

Crystal Structures of the NO and N₂O₄ Sorption Complexes of Fully Dehydrated Fully Cd²⁺-Exchanged Zeolite X (FAU): Coordination of Neutral NO and N₂O₄ to Cd²⁺

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The structures of the nitric oxide and dinitrogen tetroxide sorption complexes of dehydrated fully Cd²⁺-exchanged zeolite X (FAU) have been determined using single-crystal X-ray diffraction in the cubic space group $Fd\bar{3}m$ at 21(1) °C. Ion exchange was accomplished by allowing an aqueous stream 0.05 M in Cd²⁺ to flow past each crystal for 5 days. Each crystal was then dehydrated at 500 °C and 2×10^{-6} Torr for 2 days, followed by exposure to 100 Torr of zeolitically dry NO or NO₂/N₂O₄ gas. The structures were determined in these atmospheres. The unit cell constants at 21(1) °C are 24.877(2) Å for the dark-yellow NO complex, [Cd₄₆(NO)₁₆][Si₁₀₀Al₉₂O₃₈₄]-FAU, and 24.735(2) Å for the black N₂O₄ complex, [Cd₄₆(N₂O₄)_{25.5}][Si₁₀₀Al₉₂O₃₈₄]-FAU. The structure of the NO complex was refined to $R_1 = 0.072$ and $wR_2 = 0.134$. In this structure, Cd²⁺ ions occupy four crystallographic sites. Fifteen Cd²⁺ ions occupy site I (at the centers of the double 6-rings (D6Rs)), and one occupies site I' (in the sodalite cavity opposite a D6R). The remaining 30 Cd²⁺ ions occupy two different sites II (near 6-rings in the supercages): 16 coordinate to nitric oxide molecules and 14 do not. Sixteen NO molecules lie in the supercage where each interacts weakly with a Cd²⁺ ion: Cd–N = 2.57(22) Å. The observed N–O bond distance is 1.28(25) Å and Cd–N–O is 118(10)°. The structure of the N₂O₄ complex was refined to $R_1 = 0.084$ and $wR_2 = 0.216$. In this structure, Cd²⁺ ions occupy only three crystallographic sites. The 16 D6Rs per unit cell are filled with 11.5 Cd²⁺ ions at site I and 9 Cd²⁺ ions at site I': $11.5 + 9/2 = 16$. The remaining 25.5 Cd²⁺ ions occupy site II where each coordinates at 2.43(8) Å to a nitrogen atom of a N₂O₄ molecule. At the coordinating nitrogen atom, O–N–O is 147(10)° and the N–O bond lengths are 1.07(9) and 1.23(10) Å. At the second nitrogen atom, O–N–O is 140(10)°, and the N–O bond lengths are 1.03(13) and 1.42(12) Å. The imprecisely determined N–N bond length, 2.74(17) Å, appears to be very much lengthened by coordination to Cd²⁺. The Cd–N–N angle is 144(10)°. This appears to be the first crystallographic report of the coordination of N₂O₄ to a cation.

Introduction

Zeolites are high-capacity sorbents and effective catalysts. Because of their uniform channel systems, they are highly selective for both functions. A knowledge of the molecule–zeolite and molecule–molecule interactions within the zeolite is crucial to understanding the mechanisms of sorption and catalysis. These processes depend also on the kinds of cations present, their distribution over the available sites, and the interactions that these cations have with sorbed (guest) molecules.¹ Variations in the chemical composition and structure of the zeolite are often important.

Generally, some of the exchangeable transition-metal ions in evacuated zeolites are coordinatively unsaturated. These complex readily to a variety of guest molecules. Their complexes with CO,² CS₂,³ C₂H₂,^{4–6} C₂H₄,^{7–9} C₃H₆,¹⁰ H₂S,¹¹ NH₃,^{12,13} NO,¹⁴ and NO₂¹⁴ have been observed crystallographically.

The infrared spectra of NO sorbed onto Ca–Y, Na–Y, decationated Y, and H–Y showed that N₂O and NO₂ had been

produced from NO by disproportionation; the catalytic activity for this increased in the following order: H–Y < decationated Y = Na–Y < Ca–Y.¹⁵ Furuyama and Nagato studied the sorption of argon, oxygen, nitrogen, nitric oxide, and carbon monoxide onto magnesium, calcium, and barium mordenites; over the temperature range –50 to 150 °C, sorption affinities in the order Ar < O₂ < N₂ < NO < CO were seen; the order of gas sorbability into mordenite is Ba–M < Ca–M < Mg–M (M denotes mordenite).¹⁶ In a recent report, EPR measurements at temperatures below 40 K showed that NO is a very suitable probe molecule for characterizing Lewis acid centers on nanoporous materials such as the LTA and MFI zeolites; the relatively wide distribution of sorption energies for NO on Na–MFI showed a large variety of adsorption sites.¹⁷ Jentys et al. studied the reduction NO over Ni-exchanged mordenite in the presence of excess oxygen using propane and propene as reducing agents.¹⁸ Using MFI zeolites, NO reduction was studied using hydrocarbons such as methane, propane, and *iso*-butane.^{19,20}

Many studies have been done on the removal of nitrogen oxides (NO_x) from automobile exhaust gases. To clean the

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exhaust gas from diesel engines, an intense research effort has been focused in recent years on the design of electrochemical cells for the reduction of NO_x. Bredikhin et al. reported a novel low-voltage electrochemical cell for NO decomposition.²¹ Kono studied the dispersion of motor-vehicle exhaust gases, especially NO_x, in Osaka; annual average NO_x concentrations were calculated using the Gaussian plume model.²² Kitahara et al. studied the passive and active performance characteristics of NO_x catalysts for direct-injection diesel engines for passenger cars.²³ Liu et al. studied a new pure-oxygen internal combustion engine; by having no nitrogen gas in the intake, the NO_x in the exhaust should be very much reduced.²⁴ Yeom et al. studied the reduction of NO_x from diesel emissions over a BaNa–Y (FAU) zeolite catalyst.²⁵ DeNO_x of exhaust gas from lean-burn engines through the reversible adsorption of N₂O₃ in alkali–metal cation-exchanged faujasite-type zeolites was studied by Sultana et al.²⁶ NO_x sorbents are key control components for the emissions of transport vehicles. Basic oxides that sorb NO_x are currently in use, but they are easily poisoned by sulfur oxides.²⁶

Iranpoor et al. reported that the dinitrogen tetroxide complexes of iron(III) and copper(II) were very efficient reagents for the oxidation of hydroxy compounds, e.g., alcohols.²⁷ Addison et al. studied the molecular complexes of dinitrogen tetroxide with a wide range of organic compounds and anhydrous metal nitrates.²⁸ Roscoe and Hind have critically reviewed previous reports on the determination of the equilibrium constant of nitrogen dioxide with dinitrogen tetroxide and its temperature dependence.²⁹ Dispersive Fourier transform spectroscopy in the visible (DFTS-VIS) was used to study the complex refractive index of equilibrium mixtures of NO₂/N₂O₄ in the gas phase between 290 and 350 K and in the wavenumber range between 11000 and 19000 cm^{−1}.³⁰ With the aid of quantum-chemical MBPT/MP2 calculations of the components of the static dipole polarizability tensor of N₂O₄, the quasi-continuous spectra of the complex mean dipole polarizability of the neat components NO₂ and N₂O₄ were obtained.³⁰

Metal–nitrosyl complexes have been observed to adopt one of two limiting ground states for the MNO group, linear or bent.³¹ The linear form is considered to involve the cationic nitrosyl ligand NO⁺ and the bent form, the anionic nitrosyl ligand NO[−]. By using a fully dehydrated zeolite containing coordinatively unsaturated cations that are neither readily oxidized nor reduced, it was anticipated that the substantially weaker coordination of neutral NO molecules might be reliably observed. Cd²⁺ was chosen because it does not change oxidation state easily and because fully dehydrated, stoichiometrically Cd²⁺-exchanged zeolite X has been made and characterized.³²

Similarly, NO₂ has been observed to complex to transition-metal cations that are readily capable of oxidation, e.g., Mn²⁺, Co²⁺, Cu⁺, Au⁺, and Fe²⁺, to give nitrite complexes.^{14,33–35} The use of a zeolite as described in the preceding paragraph should allow the weaker coordination of neutral NO₂ or N₂O₄ molecules to be observed.

This work was done, in part, to understand the mechanisms by which NO_x catalysts work. The association of the odd molecules NO and NO₂ with a cation that does not promote catalysis may reveal the geometry of the first (sorpative) step in the catalytic process. Specifically, this work was done to locate the sorbed NO and NO₂ molecules, to determine the cation shifts upon sorption, to observe cation–sorbate interactions, and perhaps to detect the resultant changes in the geometry of NO and NO₂ upon sorption into Cd²⁺-exchanged zeolite X. The observation of coordinated N₂O₄ was not foreseen.

Experimental Section

Large single crystals of zeolite Na–X (FAU), stoichiometry Na₉₂Si₁₀₀Al₉₂O₃₈₄ per unit cell, were prepared in Leningrad, now St. Petersburg, Russia.³⁶ One of these, a colorless octahedron about 0.2 mm in cross-section, was lodged in a fine Pyrex capillary.

Cd₄₆-X was prepared by allowing an exchange solution of Cd(NO₃)₂ (Aldrich, 99.999%) and Cd(O₂CCH₃)₂ (Aldrich, 99.99%) in the molar ratio 1:1 with a total Cd²⁺ concentration of 0.05 M and a pH of 7 to flow past the crystal at a velocity of approximately 15 mm/s at 21(1) °C for 5 days. Each capillary containing its crystal was attached to a vacuum system, and the crystal was cautiously dehydrated at 500 °C and 2 × 10^{−6} Torr for 2 days. After cooling to room temperature, each colorless crystal was exposed for 2 h to 100 Torr of NO (Aldrich, 98.5%) or NO₂ (actually an equilibrium mixture of NO₂ and N₂O₄) (Union Carbide, 99.5%) gas that had been zeolitically dried in situ. Each crystal, still in its atmosphere, was then sealed in its capillary by torch. Upon exposure to NO and NO₂, the crystals became dark yellow and black, respectively. Subsequent diffraction experiments were performed at 21(1) °C.

The cubic space group *Fd* $\bar{3}$ was initially chosen because most crystals from this synthesis batch had been refined successfully in that space group.³⁷ However, *Fd* $\bar{3}$ was rejected and the space group *Fd* $\bar{3}m$ was chosen for both structures because only insignificant differences were seen between the mean Al–O and Si–O distances in least-squares refinement. For each crystal, the error indexes did not increase when the space group was changed to *Fd* $\bar{3}m$. The near zero difference between the mean Al–O and Si–O distances indicates that the Si/Al compositions at both the Si and Al positions are essentially the same as that for the entire crystal: the long-range Si,Al ordering has been lost.³⁷ This can occur most easily by the formation of antido-mains.³⁸

Diffraction data were collected with an automated Enraf–Nonius four-circle computer-controlled CAD-4 diffractometer equipped with a pulse-height analyzer and a graphite monochromator, using Mo radiation. The unit cell constants at 21(1) °C, determined by least-squares refinement of 25 intense reflections for which 14 < 2θ < 22, are *a* = 24.877(2) Å for the NO sorption complex and *a* = 24.735(2) Å for the N₂O₄ complex. (This work shows that the latter is a N₂O₄ complex.) All unique reflections in the positive octant of an *F*-centered unit cell, for which 2θ < 50, *l* > *h*, and *k* > *h* were recorded. Calculations were performed with XCAD4 (LP corrections)³⁹ and with the structure determination program package SHELX97.⁴⁰ An absorption correction was made empirically using a ψ scan.⁴¹ These corrections had little effect on the final *R* indices. Other details are the same as those previously reported.⁴² Table 1 provides a summary of the experimental and crystallographic data.

Structure Determination

Cd₄₆–X·16NO. Full-matrix least-squares refinement⁴⁰ was done on *F*² using all reflections. Initially the atomic parameters of the framework atoms [(Si,Al), O(1), O(2), O(3), and O(4)] in dehydrated Ca₄₆–X·30C₃H₆ were used.⁴³ These positions when refined isotropically yielded *R*₁ = 0.46 and *wR*₂ = 0.77. For the definitions of *R*₁ and *wR*₂, see the footnotes to Table 1.

A Fourier difference electron-density function yielded two strong peaks at (0.0, 0.0, 0.0) and (0.241, 0.241, 0.241), positions near framework oxygens normally occupied by cations. Isotropic refinement of the framework atoms and anisotropic refinement

TABLE 1: Summary of Experimental and Crystallographic Data

	Cd ₄₆ -X•16NO	Cd ₄₆ -X•25.5N ₂ O ₄
ion exchange <i>T</i> (°C)	21	21
ion exchange <i>t</i> (days)	5	5
space group	<i>Fd</i> $\bar{3}$ <i>m</i>	<i>Fd</i> $\bar{3}$ <i>m</i>
data collection <i>T</i> (°C)	21	21
scan technique	θ -2 θ	θ -2 θ
radiation (Mo K α) λ_1 (Å)	0.70930	0.70930
λ_2 (Å)	0.71359	0.71359
unit cell constant, <i>a</i> (Å)	24.877(2)	24.735(2)
2 θ range for <i>a</i> (deg)	14–22	14–22
no. of reflections for <i>a</i>	25	25
2 θ range in data collection (deg)	3 < 2 θ < 50	3 < 2 θ < 50
no. of unique reflections (<i>m</i>)	693	681
no. of reflections with $F_o > 4\sigma(F_o)$	323	273
no. of parameters (<i>s</i>)	48	44
data/parameter ratio (<i>m/s</i>)	14.4	15.5
weighting parameters: <i>a/b</i>	0.0981/1021	0.1376/0.00 ^a
$R_1^b/wR_2^c(F_o > 4\sigma(F_o))$	0.072/0.134	0.084/0.216
wR_2^c (all data)	0.164	0.277
goodness of fit ^d	1.09	1.07

^a *b* refined to the minimum allowed value. ^b $R_1 = \sum |F_o| / \sum F_o$. Only those reflections for which $F_o > 4\sigma(F_o)$ were used. ^c $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$. ^d Goodness-of-fit = $[\sum w(F_o^2 - F_c^2)^2 / (m - s)]^{1/2}$. All data were used.

of these two Cd²⁺ positions converged to $R_1 = 0.12$ and $wR_2 = 0.25$. The occupancies refined to 15.1(5) at Cd(1) and 25.9(9) at Cd(4), respectively. The thermal ellipsoid of Cd(4) became unreasonably elongated in subsequent refinement, indicating the presence of two nonequivalent Cd²⁺ ions at this position. These refined anisotropically as Cd(3) and Cd(4) at $x = 0.216$ and $x = 0.227$ on the three-fold axes, respectively; $R_1 = 0.088$ and $wR_2 = 0.189$.

One large peak with height 3.7 eÅ⁻³ appeared at (0.071, 0.071, 0.071) on the next difference Fourier function. Including it as Cd(2) and allowing it to refine isotropically led to convergence with $R_1 = 0.078$ and $wR_2 = 0.175$ with an occupancy of 1.0(2). The occupancy numbers were then fixed at 15, 1, 14, and 16 Cd²⁺ ions per unit cell at Cd(1), Cd(2), Cd(3), and Cd(4), respectively, integers to which they were closely refining and which sum nicely to 46 (see Table 2).

A subsequent difference Fourier function revealed two peaks at (0.254, 0.297, 0.297) and (0.307, 0.307, 0.307) with heights of 1.0 and 1.2 eÅ⁻³, respectively. Anisotropic least-squares refinement of Cd(1), Cd(3), and Cd(4), and isotropic least-squares refinement of (Si,Al), O(1), O(2), O(3), O(4), Cd(2), N(1), and O(11), treating the peak which was both smaller and closer to Cd(4) as nitrogen, N(1), and the other as oxygen, O(11), converged to $R_1 = 0.076$ and $wR_2 = 0.171$, respectively. Because the occupancies at Cd(4), N(1), and O(11) were refining almost in the ratio 1:1:1, they were fixed as shown in Table 2. Attempts to refine N(1) and O(11) at positions of lower symmetry were unsuccessful. In the final refinement, all atoms were refined anisotropically except for Cd(2), N(1), and O(5), which were refined isotropically; it converged with $R_1 = 0.072$ and $wR_2 = 0.134$. Fixed weights were used initially; the final weights were assigned using the formula $w = q/[\sigma^2(F_o^2) + (aP)^2 + bP + d + e \sin(\theta)]$, where $p = fF_o^2 + (1 - f)F_c^2$, to give $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $p = (F_o^2 + 2F_c^2)/3$; the *a* and *b* parameters were refined in least squares (see Table 1).

The largest peak on the final difference function appeared at (0.125, 0.125, 0.125) with a height of 1.1 eÅ⁻³. This peak was

not stable in least-squares refinements. There were no other peaks close to cations, NO molecules, nor framework oxygens.

Atomic scattering factors⁴⁴ for (Si,Al), O, Cd²⁺, and N were used. The scattering factor of Si, diminished by a scale factor of 0.9658 to account for its partial Al occupancy, was used for the (Si,Al) position. All scattering factors were modified to account for anomalous dispersion.^{45,46} The final structural parameters, and selected interatomic distances and angles, are presented in parts a of Tables 2 and 3, respectively.

Cd₄₆-X•25.5N₂O₄. Full-matrix least-squares refinement was done on *F*² using all reflections. It began using the framework atomic parameters determined for [Cd₄₆(NO)₁₆][Si₁₀₀Al₉₂O₃₈₄]-FAU. These positions refined isotropically to give $R_1 = 0.39$ and $wR_2 = 0.82$.

A Fourier difference electron-density function yielded three strong peaks at (0.0, 0.0, 0.0), (0.071, 0.071, 0.071), and (0.241, 0.241, 0.241), positions near framework oxygens normally occupied by cations. Isotropic refinement of the framework atoms and anisotropic refinement of these three Cd²⁺ positions converged to $R_1 = 0.113$ and $wR_2 = 0.344$. The occupancies refined to 11.9(3) at Cd(1), 10.0(7) at Cd(2), and 24.4(9) at Cd(3), respectively. These values were reset and fixed at 11.5, 9.0, and 25.5 Cd²⁺ ions at Cd(1), Cd(2), and Cd(3), respectively (see Table 2). These occupancy values fill, and do not overfill, the 16 D6Rs per unit cell: 11.5 have a Cd(1) ion at their centers and 9.0/2 = 4.5 have two Cd(2) ions, one on each side (Cd(2)···Cd(2) = 5.65 Å), at site Y'. In addition, the occupancies selected gave the lowest error indices: $R_1 = 0.108$ and $wR_2 = 0.346$. For comparison, upon fixing these occupancies at 12, 10, and 24, respectively, the error indices converged to $R_1 = 0.111$ and $wR_2 = 0.351$. Anisotropic refinement of the framework atoms and Cd²⁺ ions converged to $R_1 = 0.107$ and $wR_2 = 0.342$.

A subsequent difference Fourier function revealed three peaks at (0.236, 0.280, 0.330), (0.249, 0.249, 0.358), and (0.217, 0.324, 0.324) with heights of 1.4, 1.2, and 1.4 eÅ⁻³. Anisotropic least-squares refinement of all positions except for N(1), O(11), and O(12), which were refined isotropically, treating the peak closest to Cd(3) (0.236, 0.280, 0.330) as nitrogen and the others as oxygens, converged to $R_1 = 0.106$ and $wR_2 = 0.312$, respectively.

Another difference Fourier function revealed three more peaks at (0.170, 0.300, 0.421), (0.171, 0.419, 0.303), and (0.160, 0.242, 0.430) with heights of 1.1, 1.0, and 1.0 eÅ⁻³. Refinement including the first peak (the central peak) as nitrogen, N(2), and the remaining two as oxygens at O(21) and O(22), respectively, led to $R_1 = 0.087$ and $wR_2 = 0.254$, respectively. Guest atom positions were refined isotropically.

Because the occupancies at Cd(3), N(1), O(11), and O(12) were all refining to similar values (see Table 2), and because the occupancies at N(1), O(11), and O(12) must be equal if they are to represent NO₂ molecules, all four were constrained to be equal. Their common occupancy value refined to 24.9(7). Because 46 dipositive cations are needed per unit cell to balance its anionic charge, these occupancies were fixed at 25.5 (see Table 2). The occupancies of the atoms of the second nitrogen dioxide molecule (N(2), O(21), and O(22)), which were refining to 36(5) molecules per unit cell in constrained refinement, were each fixed at 25.5, their maximum value because only one N(2) molecule can interact with each N(1) nitrogen atom. These latter NO₂ molecules make no close approaches to framework oxygens nor Cd²⁺ ions. They interact only with the former NO₂ molecules (N(1)-N(2) = 2.74 (17) Å), and the pair may be considered an N₂O₄ molecule with an elongated N-N bond. In

TABLE 2: Positional, Thermal, and Occupancy Parameters^a

												occupancy ^c		
atom	site	Wyc. pos.	x	y	z	U_{11}/U_{iso}^b	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	varied	varied with constraints	fixed
(a) Cd ₄₆ -X · 16NO														
(Si,Al)		192(i)	−538(2)	1218(2)	356(2)	77(25)	57(27)	50(29)	−19(21)	−27(20)	−10(22)			192
O(1)		96(h)	−1071(4)	1071(4)	0	240(60)	240(60)	127(94)	−18(69)	−47(63)	−47(63)			96
O(2)		96(g)	−19(5)	−19(5)	1451(5)	121(46)	121(46)	152(82)	65(84)	30(66)	30(66)			96
O(3)		96(g)	−634(4)	−634(4)	319(6)	92(55)	92(55)	129(96)	−135(68)	71(47)	71(47)			96
O(4)		96(g)	1684(4)	1684(4)	3143(7)	61(54)	61(54)	312(109)	38(67)	26(58)	26(58)			96
Cd(1)	I	16(c)	0	0	0	99(13)	99(13)	99(13)	21(14)	21(14)	21(14)	15.0(2)		15
Cd(2)	I'	32(e)	586(22)	586(22)	586(22)	1(284)						1.0(2)		1
Cd(3)	II	32(e)	2163(3)	2163(3)	2163(3)	458(37)	458(37)	458(37)	236(45)	236(45)	236(45)	14.0(3)		14
Cd(4)	II	32(e)	2277(3)	2277(3)	2277(3)	401(30)	401(30)	401(30)	276(35)	276(35)	276(35)	15.7(5)	16.0(3)	16
N(1)		96(g)	2554(109)	2980(61)	2980(61)	1219(1038)						16.0(5)	16.0(3)	16
O(11)		32(e)	3056(38)	3056(38)	3056(38)	1454(578)						13.5(26)	16.0(3)	16
(b) Cd ₄₆ -X · 25.5N ₂ O ₄														
(Si,Al)		192(i)	−524(2)	1234(2)	358(2)	139(23)	154(23)	177(24)	−54(23)	14(20)	−31(24)			192
O(1)		96(h)	−1069(5)	1069(5)	0	322(63)	322(63)	279(102)	−218(61)	−218(61)	52(80)			96
O(2)		96(g)	−26(5)	−26(5)	1484(7)	237(57)	237(57)	274(93)	35(58)	35(58)	84(78)			96
O(3)		96(g)	−647(5)	−647(5)	302(7)	304(68)	304(68)	262(104)	128(61)	128(61)	66(85)			96
O(4)		96(g)	1698(5)	1698(5)	3210(6)	197(62)	197(62)	218(97)	22(62)	22(62)	192(78)			96
Cd(1)	I	16(c)	0	0	0	110(14)	110(14)	110(14)	22(14)	22(14)	22(14)	11.9(3)		11.5
Cd(2)	I'	32(e)	660(4)	660(4)	660(4)	382(36)	382(36)	382(36)	49(42)	49(42)	49(42)	9.1(3)		9.0
Cd(3)	II	32(e)	2424(1)	2424(1)	2424(1)	331(16)	331(16)	331(16)	70(13)	70(13)	70(13)	24.5(6)	24.9(7)	25.5
N(1)		192(i)	2376(30)	2799(32)	3332(33)	−315(185) ^d						39.0(61)	24.9(7)	25.5
O(11)		96(g)	2496(24)	2496(24)	3617(34)	547(234)						34.6(36)	24.9(7)	25.5
O(12)		96(g)	2205(48)	3261(36)	3261(36)	1058(418)						25.0(42)	24.9(7)	25.5
N(2)		192(i)	1717(41)	2959(48)	4199(48)	−301(202) ^d						39.4(64)	36(5)	25.5
O(21)		192(i)	1696(38)	4169(38)	3113(38)	207(342)						34.5(36)	36(5)	25.5
O(22)		192(i)	1714(84)	2399(98)	4311(80)	1072(663)						45.1(74)	36(5)	25.5

^a Positional and anisotropic thermal parameters are given $\times 10^4$. Numbers in parentheses are the esds in the units of the least significant digit given for the corresponding parameter. ^b The anisotropic temperature factor = $\exp[(-2\pi^2/a^2)(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + U_{12}hk + U_{13}hl + U_{23}kl)]$. ^c Occupancy factors are given as the number of atoms or ions per unit cell. ^d These physically unacceptable values were increased by 2σ in the preparation of Figures 5, 6, and 7.

TABLE 3: Selected Interatomic Distances (Å) and Angles (deg)^a

(a) Cd ₄₆ -X·16NO				(b) Cd ₄₆ -X·25.5N ₂ O ₄			
distance		angle		distance		angle	
(Si,Al)–O(1)	1.637(7)	O(1)–(Si,Al)–O(2)	113.4(7)	(Si,Al)–O(1)	1.665(8)	O(1)–(Si,Al)–O(2)	112.6(6)
(Si,Al)–O(2)	1.694(7)	O(1)–(Si,Al)–O(3)	106.8(8)	(Si,Al)–O(2)	1.674(8)	O(1)–(Si,Al)–O(3)	105.9(8)
(Si,Al)–O(3)	1.699(8)	O(1)–(Si,Al)–O(4)	113.8(8)	(Si,Al)–O(3)	1.709(9)	O(1)–(Si,Al)–O(4)	107.4(8)
(Si,Al)–O(4)	1.650(5)	O(2)–(Si,Al)–O(3)	105.8(7)	(Si,Al)–O(4)	1.653(6)	O(2)–(Si,Al)–O(3)	108.3(8)
Mean	1.670	O(2)–(Si,Al)–O(4)	105.2(8)	Mean	1.675	O(2)–(Si,Al)–O(4)	109.0(8)
Cd(1)–O(3)	2.366(14)	O(3)–(Si,Al)–O(4)	111.7(8)	Cd(1)–O(3)	2.384(18)	O(3)–(Si,Al)–O(4)	113.7(10)
Cd(2)–O(3)	2.256(25)	(Si,Al)–O(1)–(Si,Al)	130.8(11)	Cd(2)–O(3)	2.379(18)	(Si,Al)–O(1)–(Si,Al)	133.0(11)
Cd(3)–O(2)	2.169(16)	(Si,Al)–O(2)–(Si,Al)	136.1(10)	Cd(3)–O(2)	2.346(17)	(Si,Al)–O(2)–(Si,Al)	134.4(11)
Cd(4)–O(2)	2.224(15)	(Si,Al)–O(3)–(Si,Al)	126.4(9)	Cd(3)–N(1)	2.43(8)	(Si,Al)–O(3)–(Si,Al)	127.3(10)
Cd(4)–N(1)	2.57(22)	(Si,Al)–O(4)–(Si,Al)	161.8(11)	N(1)–O(11)	1.07(9)	(Si,Al)–O(4)–(Si,Al)	147.6(11)
N(1)–O(11)	1.28(25)	O(3)–Cd(1)–O(3)	89.8(5)/90.2(5)	N(1)–O(12)	1.23(10)	O(3)–Cd(1)–O(3)	88.2(6)/91.8(6)
Cd(4)···O(11)	3.36(20)	O(3)–Cd(2)–O(3)	96(3)	N(2)–O(21)	1.03(13)	O(3)–Cd(2)–O(3)	88.5(8)
		O(2)–Cd(3)–O(2)	119.9(10)	N(2)–O(22)	1.42(12)	O(2)–Cd(3)–O(2)	101.6(5)
		O(2)–Cd(4)–O(2)	115.3(3)	N(1)–N(2)	2.74(17)	Cd(3)–N(1)–O(11)	109(7)
		O(2)–Cd(4)–N(1)	111.9(18)			Cd(3)–N(1)–O(12)	103(7)
		Cd(4)–N(1)–O(11)	118(10)			O(11)–N(1)–O(12)	147(10)
						O(21)–N(2)–O(22)	140(10)
						Cd(3)–N(1)–N(2)	144(10)
						N(1)–N(2)–O(21)	120(10)
						N(1)–N(2)–O(22)	92(10)
						N(2)–N(1)–O(11)	75(13)
						N(2)–N(1)–O(12)	77(10)

^a Numbers in parentheses are estimated standard deviations in the units of the least significant digit given for the corresponding value.

the final refinement, all positions except for those of the N₂O₄ molecule were refined anisotropically: $R_1 = 0.084$ and $wR_2 = 0.216$. Fixed weights were used initially; the final weights were assigned as above with a and b values given in Table 1.

The largest peak on the final difference function appeared at (0.125, 0.125, 0.125) with a height of 0.8 eÅ^{-3} . It was not within bonding distance of any other atom, and was not considered further.

The atomic scattering factors described above were used. The final structural parameters, and selected interatomic distances and angles, are presented in parts b of Tables 2 and 3, respectively.

Discussion

Zeolite X. Zeolite X is a synthetic counterpart of the naturally occurring mineral faujasite (FAU). The 14-hedron with 24

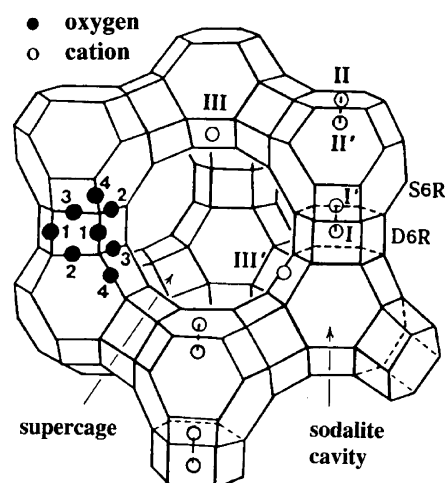


Figure 1. A stylized drawing of the framework structure of zeolite X. Near the center of each line segment is an oxygen atom. The nonequivalent oxygen atoms are indicated by the numbers 1 to 4. Silicon and aluminum atoms alternate at the tetrahedral intersections in the short range, except that Si must substitute for at least 4% of the Al atoms. Extraframework cation positions are labeled with Roman numerals.

vertices, known as the sodalite cavity or β cage, may be viewed as the principal building block of the aluminosilicate framework of the zeolite (see Figure 1). These β cages are connected tetrahedrally at six-rings by bridging oxygens to give double six-rings (D6Rs, hexagonal prisms) and, concomitantly, an interconnected set of even larger cavities (supercages) accessible in three dimensions through 12-ring (24-membered) windows. (An n -ring is composed of n O and n T (Si or Al) atoms.) The T atoms occupy the vertices of these polyhedra. The oxygen atoms lie approximately midway between each pair of T atoms but are displaced from those points to be closer to Si (farther from Al) and to give near tetrahedral angles about the T atoms. Single six-rings (S6Rs) are shared by sodalite and supercages and may be viewed as the entrances to the sodalite cavities. Each unit cell has 8 sodalite cavities, 8 supercages, 16 D6Rs, 16 12-rings, and 32 S6Rs.

The exchangeable cations that balance the negative charge of the aluminosilicate framework are found within the zeolite's windows and cavities. They are usually found at the following sites shown in Figure 1: site I at the center of a D6R, site I' in the sodalite (β) cavity on the opposite side of either of the D6R's six-rings from site I, site II' inside the sodalite cavity near a single six-ring (S6R) entrance to the supercage, II in the supercage adjacent to a S6R, III in the supercage opposite a sodalite four-ring (on a two-fold axis), and III' on the inner surface of the supercage somewhat or substantially off that two-fold axis.

Cd₄₆-X·16NO. The mean (Si,Al)-O bond length is 1.67 Å, nicely the average of the mean Si-O (1.61 Å) and Al-O (1.72 Å) distances in zeolite X.³⁷ Individual bond lengths, however, show marked variation: from 1.637(7) to 1.699(8) Å (see Table 3). These (Si,Al)-O distances depend on whether each oxygen coordinates to a Cd²⁺ ion or not. Because Cd²⁺ coordinates only to O(2) and O(3) framework oxygens in this structure, the (Si,Al)-O(2) and (Si,Al)-O(3) bonds are generally longer than (Si,Al)-O(1) and (Si,Al)-O(4). This effect is frequently observed, for example, in dehydrated Cd₄₆-X (ref 32) and is seen (less definitively) here.

The Cd²⁺ ions occupy four different crystallographic sites in this structure. In contrast, they occupied only two sites in fully dehydrated Cd₄₆-X (see Table 4). The fifteen Cd²⁺ ions per unit

TABLE 4: Number of Cd²⁺ Ions at Sites in Zeolite X

structures	site I	site I'	site II ^a	site II ^b	site II' ^b	reference
Cd ₄₆ -X ^c	16			30		[32] and [47]
Cd ₄₆ -X·29.5C ₂ H ₄	15.5	1.0	29.5			[49]
Cd ₄₆ -X·16NO	15	1	16	14		this work
Cd ₄₆ -X·89.6I ^d	14	4	25.6		2.4	[52]
Cd ₄₆ -X·28CO	13	5	28			[47]
Cd ₄₆ -X·28C ₂ H ₂	13	5	28			[48]
Cd ₄₆ -X·52S ^d	12	8	12	7	7	[51]
Cd ₄₆ -X·25.5N ₂ O ₄	11.5	9	25.5			this work
Cd ₄₆ -X·43C ₆ H ₆	11	6	27	2		[50]

^a Coordinates to a guest molecule. ^b Does not coordinate to a guest molecule. ^c Fully dehydrated. ^d The elements iodine and sulfur have disproportionated upon sorption to give monatomic anions that coordinate to Cd²⁺ and polyatomic cations.

cell at Cd(1) occupy site I at the center of D6Rs. The octahedral Cd(1)-O(3) distance, 2.366(14) Å, is just a little longer than the sum of the conventional ionic radii, 0.97 + 1.32, respectively,⁵³ = 2.29 Å. One Cd²⁺ ion at Cd(2) lies just outside the remaining D6R at site I' in the sodalite cavity. The Cd(2)-O(3) distance, 2.256(25) Å, is in agreement with the sum of the conventional radii. The fourteen Cd²⁺ ions at Cd(3) and the sixteen at Cd(4) occupy two different sites II in the supercage (see Figures 2 and 3); each Cd²⁺ ion coordinates at 2.169(16) and 2.224(15) Å, respectively, to three O(2) framework oxygens. These two distances are each a little shorter than 2.29 Å,⁵³ the sum of the conventional ionic radii of Cd²⁺ and O²⁻, in accordance with their degrees of coordinative unsaturation. The O(2)-Cd(3)-O(2) angle is 119.9(10)°, and O(2)-Cd(4)-O(2) is 115.3(3)°.

To coordinate to a nitric oxide molecule, each of the 16 Cd²⁺ ions at Cd(4) has moved 0.30 Å (0.49–0.19 Å) further, compared to dehydrated Cd₄₆-X,³² into the supercage from its six-ring plane (see Figures 2, 3, and 4, and Table 5). The Cd(4)-N distance, 2.57(22) Å, is insignificantly longer than the sum of ionic radius of Cd²⁺ and the van der Waals radius of nitrogen, 0.97 + 1.5 = 2.5 Å.⁵⁴ Similarly, the Co³⁺-NO⁻ distance in Co₄Na₄-A (LTA)·3NO, 2.23(6) Å,¹⁴ differs insignificantly from its corresponding sum, 0.72 + 1.5 = 2.22 Å.

The imprecisely determined NO bond length, 1.28(25) Å, differs insignificantly from that in NO(g), 1.151 Å⁵⁵. An NO⁻ double-bond distance of 1.47(11) Å was found in Co₄Na₄-A·3NO.¹⁴ The N-O single-bond length is 1.44 Å, and the double-bond and triple-bond lengths may be taken as 0.04 Å less than 1.24 Å for N=N and 1.10 Å for N≡N, and hence are equal to 1.20 Å and 1.06 Å, respectively.⁵⁶ Its two suggested resonance forms⁵⁶ are shown in Figure 5a. The energy difference between these two forms is small.⁵⁶ The second resonance form, formally a triple bond, would be favored upon coordination via the nitrogen atom to Cd²⁺ because it has a strong dipole moment.

If NO were to lose an electron upon coordination to a cation to form NO⁺ and Cd⁺, CdNO should be approximately linear. If NO were to gain an electron to form NO⁻ and Cd³⁺, CdNO should be bent with an angle of approximately 125°. The Cd(4)-N-O angle, 118(10)°, is far from linear, and the Cd(4)-O(2) bond length, 2.224(15) Å, does not indicate oxidation of Cd²⁺ to Cd³⁺, nor would that have been expected. This complex therefore appears to be that of NO (neutral) coordinating to Cd²⁺. This had not been seen crystallographically before with any cation because NO (neutral) is such a weak ligand.

According to VSEPR theory, the three groups of electrons about the nitrogen atom in Cd-N-O should be arranged in a trigonal-planar manner, and Cd-N-O should have an angle somewhat less than 120°. Consistent with this, 118(10)° is observed.

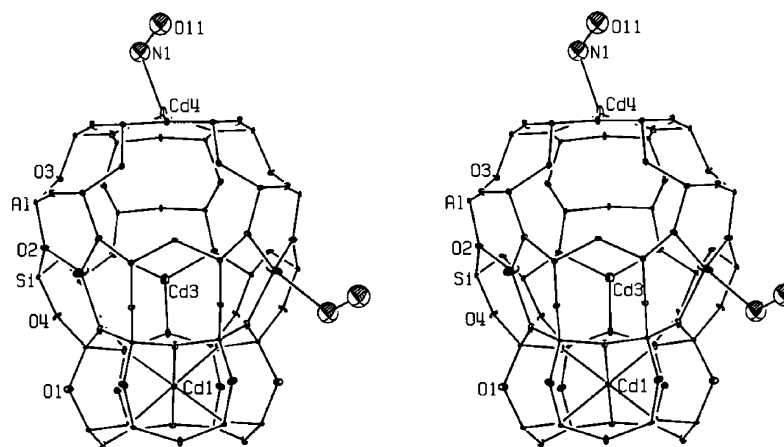


Figure 2. Stereoview of a sodalite cavity with an attached double six-ring in Cd₄₆-X·16NO. One Cd²⁺ ion at Cd(1) (site I) is shown. Two Cd²⁺ ions at Cd(3) (site II) and two at Cd(4) (also a site II) are shown. Each Cd²⁺ ion at Cd(4) coordinates to a NO molecule. Ellipsoids of 20% probability are used.

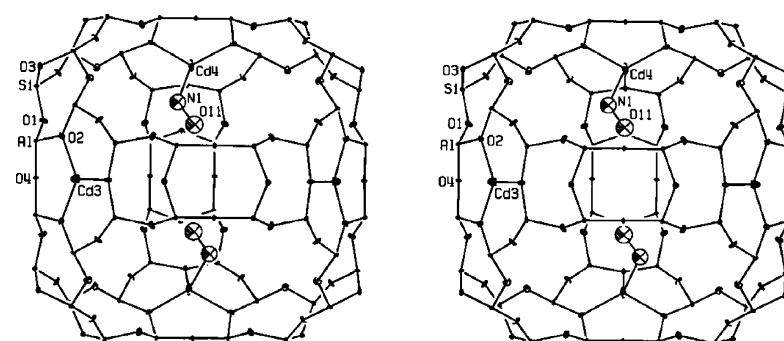


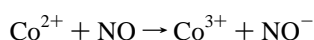
Figure 3. Stereoview of a supercage in Cd₄₆-X·16NO. Two Cd²⁺ ions at Cd(4) (site II) and two at Cd(3) (also a site II) are shown. Each Cd²⁺ ion at Cd(4) (site II) coordinates to a NO molecule. Ellipsoids of 20% probability are used.

TABLE 5: Deviations (Å) of Atoms from Six-Ring Oxygen Planes

	position	cation site	displacement
(a) Cd₄₆-X·16NO			
at O(2) ^a	Cd(3)	II	0 ^b
	Cd(4)	II	0.49 ^b
	N(1)		2.91
	O(11)		3.85
at O(3)	Cd(1)	I	-1.36 ^c
	Cd(2)	I' ^d	1.16
(b) Cd₄₆-X·25.5N₂O₄			
at O(2) ^a	Cd(3)	II	1.05 ^b
	N(1)		2.81
	O(11)		2.96
	O(12)		3.13
at O(3)	Cd(1)	I	-1.42 ^c
	Cd(2)	I' ^d	1.41

^a A positive displacement indicates that the atom or ion lies in the supercage. ^b For comparison, the site-II Cd²⁺ ions extend 0.19 Å into the supercages from the corresponding planes at O(2) in fully dehydrated Cd₄₆-X (ref 32). ^c The negative displacement indicates that the ion lies within a double six-ring. ^d Site I' is in the sodalite cavity.

In the crystal structure of the NO sorption complex of Co₄-Na₄-A (LTA), the Co-N-O angle (141(3)°) is bent.¹⁴ This is consistent with the presence of NO⁻ which would have formed by the following reaction:¹⁴



The change in color of Co₄Na₄-A from deep blue to dark brown

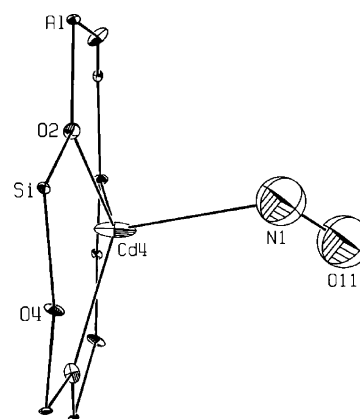


Figure 4. A Cd(NO)²⁺ complex on the inner surface of a supercage. Each of the 16 Cd²⁺ ions at Cd(4) coordinates to a NO molecule in this manner. The moderate departure of a Cd²⁺ ion at site II from the trigonal O(2) plane can be seen. Of the three equivalent positions that the NO molecule could occupy, only one (the maximum number because of packing considerations) is shown. Ellipsoids of 20% probability are used.

upon the sorption of NO and the short Co-N bond length, 2.23(6) Å (vide supra), confirm that Co²⁺ ions were oxidized to Co³⁺.

In summary, the Cd²⁺ ions are found at three sites: 15 at site I, 1 at site I', and 30 at site II. There are two kinds of site-II Cd²⁺ ions: 16 coordinate to nitric oxide molecules and 14 do not. Cd₄₆-X has sorbed 16 nitric oxide molecules per unit cell without redox.

Cd₄₆-X·25.5N₂O₄. In this structure also, the mean (Si,Al)-O bond length, 1.675 Å, is normal. The individual bond lengths,

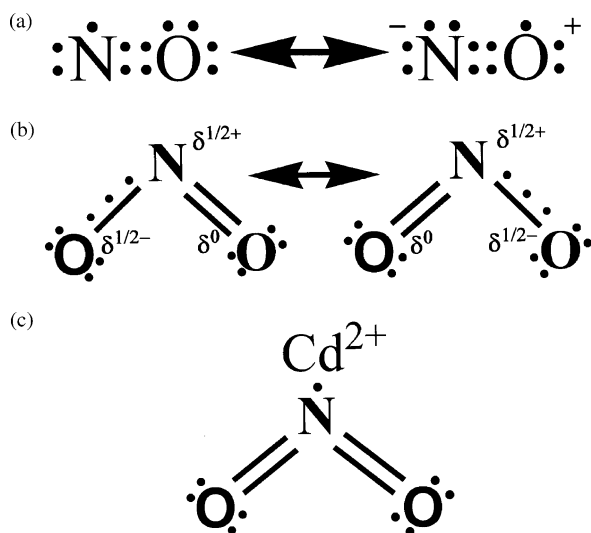


Figure 5. Resonance forms. (a) The conventional NO resonance forms. (b) The conventional NO₂ resonance forms. (c) The proposed one-electron sigma bond in a Cd(NO₂)²⁺ complex.

however, show marked variations ranging from 1.653(6) to 1.709(9) Å (see Table 3), as discussed above for Cd₄₆-X·16NO.

Cd²⁺ ions occupy three crystallographic sites in this structure (see Figure 6). Those at Cd(1) and Cd(2) do not coordinate to sorbed N₂O₄ molecules. The 11.5 Cd²⁺ ions at Cd(1) occupy site I, centering most of the D6Rs. The octahedral Cd(1)-O(3) distance, 2.384(18) Å, is just a little longer than the sum of the conventional radii, 0.97 + 1.32 = 2.29 Å.⁴³ The Cd(2)-O(3) distance is the same, 2.379(18) Å. Each of the nine Cd²⁺ ions at Cd(2) is on a three-fold axis in the sodalite cavity at site I'. Because a D6R can accommodate either one Cd²⁺ ion at site I or a maximum of two at site I', these occupancies, as discussed in the structure determination section, show that the D6Rs are full: 11.5 + 9/2 = 16. The short Cd(2)-O(2) distances seen in Cd₄₆-X·16NO are not seen in this structure because of Cd²⁺...Cd²⁺ repulsions (5.65 Å) through the D6Rs. This is responsible for the large deviation, 1.41 Å, of Cd(2) from its O(3) plane (see Table 5).

The remaining 25.5 Cd²⁺ ions are at Cd(3), site II, in the supercage (see Figure 7). Each of these extends substantially, 1.05 Å (see Table 5), into the supercage from its three-oxygen plane to coordinate to an N₂O₄ molecule. Accordingly, each of these Cd²⁺ ions is substantially farther, 2.346(17) Å, from the three O(2) framework oxygens to which it coordinates as compared to the Cd(3)-O(2) distance in the NO complex, 2.169(16) Å. The O(2)-Cd(3)-O(2) angle is 101.6(5)° (see Table 3), far from trigonal planar yet substantially less than tetrahedral. To coordinate to a nitrogen dioxide molecule, each Cd²⁺ ion at Cd(3) has moved quite far, 0.86 Å = 1.05–0.19 Å, further into the supercage from its six-ring as compared to its position, 0.19 Å from a six-ring, in the structure of dehydrated Cd₄₆-X³² (see Table 5). As compared to all other shifts upon coordination seen in the sorption complexes of Cd₄₆-X, this is the largest (see Table 6).

Each of the 25.5 Cd²⁺ ions at Cd(3) complexes to a N₂O₄ molecule (see Figures 6, 7, and 8). The Cd(3)-N distance, 2.43(8) Å, is about the same as the sum of the ionic radius of Cd²⁺ and the van der Waals radius of N: 0.97 + 1.5 = 2.47 Å,⁵⁴ indicative of a coordination bond. The O(11)-N(1)-O(12) angle, 147(10)°, agrees with that in NO₂(g), 135°. The N(1)-O(11) and N(1)-O(12) bond distances are 1.07(9) and 1.23(10) Å, respectively, in agreement with 1.19 Å, the value in N₂O₄

gas.⁵⁷ The N(2)-O(21) bond distance is 1.03(13) Å, and N(2)-O(22) = 1.42(12) Å, again in agreement with 1.19 Å, the bond length in N₂O₄(g).⁵³ The O(21)-N(2)-O(22) angle is 140(10)°, which also agrees with 135°, its value in N₂O₄(g).⁵³ Although the N(1)-N(2)-O angles are reasonable, the N(2)-N(1)-O angles are remarkably small (see Table 3); presumably the long N(1)-N(2) bond distance (vide infra) has allowed this.

The conventional resonance forms of NO₂ are shown in Figure 5b. They indicate that its nitrogen atom is positive, so it would be expected to interact electrostatically with framework oxygens; similarly NO₂ should coordinate to Cd²⁺ via one of its oxygen atoms. That, however, is not what is observed crystallographically. Figure 5c shows the unpaired electron of a NO₂ molecule forming a one-electron coordination bond with a Cd²⁺ ion. With this electronic structure, the Lewis octet rule is satisfied at both oxygens, and the odd electron at nitrogen can (1) be closer to Cd²⁺ and (2) delocalize into an empty Cd²⁺ orbital. In this form, the formal charge at each NO₂ atom is zero. The NO₂ molecule adopts this electronic structure in its dimer, N₂O₄. An MO treatment of NO₂ is supportive of the unpaired electron at N, as shown in Figure 5c.⁵⁸

The imprecisely determined N(1)-N(2) distance, 2.74(17) Å, is significantly longer than the N-N bond length in N₂O₄, 1.75 Å;⁵⁹ it appears to be very much lengthened by coordination to Cd²⁺ (see Figure 8). It is close to the sum of the van der Waals radii of two nitrogen atoms, 1.5 + 1.5 = 3.0 Å. It has presumably been very much weakened by coordination to Cd²⁺. The closest approaches of N₂O₄ to the zeolite framework are N(1) to O(2) and O(4) = 3.05 and 3.21 Å, respectively, O(12)-O(2) = 3.13 Å, and O(11)-O(4) = 3.35 Å. For comparison, the sum of the van der Waals radii of O and N is 2.9 Å and that of O and O is 2.8 Å.⁵⁴

In the NO₂ sorption complex of Co₄Na₄-A (LTA), the Co-N distance is 1.95(4) Å and the O-N-O angle is 88(6)°. In the present "NO₂" sorption complex of dehydrated Cd₄₆-X, the Cd-N distance is much longer, 2.43(3) Å, and the O-N-O angle is larger, 147(10)°. Even after considering the difference in the ionic radii of Co²⁺ and Cd²⁺ (0.72 and 0.97 Å, respectively),⁵³ it can be seen that the Co-N interaction is much shorter than Cd-N. This is consistent with the oxidation of Co²⁺ to Co³⁺ with the reduction of NO₂ to NO₂⁻.¹⁴ The change in color of Co₄Na₄-A from deep blue to dark brown (nearly black) upon the sorption of NO₂, and the short Co-N bond length, 1.95(4) Å (vide supra), indicate clearly that Co²⁺ ions were oxidized to Co³⁺. In addition, only the O-N-O angle in Cd₄₆-X·25.5N₂O₄ (not that in Co₄Na₄-A·2NO₂) is close to that in NO₂(g), 134.1°. This indicates that our objective, of sorbing NO₂ (N₂O₄) onto a zeolite without redox, was achieved.

In summary, a total of 25.5 N₂O₄ molecules have been sorbed asymmetrically per unit cell. Each coordinates via one nitrogen atom to a Cd²⁺ ion (Cd(3)) at site II in the supercage (see Figure 8). Previous crystallographic reports of the coordination of N₂O₄ to cations, with or without electron transfer, for comparison with the results reported here, could not be found. The uniqueness of zeolite sorption chemistry, where no solvent molecules are present to compete for coordination sites, has facilitated the formation of this complex.

The concentrations of N₂O₄ and NO₂ were almost equal in the NO₂/N₂O₄ equilibrium mixture used for sorption. A value of 0.75 can be calculated for [N₂O₄]/[NO₂] at *P*_{total} = 100 Torr using *K*_p (atm) = 0.104 at 21 °C.²⁹ It may be said that N₂O₄ is selected for sorption over NO₂ by the zeolite. However, because the structure of the sorbed N₂O₄ is so unusual and has such a long N-N bond, it may also be said that it is a NO₂ molecule

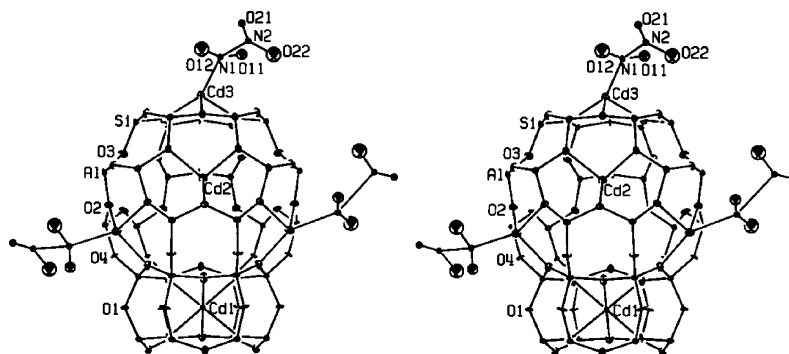


Figure 6. Stereoview of a sodalite cavity with an attached double six-ring in Cd₄₆-X·25.5N₂O₄. One Cd²⁺ ion at Cd(1) (site I) is shown. One Cd²⁺ ion at Cd(2) (site I') and three Cd²⁺ ions at Cd(3) (site II) are shown. Each Cd²⁺ ion at Cd(3) coordinates to a N₂O₄ molecule. Ellipsoids of 20% probability are used.

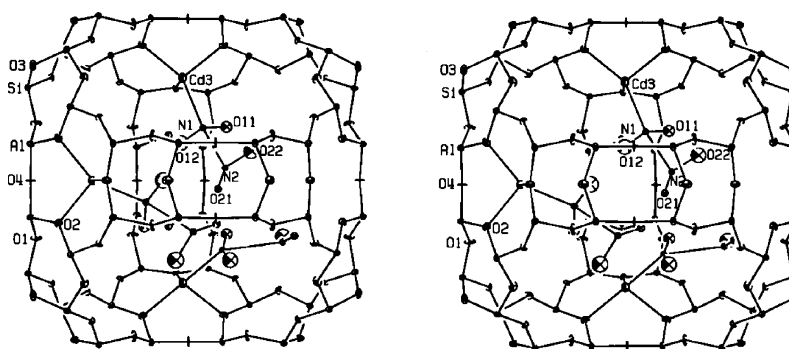


Figure 7. Stereoview of a supercage in Cd₄₆-X·25.5N₂O₄. Three Cd²⁺ ions at Cd(3) (site II) are shown. Each Cd²⁺ ion at Cd(3) coordinates to a N₂O₄ molecule. Ellipsoids of 20% probability are used.

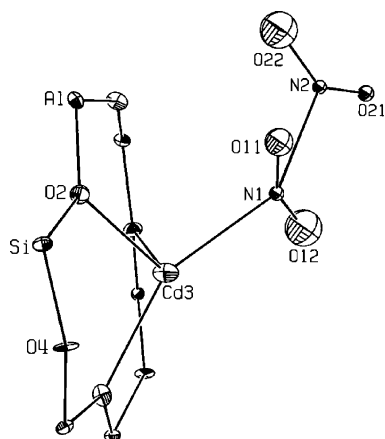


Figure 8. A Cd(N₂O₄)₂²⁺ complex on the inner surface of a supercage. Each of the 25.5 Cd²⁺ ions at Cd(3) coordinates to a N₂O₄ molecule whose N–N bond, 2.7(2) Å, appears to have been very much elongated by coordination to Cd²⁺. The large 1.05 Å displacement of the Cd²⁺ ion at site II from the trigonal O(2) plane can be seen. Of the six equivalent positions that the N₂O₄ molecule could occupy, only one (the maximum number because of packing considerations) is shown. Ellipsoids of 20% probability are used.

that has coordinated to a Cd²⁺ ion, with a second NO₂ molecule associating itself weakly with each first one.

Comparison of the Two Structures. The unit cell constant decreased upon the sorption of NO and NO₂ from $a = 24.935(8)$ Å for empty Cd₄₆-X,³² to 24.877(2) Å for Cd₄₆-X·16NO, and to 24.735(2) Å for Cd₄₆-X·25.5N₂O₄. From the extent of sorption, it appears that Cd₄₆-X has a greater affinity for N₂O₄ (gas-phase dipole moment $\mu = 0.55$ D)⁶⁰ than for NO (0.159 D)⁶¹ (or for NO₂ (0.316 D)).⁶¹

TABLE 6: Descriptors of the Shifts in Position of the Coordinating Cd²⁺ Ions in Cd₄₆-X

structures	Cd–O(2) (Å)	O(2)–Cd–O(2) (deg)	deviation from O(2) plane	reference
Cd ₄₆ -X	2.16(1)	119.2(5)	0.19	[32] and [47]
Cd ₄₆ -X·28CO	2.16(1)	117.7(4)	0.33	[47]
Cd ₄₆ -X·28C ₂ H ₂	2.192(8)	115.7(3)	0.46	[48]
Cd ₄₆ -X·16NO	2.224(15)	115.3(3)	0.49	this work
Cd ₄₆ -X·29.5C ₂ H ₄	2.221(6)	115.1(3)	0.50	[49]
Cd ₄₆ -X·89.6I	2.218(7)	113.5(2)	0.58	[52]
Cd ₄₆ -X·43C ₆ H ₆	2.224(10)	112.9(4)	0.60	[50]
Cd ₄₆ -X·52S	2.251(7)	111.2(3)	0.68	[51]
Cd ₄₆ -X·25.5N ₂ O ₄	2.346(17)	101.6(5)	1.05	this work

TABLE 7: Bond Angles (deg) at Framework Oxygens

	Cd ₄₆ -X ^a	Cd ₄₆ -X·16NO	Cd ₄₆ -X·25.5N ₂ O ₄
(Si,Al)-O(1)–(Si,Al)	129.2(8)	130.8(11)	133.0(11)
(Si,Al)-O(2)–(Si,Al)	134.7(7)	136.1(10)	134.4(11)
(Si,Al)-O(3)–(Si,Al)	115.7(3)	126.4(9)	127.3(10)
(Si,Al)-O(4)–(Si,Al)	163.7(9)	161.8(11)	147.6(11)

^a Reference 32. The angles given are Si–O(*n*)–Al, *n* = 1–4, respectively, because the space group *Fd* $\bar{3}$ was used.

The zeolite framework geometry changed substantially more for the N₂O₄ complex than for the NO complex. The bond angles at oxygen changed the most and are indicative (see Table 7).

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Supporting Information Available: Tables of calculated and observed structure factors with esds (13 pages). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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