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Crystal Structures of Nitric Oxide and Nitrogen Dioxide Sorption Complexes of Partially Cobalt(II)-Exchanged Zeolite A

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The crystal structures of the nitric oxide and nitrogen dioxide complexes 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 the cubic space group *Pm*3*m*; at 24 °C the unit cell constants are 12.187 (4) Å for the NO complex, stoichiometry $Co_4Na_4Si_{12}Al_{12}O_{48}\cdot 3NO$, and 12.143 (2) Å for the NO_2 complex, stoichiometry $Co_4Na_4Si_{12}Al_{12}O_{48}\cdot 2NO_2$. Each of the complexes was prepared by dehydration (activation) of a single crystal of the zeolite at 1×10^{-5} torr and 350 °C for 48 h, followed by exposure to NO or NO_2 at 23 °C. In the NO complex, the formation of Co(III)–NO^- is indicated by a severe redistribution of cations: three of the four Na^+ ions have moved about 5.1 Å to the planes of oxygen 8-rings. Of the four threefold-axis cobalt ions, only one, a three-coordinate Co(II) ion, remains uncomplexed near the plane of a 6-ring. The other three ions, complexed to NO, are Co(III) and are four-coordinate, 0.39 Å from the O(3) plane, the shortest such distance reported for a sorption complex of dehydrated $Co_4Na_4Si_{12}Al_{12}O_{48}$. The Co^{III}–N–O angle is bent (141 (3)°), further indicating the oxidation of Co(II), and the Co^{III}–N distance is 2.23 (6) Å. In the NO_2 complex, only two of the four Co(II) ions are complexed to an NO_2 molecule; the Co^{II}–N distance is 1.95 (4) Å. The Co^{II}–NO_2 moiety is planar, indicating a synergic π interaction between NO_2 and Co(II). No NO or NO_2 interaction with Na^+ is observed. Full-matrix least-squares refinement converged to the final weighted *R* indices of 0.038 and 0.053 for the NO and NO_2 complexes, respectively.

Introduction

Exchangeable transition-metal ions in evacuated zeolites are generally coordinatively unsaturated. To satisfy their coordination requirements, they form complexes with a large variety of ligands. To characterize the activity of transition-metal ions in this unusual environment, we carried out structural studies of sorption complexes of cation-exchanged zeolite A. Among the structures which have been completed are complexes involving the cations Co(II), Mn(II), Ni(II), Fe(II), Eu(II), Cd(II), and Ag(I) and the small molecules H_2O, CO, C_2H_2, C_2H_4, C_3H_6, Cl_2, Br_2, and O_2.[1-14]

Metal–nitrosyl complexes have been observed to adopt one of two limiting ground states for the MNO (M is the metal) group, linear or strongly bent.[15] The linear form is considered to involve a cationic nitrosyl ligand and the bent form, an anionic nitrosyl ligand. Enemark and Feltham[16] have pointed out that the geometry assumed by the MNO group is dependent on several factors among which are the total number of electrons and the nature of the highest occupied molecular orbital. It has been determined by ESR methods that nitric oxide reacts with the cobalt(II)–ammonia complex in zeolite Y to form a nitrosyl complex $(Co^{III}(NH_3)_n(NO)^-)$.[17]

At room temperature, nitric oxide in zeolite Y undergoes disproportionation to form N_2, NO_2, and N_2O at pressures greater then 10 torr.[17] Furthermore, a Co^{II}–NO_2 complex, formed as a product of the disproportionation, poisons the catalytic site and terminates the reaction.[17] Hence by determining the crystal structures of the NO and NO_2 complexes of Co(II)-exchanged zeolite A, we gained some insight into the nature of bonding and the source of the catalytic activity.

If the structure of the NO_2 complex is found to be different from that of the NO complex, it would have been shown that the catalytic reaction had not already occurred in the latter and that the NO complex had been successfully prepared.

Experimental Section

Crystals of sodium zeolite 4A, stoichiometry $Na_{12}Si_{12}Al_{12}O_{48}\cdot 27H_2O$, were prepared according to Charnell's method[18] modified to include a second crystallization by using seed crystals from a previous synthesis. The ion exchange of the crystals of zeolite 4A was conducted as described before[2] with 0.1 M $Co^{II}(NO_3)_2$ solutions. The exchange yielded a material with approximate stoichiometry $Co_4Na_4Si_{12}Al_{12}O_{48}\cdot xH_2O$ per unit cell, henceforth to be referred to as Co_4Na_4-A, exclusive of water molecules. A single crystal, a cube about 0.08 mm on an edge, was used for the preparation of each complex and for the subsequent X-ray diffraction studies. Each crystal was placed into a finely drawn Pyrex capillary, attached to a vacuum system and then dehydrated by gradually increasing the temperature at increments of 25 °C/h up to 350 °C at a pressure of 1×10^{-5} torr (conditions previously determined[2] to be adequate for the complete dehydration of Co_4Na_4-A). In each preparation, the single crystal was maintained at these conditions for a period of 48 h to ensure complete dehydration.

After the crystals were returned to room temperature (23 °C), each crystal was exposed to zeolitically dried NO or NO_2 gas (Matheson Gas Products), at pressures of 10 and 20 torr, respectively, for 2 h, after which each was removed from the vacuum system by torch. Each crystal remained inside its capillary, in contact with its absorbent gas and sealed from the atmosphere, throughout subsequent X-ray diffraction experiments.

Microscopic examination indicated that neither crystal was damaged by dehydration and subsequent exposure to NO or NO_2 gas. Upon exposure to NO, the dehydrated Co_4Na_4-A crystal quickly changed color from deep blue to dark brown, and exposure to NO_2 caused the second crystal to become an even darker brown, nearly black.

X-Ray Diffraction Experiments and Data Collection. The cubic space group *Pm*3*m* (no systematic absences) was chosen for both X-ray diffraction studies for reasons previously cited.[14,19,20] An automated Syntex four-circle $P\bar{1}$ diffractometer with a graphite monochromator and a pulse-height analyzer was used for preliminary crystallographic experiments and for data collection. Molybdenum radiation ($K\alpha_1$, λ 0.709 30 Å; $K\alpha_2$, λ 0.713 59 Å) was used throughout. Least-squares refinement of 15 intense reflections for which $20° < 2\theta < 24°$ yielded the cubic cell constants $a = 12.187$ (4) Å for Co_4Na_4-A·3NO and $a = 12.143$ (2) Å for Co_4Na_4-A·$2NO_2$.

For each crystal, reflections from the two intensity-equivalent regions of reciprocal space (hkl, $h \leq k \leq l$; lhk, $l \leq h \leq k$) were examined by using the θ–2θ scan technique, for $2\theta < 70°$. For the NO complex, each reflection was scanned at a constant rate of 1.0° min^{-1} (0.5° min^{-1} for the NO_2 complex) over a symmetric range from 1° (in 2θ) below the calculated $K\alpha_1$ peak to 1° above the $K\alpha_2$ maximum. At each end of a scan range, background intensity was counted for a time equal to half the time required to scan 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 observed 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.[21] The mean intensity for a

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Table I. Positional, Thermal, and Occupancy Parameters[a]

	Wyckoff position	x	y	z	U_{11} or U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	occupancy factor
					(a) Co_4Na_4-A·3NO						
(Si,Al)	24(*k*)	0	1825 (2)	3692 (1)	276 (13)	213 (12)	139 (11)	0	0	36 (10)	1[b]
O(1)	12(*h*)	0	2098 (7)	1/2	754 (64)	662 (61)	227 (42)	0	0	0	1
O(2)	12(*i*)	0	2949 (4)	2949 (4)	721 (64)	267 (28)	267 (28)	0	0	194 (38)	1
O(3)	24(*m*)	1126 (3)	1126 (3)	3322 (4)	422 (23)	422 (23)	568 (40)	145 (32)	−66 (23)	−66 (23)	1
Co(1)	8(*g*)	2044 (6)	2044 (6)	2044 (6)	316 (25)	316 (25)	316 (25)	168 (22)	168 (22)	168 (22)	3/8
Na(1)	8(*g*)	1498 (32)	1498 (32)	1498 (32)	650 (173)	650 (173)	650 (173)	−105 (213)	−105 (213)	−105 (213)	1/8
Na(2)	12(*i*)	0	4248 (23)	4248 (23)	3485 (649)	2391 (368)	2391 (368)	0	0	−928 (394)	1/4
N	8(*g*)	3102 (30)	3102 (30)	3102 (30)	1627 (277)	1627 (277)	1627 (277)	−252 (296)	−252 (296)	−252 (296)	3/8
O(4)	24(*m*)	3027 (115)	3951 (55)	3951 (55)	3113 (1664)	4279 (1484)	4279 (1484)	−402 (886)	−402 (886)	−2052 (1066)	1/8
Co(2)	8(*g*)	2023 (51)	2023 (51)	2023 (51)	1442 (260)						1/8
					(b) Co_4Na_4-A·$2NO_2$						
(Si,Al)	24(*k*)	0	1821 (1)	3669 (1)	272 (9)	121 (7)	83 (7)	0	0	7 (6)	1[b]
O(1)	12(*h*)	0	2005 (5)	1/2	739 (50)	344 (39)	190 (32)	0	0	0	1
O(2)	12(*i*)	0	2972 (4)	2972 (4)	1118 (67)	176 (21)	176 (21)	0	0	67 (29)	1
O(3)	24(*m*)	1126 (3)	1126 (3)	3236 (3)	499 (20)	499 (20)	324 (27)	212 (26)	−139 (18)	−139 (18)	1
Co	8(*g*)	2071 (2)	2071 (2)	2071 (2)	300 (9)	300 (9)	300 (9)	45 (11)	45 (11)	45 (11)	1/2
Na	8(*g*)	1789 (16)	1789 (16)	1789 (16)	2055 (192)	2055 (192)	2055 (192)	1480 (200)	1480 (200)	1480 (200)	1/2
N	8(*g*)	2999 (19)	2999 (19)	2999 (19)	346 (96)						1/4
O(4)	24(*m*)	2997 (65)	2997 (65)	3893 (85)	1052 (313)						1/12
O(5)	24(*m*)	3034 (80)	3737 (76)	3737 (76)	1580 (580)						1/12

[a] All positional and thermal parameters are given × 10^4; standard deviations are in units of the least significant digit given for the corresponding parameter. The anisotropic temperature factor is $\exp[-2\pi^2(h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + l^2(c^*)^2U_{33} + 2hk(a^*b^*)U_{12} + 2hl(a^*c^*)U_{13} + 2kl(b^*c^*)U_{23})]$. [b] Occupancy factor for (Si) = $^1/_2$; occupancy factor for (Al) = $^1/_2$.

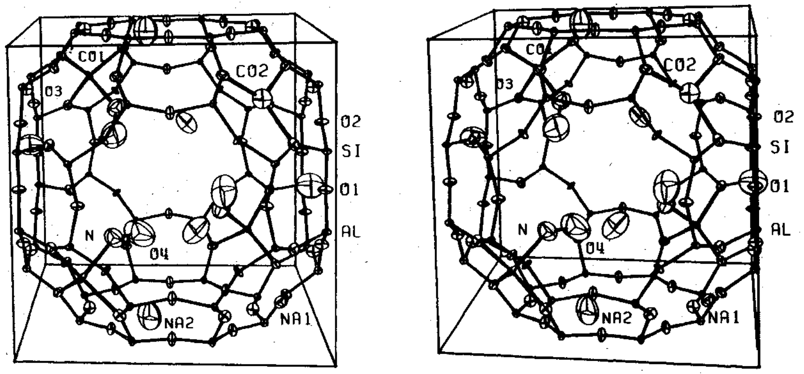

Figure 1. Stereoview of the Co_4Na_4-A·3NO unit cell. Heavy bonds indicate the approximate tetrahedral or trigonal-planar coordination about the two kinds of cobalt ions. Ellipsoids of 20% probability are used.

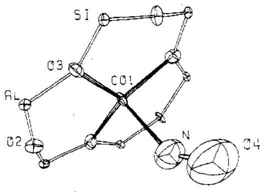

Figure 2. Coordination environment of the Co(III) ion in its $(CoNO)^{2+}$ complex. Ellipsoids of 20% probability are used.

reflection was calculated as $I = (I_{hkl} + I_{lhk})/2$, where $I_{hkl} = [\mathrm{CT} - 0.5(t_c/t_b)(B_1 + B_2)](\omega)$, 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 taken to be

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

and the standard deviation of each unmerged reflection is

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

The value of p was taken as 0.02,[22] a value found to be appropriate for the instrumentation used. No absorption correction was applied to the data; the linear absorption coefficients are 13.9 and 14.1 cm^{-1} for the NO and the NO_2 complexes, respectively, and the total range of transmission coefficients is estimated to be less than 2% for each crystal. Only those reflections whose net counts exceeded 3 times their corresponding esd's were used in structure solution and refinement. This amounted to 268 of the 864 reflections for Co_4Na_4-A·3NO and 464 of the 852 reflections for Co_4Na_4-A·$2NO_2$. Other details of the data reduction have been discussed previously.[4]

Structure Determination. Co_4Na_4-A·3NO. Initial full-matrix least-squares refinement of the structure began by using the atomic parameters of the framework ions ((Si,Al), O(1), O(2), O(3)) and of the cations (Co(II) and Na^+) previously determined for Co_4Na_4-A·4CO.[2] Refinement of these ions led to an R_1 index, $\sum|F_o - |F_c||/\sum F_o$, of 0.072 and a weighted R_2 index, $(\sum w(F_o - |F_c|)^2/\sum wF_o^2)^{1/2}$, of 0.067.

Isotropic refinement of four nitrogen atoms, at guessed positions on the threefold axis in the large cavity bonded to cobalt, lowered the R_1 and R_2 indices to 0.066 and 0.059, respectively. Refer to Table Ia and Figures 1 and 2 to identify the atoms.

With phases calculated from only the framework and Co parameters, a difference electron density function was generated, the standard deviation of which was 0.1 e $Å^{-3}$. Five significant peaks were located (i) at 0, x, x ($x = 0.42$; density = 1.10 e $Å^{-3}$), (ii) at x, x, x ($x = 0.15$; density = 2.02 e $Å^{-3}$), (iii) at x, x, x ($x = 0.30$; density = 1.21 e $Å^{-3}$), (iv) at x, y, y ($x = 0.30$, $y = 0.38$; density = 0.54 e $Å^{-3}$), and (v) at x, x, y ($x = 0.23$, $y = 0.40$; density = 0.34 e $Å^{-3}$). The first four of these positions were identified as Na(2), Na(1), N, and O(4), respectively. Occupancy refinement of the Na(1) and Na(2) positions led to values of approximately two each per unit cell. It was assumed at this stage that the occupancy factors of N and O(4) were 4, corresponding to one NO molecule per cobalt ion. Subsequent anisotropic refinement of these positions, except O(4) which refined only isotropically, converged with $R_1 = 0.056$ and $R_2 = 0.040$.

Because some of the resulting interatomic distances appeared to be in error, all reflections for which $(\sin\theta)/\lambda < 0.3$ were initially removed. With this data set, the positional parameter of O(4) changed from (x, x, y; $x = 0.30$, $y = 0.38$) to (x, y, y; $x = 0.26$, $y = 0.39$). Occupancy refinement of N and O(4) led to approximately four atoms per unit cell and that of Na(1) and Na(2) to about two ions per unit cell. Anisotropic refinement of O(4) failed to converge. The refinement of the initially proposed structure consisting of the zeolite framework, four Co(II) and four Na^+ cations, and four NO molecules led to $R_1 = 0.048$ and $R_2 = 0.033$.

Using all observed reflections, we found that occupancy and anisotropic refinement of the structure (excluding O(4) and with the Na(2) position fixed) resulted in 3.1 Co, 2.4 Na(1), and 1.7 Na(2) cations and 3.1 N atoms per unit cell. Inclusion of O(4) (isotropic) at 0.28, 0.38, 0.38 with the occupancy factors of the exchangeable atoms fixed at Co = 4, Na(1) = 2, Na(2) = 2, and N = 4 resulted in very large thermal parameters for Na(1) and higher error indices. Resetting the occupancy factors of Na(1) and Na(2) to 1.5 and 2.5 atoms/unit cell gave smaller thermal parameters for Na(1) with slightly larger R_1 and R_2 values. However, the thermal parameters of Na(2) were smaller than those of Na(1) despite the 2.5 ions at the Na(2) position, indicating that more ions could be placed at that position.

With the occupancy factors obtained for Co and N in the previous occupancy refinement, the model was reset to three atoms each per unit cell for Co(1), Na(2), N, and O(4) and one atom per unit cell for Na(1). Another atom at Co(2) was included at $x = 0.190$ on the threefold axis. Simultaneous positional and thermal parameter refinement of this model (with N, O(4), and Co(2) varying isotropically) led to $R_1 = 0.053$ and $R_2 = 0.038$. Subsequent refinements with the parameters of N and O(4) varying anisotropically converged to the final R_1 and R_2 indices of 0.052 and 0.038, respectively.

To determine whether Co(1) is coordinated by the oxygen or the nitrogen of the NO molecule, we carried out refinement for both structures. Coordination of the metal ion to the nitrogen end converged to an R_2 index of 0.037 64 while coordination to the oxygen end converged to $R_2 = 0.038 02$. By use of the significance test based on the R_2-factor ratio,[23,24] $\mathcal{R}$, it was established, at the 99.5% confidence level, that it is the nitrogen atom of NO which coordinates to cobalt.

The goodness-of-fit, $(\sum w(F_o - |F_c|)^2/(m - s))^{1/2}$, is 1.94; m (268) is the number of observations, and s (42) is the number of independent variables in least squares. All shifts in the final cycle of refinement were less than 6% of their respective standard deviations except those of some Co(2) parameters.

The most significant peak on the final difference Fourier function, whose estimated standard deviation is 0.06 e $Å^{-3}$ at a general position, was 0.9 (3) e $Å^{-3}$ in height and was located at (0.156, 0.156, 0.156), unreasonably close to the Na(1) 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. The proposed atomic arrangement in a particular unit cell is shown in Figure 1, and the coordination environment of Co(1) can be seen in Figure 2.

Co_4Na_4-A·$2NO_2$. Initial least-squares refinement began by using the framework atomic parameters determined for the NO complex. Rapid convergence to $R_1 = 0.33$ and $R_2 = 0.40$ was observed. A difference electron density function revealed possible positions for the Co ions at x, x, x ($x = 0.20$; density = 20.2 (4) e $Å^{-3}$). Isotropic refinement of four Co ions per unit cell reduced both R indices to 0.10.

A subsequent electron density function with phases calculated from the framework and Co parameters indicated a possible position for Na^+ at x, x, x ($x = 0.17$; density = 2.2 e $Å^{-3}$), a second maximum at x, x, x ($x = 0.30$; density = 3.0 e $Å^{-3}$) which was later identified as the N position, and several other density maxima in the large cavity which were possible positions for the oxygen atoms of the NO_2 group. Successive inclusion of four Na^+ and four N atoms (with anisotropic thermal parameters for Co), corresponding to an initially proposed model of one NO_2 molecule associated with each of the four Co cations, reduced R_1 to 0.091 and R_2 to 0.075. Inclusion of four oxygens per unit cell at O(4) with anisotropic thermal parameters for Na^+ and N led to the R_1 and R_2 indices of 0.082 and 0.062, respectively (see Table Ib to identify the atoms). Further inclusion of four oxygen atoms at O(5) with an isotropic thermal parameter caused large shifts in the thermal and positional parameters of the oxygen atoms and led to an unacceptable structure for the $CoNO_2$ complex. It was noted that when the number of NO_2 ligands was decreased, acceptable geometries and lower R indices resulted, indicative of the presence of only two NO_2 molecules per unit cell. Simultaneous positional and thermal parameter refinement of the structure led to $R_1 = 0.078$ and $R_2 = 0.052$ with, however, very large esd's for the anisotropic thermal parameters of O(4) and O(5). Consequently, the structure was refined with N, O(4), and O(5) isotropic. Least-squares refinement of the final model, Co_4Na_4-A·$2NO_2$, converged to the final R_1 and R_2 indices of 0.078 and 0.053, respectively.

An attempt was made to refine the structure with three molecules of NO_2. However, the N–O(4) distances became unreasonable and the error indices increased slightly. The goodness-of-fit is 2.77. The number of observations is 464, and the number of parameters is 35. All shifts in the final cycle of least-squares refinement were less than 1% of their respective standard deviations. The most significant peak on the final difference Fourier function (esd at a general position = 0.10 e $Å^{-3}$) was 1.7 (2) e $Å^{-3}$ at (0, 0.19, 0.36), too close to the framework Si and Al atoms to be acceptable as a new atomic position.

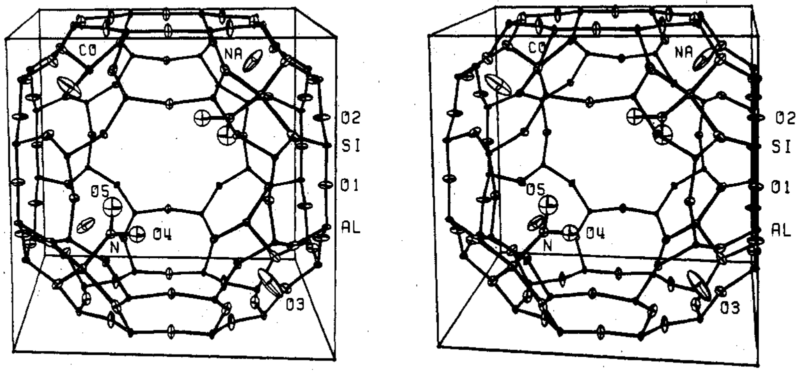

Figure 3. Stereoview of the Co_4Na_4-A·$2NO_2$ unit cell. Heavy bonds indicate the approximately tetrahedral or trigonal-planar coordination about the Co(II) ions. Ellipsoids of 20% probability are used.

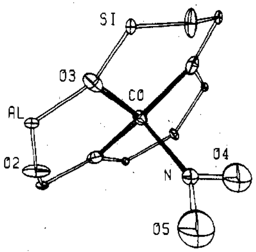

Figure 4. Coordination environment of the Co(II) ion in its $(CoNO_2)^{2+}$ complex. Ellipsoids of 20% probability are used.

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

In Co_4Na_4-A·3NO			
(Si,Al)–O(1)	1.628 (3)	Co(2)–O(3)	2.213 (18)
(Si,Al)–O(2)	1.643 (6)	Co(2)–O(2)	2.937 (6)
(Si,Al)–O(3)	1.677 (2)	Na(1)–O(3)	2.31 (2)
Co(1)–O(3)	2.220 (5)	Na(1)–O(2)	3.10 (2)
Co(1)–O(2)	2.939 (4)	Co(1)–N	2.23 (6)
		N–O(4)	1.47 (11)
O(1)–(Si,Al)–O(2)	111.7 (4)	(Si,Al)–O(3)–(Si,Al)	139.3 (3)
O(1)–(Si,Al)–O(3)	111.5 (2)	O(3)–Co(1)–O(3)	116.9 (6)
O(2)–(Si,Al)–O(3)	106.0 (3)	O(3)–Co(2)–O(3)	118 (4)
O(3)–(Si,Al)–O(3)	109.9 (3)	O(3)–Na(1)–O(3)	110 (3)
(Si,Al)–O(1)–(Si,Al)	156.4 (6)	O(3)–Co(1)–N	100.2 (5)
(Si,Al)–O(2)–(Si,Al)	156.9 (5)	Co(1)–N–O(4)	141 (3)
In Co_4Na_4-A·$2NO_2$			
(Si,Al)–O(1)	1.632 (2)	Na–O(3)	2.094 (4)
(Si,Al)–O(2)	1.634 (2)	Na–O(2)	2.974 (6)
(Si,Al)–O(3)	1.690 (2)	Co–N	1.95 (4)
Co–O(3)	2.153 (4)	N–O(4)	1.09 (11)
Co–O(2)	2.953 (3)	N–O(5)	1.27 (10)
O(1)–(Si,Al)–O(2)	113.3 (3)	O(3)–Co–O(3)	114.6 (3)
O(1)–(Si,Al)–O(3)	112.1 (2)	O(3)–Na–O(3)	120 (2)
O(2)–(Si,Al)–O(3)	105.4 (2)	O(3)–Co–N	103.6 (2)
O(3)–(Si,Al)–O(3)	108.0 (2)	Co–N–O(4)	125 (6)
(Si,Al)–O(1)–(Si,Al)	164.2 (3)	Co–N–O(5)	147 (6)
(Si,Al)–O(2)–(Si,Al)	152.4 (4)	O(4)–N–O(5)	88 (6)
(Si,Al)–O(3)–(Si,Al)	135.3 (3)		

[a] Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

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

The quantity minimized in the full-matrix least-squares program used was $\sum w(\Delta|F|)^2$; the weight (w) of an observation was the reciprocal square of $\sigma(F_o)$, its standard deviation. Atomic scattering factors[25,26] for Na^+, Co^{2+}, O^-, N (valence), O (valence), 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. These scattering factors were modified to account for the real components ($\Delta f'$) of the anomalous dispersion correction.[27,28]

Discussion

Co_4Na_4-A·3NO. In dehydrated Co_4Na_4-A,[2] four Co(II) and four Na^+ ions are located on the threefold axes close to the plane of the oxygen 6-rings. Both the Co(II) and Na^+ ions possess near trigonal-planar geometry and each is strongly bound to three framework oxide ions at O(3). Upon the introduction of NO gas at a pressure of 10 torr, a severe redistribution of exchangeable cations occurs, suggesting the formation of Co(III) and NO^-. The nonlinear Co–N–O bond angle of 141 (3)° further shows the presence of NO^-, which in turn indicates the oxidation of Co(II).

The oxidation of three Co(II) ions to Co(III) would lead to a sharp increase in cationic charge near the surface of the sodalite unit, from a formal charge of +12 (four Co(II) and four Na^+ ions) to +15 (three Co(III), one Co(II), four Na^+ ions). To alleviate this charge imbalance, three Na^+ ions have moved about 5.1 Å to the previously less favorable sites in the oxygen 8-rings which are occupied to the limit of one Na^+ ion per available 8-ring. Because the fourth Na^+ ion cannot be so promoted, it remains in the sodalite unit. It is perhaps for this reason that the oxidation of the fourth Co(II) ion does not occur.

The complexed Co(III) ions, at Co(1), are 0.39 Å from the O(3) plane. This distance is the smallest reported for sorption complexes of dehydrated Co_4Na_4-A. Cobalt(II) ions in dehydrated Co_4Na_4-A complexed with CO, C_2H_2, C_2H_4, Cl_2, or C_3H_6[2–4,6,14] are all more than 0.50 Å from their respective O(3) planes. The unusually small deviation observed in this work is consistent with the proposed oxidation of Co(II) to Co(III).

A strong metal ion to ligand interaction is likewise indicated by the color change from deep blue in the dehydrated form to dark brown upon sorption of NO.

The Co^{III}–O^{2-} bond length (2.220 (5) Å) is here found to be longer than the Co^{II}–O^{2-} bond length (2.077 (18) Å) in dehydrated Co_4Na_4-A.[2] This distance could be virtual, a result of the "averaging" of the atomic positions of the variously occupied (by Co(III), Co(II), or Na^+) oxygen 6-rings. The triply charged Co(III) ion with its smaller radius should cause a larger deformation of the 6-ring O(3)'s toward the center than would Co(II) or Na^+, so the actual Co^{III}–O^{2-} distance should be somewhat shorter than the value observed.

In a recent article, Lunsford et al.[29] concluded on the basis of IR and photoelectron spectra of the cobalt ions that the nitrosyl ligand is effectively neutral in the NO complex of dehydrated Co_4Na_4-A zeolite, contrary to findings in this work. Their report, however, also included data from diffuse-reflectance spectra and X-ray photoelectron spectra of the nitrogen 1s level, which did not unequivocally support their conclusion. It was stated in the same report that the diffuse-reflectance spectra, which provided information on the

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

	Co_4Na_4-A·3NO	Co_4Na_4-A·$2NO_2$
Co(1)	0.393	0.508
Co(2)	0.347	
Na(1)	−0.76	−0.08
N	2.62	2.46

[a] A negative deviation indicates that the atom lies on the same side of the plane as the origin.

metal ions, indicated that "the nitrosyl group has a significant effect on the electronic structure of the cobalt ion".[29] The spectra showed large decreases in absorbance and small modifications in band positions upon introduction of NO, accompanied by a change in sample color from blue to almost black. The latter observation is consistent with the observed color changes in this work. Furthermore, Lunsford et al. observed that the zeolite sample returned to its original blue color upon evacuation of NO. These results were attributed to possible charge-transfer bands.

In their measurements of binding energies, Lunsford et al. obtained a value of 400.6 ± 0.1 eV for the nitrogen 1s peak,[29] a value similar to that reported by Finn and Jolly[30] for the $[Co(NO)(NH_3)_5]Cl_2$ complex (BE = 400.7 eV) which has an anionic NO ligand and a Co–N–O angle of 119°. However, Lunsford et al. argued that because Finn and Jolly did not report the value adopted by their carbon (pump oil) standard, no valid comparisons could be made between the results of the two groups. It now appears to us that the calibrations of Finn and Jolly were adequate and that their reported value of the N 1s binding energy is reliable; it is consistent with our finding that the NO ligand in this zeolite is anionic and that Co–N–O is bent.

Finn and Jolly,[30] in the study of several metal nitrosyl compounds, established a definite correlation between the N 1s binding energy of a nitrosyl group, the structure, and the electron density of that group. Complexes with high electron density on the NO ligand were characterized by a bent metal–N–O bond angle. Such bent nitrosyls also exhibited low binding energies (about 400.3 ± 0.4 eV). In addition, Finn and Jolly concluded that the NO binding energies correlated imprecisely with N–O stretching frequencies.[30]

Enemark and Feltham[16] have pointed out that the geometry (linear or bent) adopted by a NO group coordinated to a metal ion is governed by four factors: the coordination number, the coordination geometry, the number of electrons, and the nature of the highest occupied molecular orbital.

Mingos[31] has reported a molecular orbital correlation diagram for tetrahedral complexes with linear and bent nitrosyls. Relatively few structures of four-coordinate metal–nitrosyl complexes have been determined and all of the known structures are $(MNO)^{10}$ complexes (a notation using the sum of the number of d electrons from the metal ion and electrons from π^* NO orbital). These $(MNO)^{10}$ complexes have pseudotetrahedral geometries with linear or nearly linear MNO groups (C_{3v} symmetry) as expected due to the molecular orbital energies of these complexes.[16] The CoNO complex in Co_4Na_4-A·3NO is a $(MNO)^8$ system. On the basis of correlation diagrams such as that reported by Mingos, a tetrahedral coordination with a bent nitrosyl group (C_s symmetry) for this system is not energetically unfavorable.

Co_4Na_4-A·$2NO_2$. Each Co(II) ion which has complexed to an NO_2 molecule has shifted 0.17 Å into the large cavity along a threefold axis. The cation to framework interaction is weakened as evidenced by the lengthening of Co–O(3) bond length from 2.077 (18) Å in dehydrated Co_4Na_4-A[2] to 2.153 (4) Å and the increase in (Si,Al)—O(3)—(Si,Al) bond angle to 135.3 (3)°. (As before, these values are averages over all O(3) ions in the structure and are likely to describe the actual environment of Co inaccurately.) As with the NO complex, no interaction of sorbed molecules with Na^+ is observed; an alternative approach distance of Na^+ to N, 2.54 Å, is judged to be too long. A strong Co(II) to NO_2 interaction is further indicated by the short Co(II) approach distance to nitrogen of 1.95 (4) Å.

The positions for Co, N, O(4), and O(5) are planar by symmetry, indicating a significant π interaction between the NO_2 π system and the Co(II) d orbitals. Hence the stability of this complex can be attributed, in part, to synergic bonding. The lone electron in NO_2, located mainly on nitrogen, can delocalize into Co(II) d orbitals, which can, in turn, "back-bond" to the π^*-acceptor orbitals of NO_2. That the Na^+ ions have not relocated from the sodalite unit indicates that the extent of charge transfer is much less than that in the NO complex.

Because the structures of the NO and NO_2 complexes of dehydrated Co_4Na_4-A are significantly different (see Table I to compare positional parameters and Table II for bond lengths and angles), the possibility that NO in Co_4Na_4-A had disproportionated before the diffraction data was collected, to give N_2, N_2O, and NO_2 which would have led to the unintentional formation of the NO_2 complex, can be dismissed. The difference in the cell constants of the two complexes also ensures that the first is not an NO_2 complex.

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Registry No. Co_4Na_4-A·3NO, 69991-07-7; Co_4Na_4-A·$2NO_2$, 69991-06-6; Co_4Na_4-A, 50940-66-4.

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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