically and crystallographically equivalent. The cyclopropane complexes of Co₄Na₄-A and Mn₄Na₄-A are isostructural. As in the Co(II) complex, a Mn(II) and a Na⁺ ion cannot simultaneously occupy a single 6-ring; that would lead to a Mn(II)-Na⁺ distance of 1.06 Å. Furthermore, to maximize the distribution of charge, the Mn(II) and Na⁺ ions should occupy alternate 6-rings. The cyclopropane molecules, each associated with a Mn(II) ion, are therefore arranged tetrahedrally in the unit cell.

The Na⁺-O(3) distance, 2.160 (9) Å, is too short for reasons discussed in the previous section. The true Mn(II)-O(3) distance should be less, and the Na⁺-O(3) distance more, than the values given in Table II. The intramolecular C-C distance is short (1.10 (12) Å) as compared to 1.51 Å in the free C₃H₆ molecule,²⁸ but this is not significant, as was discussed in the preceding section.

It has been found in previous work¹ that the stoichiometry of Mn_4Na_4-A is $Mn_{4.5}Na_3Si_{12}Al_{12}O_{48}$ (exclusive of water molecules) per unit cell. Only four Mn(II) ions (and four Na^+ ions) were located in this work. Several reasons for this discrepancy are possible. While the former stoichiometry is based upon elemental analysis of a larger sample, the large individual single crystal studied could have had a somewhat different composition. It is also possible that this crystal has a different stoichiometry because it was selected from a different (more recently exchanged) batch, which was too small (ca. 50 mg) for elemental analysis. A third and favored alternative is that the stoichiometry of this crystal is indeed the same as that determined previously. Only four Mn(II) ions are located at the Mn position because only the four-coordinate Mn(II) ions shift into the large cavity; the remaining half Mn(II) ion (one ion per two unit cells) cannot coordinate to cyclopropane for packing reasons, and would occupy a position perhaps indistinguishable from that of the Na^+ ions, increasing the occupancy at the Na^+ position. The Mn_4Na_4-A model would then be a good representation of the distribution of electron density near the 6-rings.

Further Discussion of the Choice of Space Group

As was noted in the initial report³² of the structure of the aluminosilicate framework of zeolite A, the requirement that silicon and aluminum ions alternate does not allow the space group of zeolite A to be $Pm3m$, as it would be if those ions were equivalent, and it requires a doubling of the ca. 12.3 Å unit cell edge length. Other workers confirmed this expectation by observing superstructure diffraction lines which could be attributed to this larger (ca. 24.6 Å) cubic unit cell.^{33,34} Later it was proposed that the space group of the superstructure is $Fm3c$.³⁵ Finally, Gramlich and Meier³⁶ determined the structure of hydrated $Na_{12}-A$ in $Fm3c$ using single-crystal diffraction data by a constrained least-squares procedure which included many weak superstructure reflections. Unfortunately, this method could not be extended to other forms of zeolite A, such as hydrated Ca_6-A .^{37,38} However, because the scattering factors of aluminum and silicon ions for X-rays are so similar, because the Al-O and Si-O bond lengths are similar, and because both ions are tetrahedrally coordinated, the space group $Pm3m$ is approximately correct and can be used.³⁸⁻⁴¹

Symmetry considerations involving only the aluminosilicate framework of the zeolite are necessarily incomplete. The exchangeable cations within zeolite A nearly always, by their numbers and by the sites they select within the structure, modify the symmetry indicated by the framework, so that $Fm3c$ is also incorrect. Framework decomposition or modification may have the same effect, as can sorbed molecules by their numbers, symmetry, and sorption sites. For example, the $Pm3m$ unit cell of dehydrated Cs_7K_5-A appears to contain only a single threefold axis of symmetry,³⁹ and that of dehydrated $Rb_{11}Na-A$ appears to have no symmetry at all.⁴⁰ However, if these structures were disordered so that the contents of one 12.3- or 24.6-Å unit cell were not strictly related only by translation to those in other unit cells, some or all of the lost symmetry would be recovered. Without such disordering, even the structure of dehydrated $Na_{12}-A$ ⁴¹ could contain no more than a single twofold axis per 12.3-Å unit cell. Even the sorption of a single asymmetric molecule per unit cell would reduce the symmetry of the zeolite crystal to $P1$ unless disorder were present.

The effects of these considerations on the single crystal diffraction pattern are small and various. Cations placed on n -fold axes are not better described by $Fm3c$ than by $Pm3m$, and most cations (these have generally been the largest scatterers of X-rays in these structures) occupy such positions in each of the zeolite A crystal structures which has been reported. Cations placed elsewhere may easily have a greater

influence in describing deviations from $Pm3m$ symmetry than the silicon/aluminum ordering. Always, nearly all of the diffraction data are consistent with the space group $Pm3m$ and one must be quite careful to reliably observe additional weak reflections or deviations from cubic intensity symmetry. Both of the hydrated $Na_{12}-A$ crystals, and one of hydrated Co_4Na_4-A , which have been examined in this laboratory for unit cell doubling have been found to have it, and to support the space group $Fm3c$, the group which describes the silicon/aluminum ordering. Generally the amount of available data has been so small, however, and its reliability so low, that its incorporation into structure calculations has not appeared to be a useful exercise. Even when such a procedure was followed,³⁶ it was with 1σ data, and it required that structural constraints be imposed to keep least squares from diverging.

For the present work, the details of the thermal parameters of the aluminosilicate framework or of the Si-O and Al-O distances are of relatively little interest. With constrained least squares, which would have been necessary, these distances would have been held fixed anyway. The R values which are attainable in least squares are generally acceptable, indicating that the level of disorder contracted by the choice of the $Pm3m$ space group is only moderate, and that it is reasonably compensated for by the thermal parameters of the zeolite framework which have refined to include the effects of this disorder. Finally, and quite generally, one must view with some suspicion the results of constrained least-squares refinement. For these reasons, all results from this laboratory are reported using the highest group $Pm3m$.

In order to visualize each structure, atoms are placed in partially occupied equipoints in a manner which is most reasonable on chemical grounds. Usually this is most reasonable on chemical grounds. Usually this can be done quite unambiguously to reveal the general situations of the cations and of the sorbed molecules. Unfortunately, this constitutes a result which is less than the full and complete determination of a crystal structure. However, the use of the alternative space group $Fm3c$ does not offer relief from this dilemma for several reasons, the principal one being that cations generally arrange themselves according to considerations of coordination and charge distribution, and not so as to continue the silicon/aluminum ordering. These cations further distort the zeolite framework away from $Fm3c$ symmetry and usually direct the positions of sorbed molecules, which further diminishes the applicability of that group.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE 76-81586). We are indebted to the University of Hawaii Computer Center.

Supplementary Material Available: Listings of the observed and calculated structure factors for both structures (Supplementary Tables I and II) (5 pages). Ordering information is given on any current masthead page.

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^1H , ^{31}P , and ^{13}C Nuclear Magnetic Resonance Nonequivalence of Diastereomeric Salts of Chiral Phosphorus Thio Acids with Optically Active Amines. A Method for Determining the Optical Purity and Configuration of Chiral Phosphorus Thio Acids^{1,2}

Marian Mikołajczyk,* Jan Omelańczuk, Mirosława Leitloff, Józef Drabowicz,
Andrzej Ejchart,³ and Janusz Jurczak³

Contribution from the Center of Molecular and Macromolecular Studies,
Polish Academy of Sciences, Department of Organic Sulfur Compounds,
90-362 Łódź, Boczna 5, Poland. Received April 7, 1978

Abstract: It was shown that diastereomeric salts of chiral phosphorus thio acids with optically active amines have different proton, phosphorus, and carbon NMR spectra in nonpolar solvents. The magnetic nonequivalence observed has been utilized for the first time for the direct determination of the enantiomeric content and optical purity of chiral phosphorus thio acids. In order to test the sensitivity of this method methylmethyl-*d*₃-phosphinothioic acid and *O*-methyl-*O*-methyl-*d*₃-phosphorothioic acid, which are chiral because of deuterium substitution, have been synthesized. The diastereomeric (–)– or (+)–1-(1-naphthyl)ethylamine salts of both acids exhibit different ^1H NMR spectra. The effect of solvent and optically active amines on the magnitude of magnetic nonequivalence, $\Delta\delta$, was investigated and pyridine was found to be a very good solvent for the investigated diastereomeric salts. A correlation between the absolute configuration of *O*-alkylalkylphosphonothioic acids and the NMR chemical shifts of their (–)–1-phenylethylamine salts has been observed in proton and phosphorus NMR spectra.

The recently developed NMR methods for determining enantiomeric or diastereomeric purity are based on the fact that diastereotopic nuclei are, in principle, anisochronous and should have different chemical shifts and different coupling constants.⁴

The magnetic nonequivalence of diastereomers in which the chiral centers are linked covalently in a single molecule was noted for the first time by Mateos and Cram.⁵ This phenomenon was widely used to establish the composition of diastereomeric mixtures and thereby the enantiomeric purity of chiral substances from which these stereoisomers were prepared by means of *chiral derivatizing agents*.⁴ In some cases empirically derived correlations of configuration and NMR chemical shifts for diastereomeric esters and amides have been reported.⁶

Similar nonequivalence of the NMR spectra was observed by Pirkle^{7,4c} for a mixture of enantiomers in *chiral solvents*. In this case, unstable solvation diastereomers are formed as a consequence of interactions between the solute and solvent. Because of this, the enantiomers have different chemical environments and show different chemical shifts. Their inte-

gration provides a direct measure of the enantiomeric purity of the solute. In addition to the determination of enantiomeric or optical purities, Pirkle has also reported on the correlation of absolute configuration of chiral carbon,⁸ sulfur,⁹ and nitrogen¹⁰ centers with the relative chemical shifts of enantiotopic nuclei in optically active solvents.

Recently, *chiral lanthanide shift reagents* have been prepared and found to induce the NMR spectral nonequivalence of enantiomers.^{4c,11} The approach to determination of optical purity utilizing diastereomeric complexes with chiral shift reagents is very advantageous because the chemical shift differences observed are generally large and a wide range of chiral compounds can be studied.

In addition to diastereomeric solvates and complexes with chiral shift reagents, *diastereomeric salts* belong to dynamic diastereomeric systems the NMR spectra of which should be different provided that they are taken in nonpolar solvents. It is interesting to note that diastereomeric salts are systems in which there are stronger interactions between the components (acid–amine) than in the solvates investigated by Pirkle and, therefore, the NMR chemical shift differences ($\Delta\delta$) should be