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New Different Forms of Ammonium Loaded and Partly Deammoniated Zeolite Rho Studied by Neutron Powder Diffraction

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Abstract. Zeolite ND₄-Rho, prepared by shallow-bed calcination of ammonium-exchanged Rho under flowing dry nitrogen at 873 K, subsequently reloaded with ammonium, deuterium exchanged and dehydrated: D_{2.5}(ND₄)_{7.4}Cs_{0.7}Al_{10.9}Si_{37.1}O₉₆, $M_r = 3073.45$, cubic, $I43m$, $a = 14.5265$ (7) Å, $V = 3065.37$ Å³, $Z = 1$, $D_x = 1.665$ g cm⁻³, $R_{wp} = 3.9\%$, Rietveld refinement based on time-of-flight neutron powder diffraction data collected at room temperature. Zeolite ND₄-Rho, prepared by deep-bed calcination of ammonium-exchanged Rho in air at 633 K, yielding a partly deammoniated sample, subsequently deuterium exchanged and dehydrated: D_x(ND₄)_{4.6}Cs_{0.55}Al_{10.1}Si_{37.9}O₉₆, $M_r = 3047.28$, cubic, $I43m$, $a = 14.4247$ (5) Å, $V = 3001.38$ Å³, $Z = 1$, $D_x = 1.685$ g cm⁻³, Rietveld refinement based on fixed-wavelength neutron powder diffraction data collected at room temperature, $\lambda = 1.5423$ (6) Å. Shallow-bed calcined zeolite Rho when

exposed to ND₃ and partly deammoniated deep-bed calcined zeolite Rho (both designated ND₄*-Rho) yield a form of ammonium Rho with much smaller cell constants compared to its precursor ammonium form. The N atoms of the ND₄⁺ groups are located close to position $\frac{1}{2}, 0, 0$, in the center of the double-eight ring, and are surrounded in approximately tetrahedral fashion by four O atoms of the double-eight ring. This location of the ammonium group distorts that ring more than has so far been observed in any other zeolite Rho except for Ag-Rho, and causes the cell constant to become very short. The results for ND₄*-Rho are clearly different from previous refinements obtained for NH₄-exchanged Na,Cs-Rho, where the ammonium group resides on the faces of the double-eight rings and contributes less to their distortion. The ellipticities of the eight-rings in the noncentrosymmetric structures of zeolite Rho can be estimated with good accuracy using a regression equation based on the relation between the ellipticity and the cell constants of zeolite Rho.

† Contribution No. 4427.

Introduction. The acid form of zeolite Rho is a highly active and selective catalyst. It can be used commercially for the selective production of dimethylamine (DMA) from ammonia and methanol (Keane, Sonnichsen, Abrams, Corbin, Gier & Shannon, 1987). Pore sizes and channel openings determine the shape-selective properties of the zeolite, whether reactant molecules can enter the interior of the zeolite cages and product molecules can exit the three-dimensional channel systems. The apertures of the cavities are controlled by nonframework cations, in this case ammonium, which causes an extreme distortion of the highly flexible (Si,Al)O₂ framework of Rho.

When Na,Cs-Rho zeolite prepared in the usual way is exchanged with NH₄NO₃, a zeolite of approximate composition (NH₄)₁₂Al₁₂Si₃₆O₉₆ is obtained (Robson, Shoemaker, Ogilvie & Manor, 1973). This ammonium-Rho crystallizes in the noncentrosymmetric space group $I\bar{4}3m$ with cell constants *a* from about 14.82 to 14.86 Å (Flank, 1977; McCusker, 1984). It can be transformed into an H-Rho form by calcination at temperatures between 673 and 1023 K. During calcination the zeolite is dehydroxylated and some of the aluminium is removed from the aluminosilicate framework, thus making it more siliceous. Zeolite H-Rho calcined under these conditions crystallizes in the centrosymmetric space group $Im\bar{3}m$ and has cell constants of ~15 Å (Baur, Fischer & Shannon, 1988). Ammonium-Rho prepared either by partial deammoniation or by exposure of shallow-bed calcined H-Rho to ND₃ differs from its precursor NH₄-Rho. Like the precursor, it crystallizes in $I\bar{4}3m$, but surprisingly has cell constants *a* close to 14.5 Å, or 2.5% smaller than for NH₄-Rho (Abrams, Jones & Stucky, 1982, unpublished results). In order to distinguish between the precursor NH₄-Rho and the forms obtained by partial deammoniation or by reloading we designate the latter as NH₄*-Rho and ND₄*-Rho. We wish to elucidate the differences in the crystal structures of the two forms of ammonium-Rho. Sample designations are explained by Fischer, Baur, Shannon, Staley, Vega, Abrams & Prince (1986a). They include both the calcination temperature and data-collection temperature in K separated by a slash; S refers to shallow-bed calcination, D to deep-bed calcination, RT is room temperature.

Experimental.

Sample preparation

Sample ND₄*-Rho-S873/RT was prepared from Na,Cs-Rho using AlOOH (Catapal SB), NaOH, CsOH, and Ludox LS-30 according to the method described by Robson *et al.* (1973). Scanning electron micrographs showed typical dodecahedral Rho crystals approximately 0.5 μm in diameter and spherical aggregates of chabazite of about the same size. The chabazite fraction was ~10% of the total sample volume. X-ray

Table 1. *Experimental conditions, crystallographic data and definitions used in data refinement*

E.s.d.'s are given in parentheses. The approximate chemical composition of the samples is D_{2.5}(ND₄)_{7.4}Cs_{0.7}Al_{10.9}Si_{37.1}O₉₆ for ND₄*-Rho-S873/RT and D_{4.95}(ND₄)_{4.6}Cs_{0.55}Al_{10.1}Si_{37.9}O₉₆ for ND₄*-Rho-S663/11.

Sample designations used in text	ND ₄ *-Rho-S873/RT	ND ₄ *-Rho-D633/11
Beam	Time-of-flight	Monochromatized on (222) of Cu
Wavelength of radiation	White	1.5423 (6) Å
Detector position	±90°	5 counters at 7–30, 27–50, 47–70, 67–90, 87–110°
Sample container	Vanadium can of ~11.3 mm diameter	Aluminium can of ~10 mm diameter
Interval between consecutive profile points	7 μs	0.05° in 2θ
Data-collection temp. (K)	RT	11
Calcination temp. (K)	873	633
Range of <i>d</i> values (Å)	1.03–3.90	1.01–12.6
Number of observations	2234	1929
Number of reflections	173	180
Number of variable profile parameters	8	14
Number of variable structural parameters†	22	24
R _{wp} (%)	3.9	4.8
R _e (%)	2.0	3.2
R _i (%)	12.1	9.3

Definitions‡:

$$R_{wp} = [\sum w_i (y_{oi} - 1/Cy_c)^2 / \sum w_i y_{oi}^2]^{1/2}$$

$$R_e = [(N-P) / \sum w_i y_{oi}^2]^{1/2}$$

$$R_i = \sum |I_{oi} - 1/C I_{ci}| / \sum I_{oi}$$

† Including scale factor.

‡ R_{wp} = weighted residual including profile intensities; R_e = statistically expected residual; R_i = residual including integrated intensities; N = number of statistically independent observations; P = number of variable least-squares parameters; y_o, y_c = observed and calculated profile intensities; I_o, I_c = observed and calculated integrated intensities; C = scale factor; w = weight = 1/y_o.

diffraction powder patterns of the product displayed weak chabazite lines. The product was exchanged four times with 10% NH₄NO₃. With the assumption that the NH₄ content is the difference between the Al and Cs contents, wet chemical analysis showed the composition to be approximately (NH₄)_{9.9}Cs_{0.70}Al_{10.6}Si_{37.4}O₉₆.xH₂O with an Si/Al ratio of 3.5. H-Rho was prepared by deammoniation of a 10 g sample of NH₄-Rho for 4 h at 873 K in a shallow-bed configuration using a belt furnace and a quartz boat with an area of 110 cm². Rapid removal of H₂O and NH₃ was assured by a flow of 20 l min⁻¹ N₂. The chabazite lines were no longer visible, implying that the chabazite fraction had been rendered amorphous. The deuterium form of the sample was prepared as described by Fischer *et al.* (1986a). Deuteration was necessary for the neutron powder experiment. Exposing it to ND₃ in a closed vacuum system yielded a zeolite ND₄*-Rho with the composition, according to bulk chemical analysis, D_{2.5}(ND₄)_{7.4}Cs_{0.7}Al_{10.9}Si_{37.1}O₉₆ assuming that cations not determined are deuterons.

The preparation of NH₄-Rho used for sample ND₄*-Rho-D633/11 was described by Fischer *et al.* (1986a). Wet chemical analysis proved it to be approximately (NH₄)_{9.4}Cs_{1.1}Al_{10.5}Si_{37.5}O₉₆.43H₂O. It was exchanged in a D₂O solution containing 10% ND₄Cl, heated in a 20 mm-diameter quartz tube at

Table 2. ND_4^* -Rho-S873/RT (first line, A) and ND_4^* -Rho-D633/11 (second line, B), positional parameters in fractional coordinates, isotropic temperature factors (\AA^2), site symmetry, Wyckoff positions and occupancies

The e.s.d.'s are given in parentheses following the values in units of the least significant digit.

		x	y	z	B	Site symmetry†	Position†	Number of atoms in unit cell
Si/Al	A	0.2712 (7)	0.1242 (8)	0.4256 (5)	0.8 (2)	1	48(h)	37/11‡
	B	0.2735 (6)	0.1241 (7)	0.4265 (5)	1.3 (2)			38/10‡
O(1)	A	0.0342 (4)	0.2140 (5)	0.3853 (6)	1.9 (2)	1	48 (h)	48
	B	0.0381 (3)	0.2070 (5)	0.3881 (4)	1.3 (2)			
O(2)	A	0.2197 (5)	x	0.3999 (7)	3.2 (3)	..m	24(g)	24
	B	0.2212 (4)	x	0.4018 (7)	1.7 (2)			
O(3)	A	0.1309 (5)	x	0.6227 (8)	1.6 (2)	..m	24(g)	24
	B	0.1248 (5)	x	0.6219 (7)	1.7 (1)			
N(1)	A	0.530 (2)	0	0	6.0 (7)	2.mm	12(e)	6
	B	0.519 (2)	0	0	0.9 (6)			3.8 (1)
N(2)	A	0.214 (3)	0.077 (3)	0.033 (3)	B N(1)			6.6 (6)
	B	0.229 (7)	0.109 (7)	0.969 (7)	1 (3)			1.7 (3)

† From *International Tables for Crystallography* (1983).

‡ From chemical analysis.

Table 3. Selected interatomic distances (\AA) and angles ($^\circ$) in ND_4^* -Rho-S873/RT (A), ND_4^* -Rho-D633/11 (B) and NH_4 -Rho (McCusker, 1984)

The averages of the T—O—T angles are weighted according to the frequency of occurrence of the O atoms.

	A	B		A	B		
Si/Al—O(1)	1.598 (11)	1.644 (9)	O(1)—O(2)	2.66 (1)	111 (1)	2.72 (1)	112.7 (7)
Si/Al—O(2)	1.620 (13)	1.630 (11)	O(1)—O(3)	2.69 (1)	112 (1)	2.64 (1)	106.6 (6)
Si/Al—O(3)	1.642 (13)	1.643 (12)	O(1)—O(1)	2.67 (1)	110 (1)	2.71 (1)	110.2 (6)
Si/Al—O(1)	1.657 (13)	1.663 (11)	O(2)—O(3)	2.63 (1)	107 (1)	2.67 (1)	109.4 (6)
Mean	1.629	1.645	O(2)—O(1)	2.70 (1)	111 (1)	2.66 (1)	107.5 (6)
			O(3)—O(1)	2.61 (1)	104 (1)	2.72 (1)	110.5 (6)
	A	B	NH_4 -Rho	A	B	NH_4 -Rho	
2 × N(1)—O(3)	3.01 (2)	2.94 (1)	2.887 (6)	Si/Al—O(1)—Si/Al	138 (1)	131.9 (7)	136.2 (3)
4 × N(1)—O(1)	3.38 (1)	3.32 (1)	3.140 (6)	Si/Al—O(2)—Si/Al	138 (1)	138.4 (7)	160.7 (7)
2 × N(1)—O(3)	3.49 (2)	3.26 (2)	4.522 (11)	Si/Al—O(3)—Si/Al	150 (1)	143.5 (7)	142.0 (3)
4 × N(1)—O(1)	3.78 (2)	3.58 (1)	—	Weighted mean T—O—T	141.0	136.4	143.8
N(2)—O(1)	3.19 (4)	2.9 (1)	—				
N(2)—O(3)	3.45 (5)	2.6 (1)	—				
N(2)—O(2)	3.66 (4)	2.7 (1)	—				
N(2)—O(1)	3.67 (4)	—	—				
N(2)—O(2)	—	3.6 (1)	—				

633 K in vacuum for 66 h, exposed four times to D_2O at 473 K and heated again to 633 K in vacuum for 18 h. Chemical analysis of the sample yielded the bulk composition $\text{D}_x(\text{ND}_4)_{4.6}\text{Cs}_{0.55}\text{Al}_{10.1}\text{Si}_{37.9}\text{O}_{96}$. NMR experiments were not performed on this sample.

Neutron diffraction

(a) Sample ND_4^* -Rho-S73/RT

The sample was sealed in a vanadium can. Neutron diffraction data were collected on the General Purpose Powder Diffractometer at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory (Jorgensen & Faber, 1983). Experimental conditions, crystallographic data and basic equations and definitions are listed in Table 1. After irregular background effects (caused by scattering by an amorphous component in the sample) were corrected by fitting polynomials of fifth degree (Baur & Fischer, 1986), the framework refined to more reasonable values than it did after applying the standard correction procedure (fitting a Chebyshev polynomial with five refineable parameters). The minimum and maximum

values of the T—O distances ($T=\text{Si,Al}$) within one TO_4 tetrahedron were 1.3 and 2.0 \AA after the standard correction and 1.60 and 1.66 \AA after the polynomial fitting. All thermal parameters changed from negative to positive values. Peaks probably due to impurities at d values of 3.49 and 2.68 \AA were excluded.

It has been shown recently (Baur & Fischer, 1986; Fischer, Baur, Shannon & Staley, 1987; Fischer, Baur, Shannon, Staley, Abrams, Vega & Jorgensen, 1988) that difference Fourier methods are not always successful in finding additional atomic positions in powder refinements of partly known structures. Therefore, we searched for nonframework positions by refining the occupancy of a dummy atom on a grid net with a step size of 0.3 \AA . The two strongest peaks in the grid-search map were assigned to N atoms. The refinement of the occupancy of N(1) yielded within the e.s.d.'s the maximum number of N atoms possible at this location. One of these, N(1) at 0.530 (2), 0, 0, is only 0.8 \AA from a symmetrically equivalent position at 0.470, 0, 0, so that both cannot be simultaneously occupied. The maximum number in the unit cell is therefore six.

Refinement of the occupancy of N(1) yielded a value slightly higher than six, so its occupancy was subsequently held fixed at six atoms per unit cell.

The isotropic temperature factor of the N atoms and the occupancy of N(2) could not be refined independently in one cycle because of large correlations between these parameters. Therefore, the temperature factors of N(1) and N(2) were constrained to be equal, while the occupancy of N(2) was refined independently. Obviously, the poor crystallinity of the sample, which resulted in very broad peaks, did not allow a more detailed analysis of the structure. A second pattern of the same sample taken at 496 K was clearly resolved into two phases, where the second phase ($a \approx 14.76 \text{ \AA}$) apparently was generated either by a chemical reaction or by a change in the position of an atom or group that occurred during the heating of the sample. At 496 K the cell constant of the first phase is about 14.6 \AA . The simultaneous presence in one sample of two phases of zeolite Rho was observed previously in the case of a D-Rho deep-bed calcined at 773 K (Fischer *et al.*, 1986a). Scattering from impurity phases also affected the refinements. These effects cannot be corrected in the TOF data because peaks belonging to impurities are superimposed with overlapping peaks of zeolite Rho. Table 2 contains the structural parameters used in calculating the final profile; selected interatomic distances and angles are listed in Table 3.

(b) Sample $\text{ND}_4^*\text{-Rho-D633/11}$

For the neutron diffraction experiment the sample was loaded into an aluminium can and sealed under vacuum. The neutron diffraction data were collected at the National Bureau of Standards Reactor (NBSR), Gaithersburg, Maryland, on a high-resolution five-counter powder diffractometer (Prince & Santoro, 1980). Experimental conditions, crystallographic data and basic equations and definitions are listed in Table 1. Peaks corresponding to chabazite ($d = 9.3, 6.9$ and 4.35 \AA), a common impurity in zeolite Rho (Shannon *et al.*, 1988), and to aluminium were excluded from the refinement. The profile exhibited an irregular and nonlinear background owing to diffuse scattering by the sample can. This was corrected by the polynomial fitting method, as described by Baur & Fischer (1986) and applied to deep-bed calcined Rho and ZK-5 (Fischer *et al.*, 1986a,b) which showed similar effects. After these corrections the residuals dropped significantly. Further refinements with nonframework atoms similar to $\text{ND}_4^*\text{-Rho-S873/RT}$ gave the final results with residuals of $R_{wp} = 4.8$ and $R_f = 9.3\%$. The refined structural parameters are listed in Table 2, and the distances and angles in Table 3. The background correction allowed us to include in the refinement many more Bragg peaks with low values of d than would otherwise have been possible. This improved the available precision.

Computations

The coherent neutron scattering lengths used in the refinements are $b(\text{Si}) = 4.1491$, $b(\text{Al}) = 3.449$, $b(\text{O}) = 5.803$ and $b(\text{N}) = 9.36 \text{ fm}$ (Koester, 1977). The scattering length of the Si and Al atoms occupying statistically the tetrahedral site T was calculated by linear interpolation according to the Si/Al ratio determined by MAS NMR (magic-angle-spinning NMR) spectroscopy or by chemical analysis. The structure refinements† on the IPNS data were performed with a local version (Rotella, 1982) of Rietveld's (1969) program adapted to the time-of-flight method by Von Dreele, Jorgensen & Windsor (1982). The crystal structure refinement based on the data collected at NBS was performed with a modified version (Prince, 1980) of the Rietveld program (Rietveld, 1969), which provides for the simultaneous processing of the five separate data sets collected by different detectors, and which includes background parameters in the least-squares procedure.† Interatomic distances and angles were calculated with the program *SADIAN86* (Baur, Wenninger & Roy, 1986) and the crystal structure illustrations were drawn with the plot program *STRUPLO84* (Fischer, 1985).

Discussion. Both data sets suffered from irregular background effects. In the $\text{ND}_4^*\text{-Rho-D633/11}$ pattern the irregular background was due to scattering from the aluminium sample can. In the case of $\text{ND}_4^*\text{-Rho-S873/RT}$ this additional background, which had to be corrected for, was due to the presence of an amorphous phase in the sample. Sample $\text{ND}_4^*\text{-Rho-D633/11}$ probably also contained an amorphous component. However, its scattering was not visible in the fixed-wavelength instrument at NBSR because the relative intensity of the pattern at the d values in question ($\sim 1.2 \text{ \AA}$) is very small when compared with the intensities at high d values. For a time-of-flight instrument the situation is reversed; the available intensity is approximately one hundred times larger at a d value of 1 \AA than at a d value of 2.5 \AA . Any additional background caused by an amorphous component will have an effect clearly discernible in the profile.

The N atoms are located in different positions in the $\text{ND}_4^*\text{-Rho}$ zeolites (this work) and in $\text{NH}_4^*\text{-Rho}$ (McCusker, 1984). The NH_4^+ group in $\text{NH}_4^*\text{-Rho}$ resides on the face of a single eight-ring at $0.38, 0, 0$. We determined two crystallographically different ND_4^+ groups in our samples. One of them is close to the center of the double eight-rings (D8R); the other one is

† Lists of observed and calculated intensities and the corresponding profile plots have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51708 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

outside the D8R in the α -cage, with a distance of 1.63 and 1.22 Å from the center axis of the eight-ring channels in ND_4^* -Rho-D633/11 and ND_4^* -Rho-S873/RT, respectively (Figs. 1 and 2). The N–N distance in NH_4 -Rho is 3.433 Å, a distance large enough for the position to be fully occupied. The NH_4^+ group in NH_4 -Rho (McCusker, 1984) is surrounded in a plane by two O(3) atoms at 2.887 Å and four O(1) atoms at 3.140 Å. Four of the eight possible O(3)–N–O(1) angles measure 129.6°. A comparison with other NH_4^+ -containing oxygen compounds (Khan & Baur, 1972) shows it to be likely that two of the four H atoms of the NH_4^+ group lie in the O(3)–N–O(1) plane and form N–H...O bonds. Because of the tetrahedral geometry of NH_4^+ this immediately determines the positions of the remaining two H atoms. If we assume an N–H distance of 1.01 Å (Baur, 1970) and further assume that the two NH_4^+ groups on opposite sides of the double eight-ring are related by an inversion center, the minimum possible H...H distance between the two ammonium groups is 2.14 Å, which is longer than twice the van der Waals radius of the H atoms of 1.0 Å (Baur, 1972). The NH_4^+ (ND_4^+) ions are distorted from tetrahedral symmetry and rotate rapidly as determined by MAS NMR spectroscopy (Vega & Luz, 1987), and by inelastic neutron scattering studies (Udovic *et al.*, 1987). This explains why the D atoms of the ND_4 groups cannot be located in the crystal structure analysis.

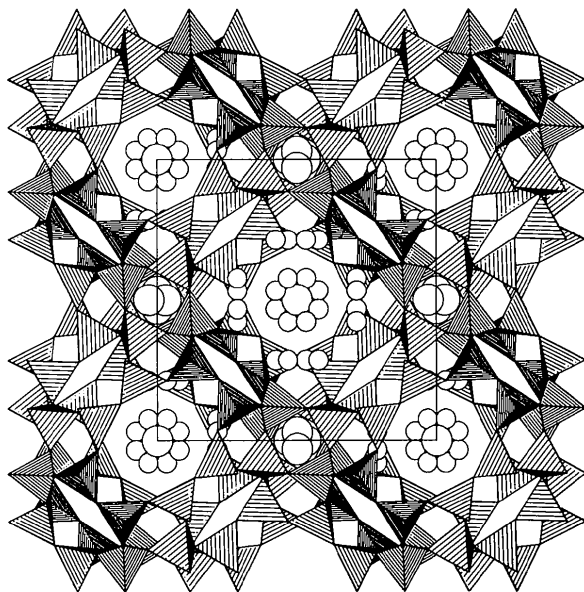


Fig. 1. Projection of the crystal structure of ND_4^* -Rho-S873/RT from -0.5 to 1.5 in all crystallographic directions in polyhedral representation. The outline of the unit cell is indicated, its origin is in the upper left corner, x pointing down, y pointing right and z pointing up. Large circles represent N(1) and small circles N(2).

In ND_4^* -Rho the ND_4^+ groups in the center of D8R are surrounded in approximately tetrahedral fashion by four O(3) atoms, two at 2.94 and two at 3.26 Å in ND_4^* -Rho-D633/11, and two at 3.01 and two at 3.49 Å in ND_4^* -Rho-S873/RT. If ND_4^+ were located at 0.5, 0, 0 it would have four equidistant O(3) neighbors at 3.12 Å, but this distance is too long for a strong N–D...O bond (Khan & Baur, 1972). Therefore, the ammonium group is moved towards two of the O(3) neighbors. This central location of ND_4^+ distorts the double eight-ring more than in any other well determined noncentrosymmetric Rho structure except for Ag-Rho (Stucky, Eddy, Prince, Abrams, Corbin & Jones, 1986). The stronger distortion (Fig. 2) of ND_4^* -Rho as compared with NH_4 -Rho is reflected in the differences in the mean angles T –O– T : 136.4° in ND_4^* -Rho-D633/11, 140.8° in ND_4^* -Rho-S873/RT versus 143.8° in NH_4 -Rho. The cell constants are directly related to the sines of half of these angles.

The difference in cell constants between our two ND_4^* -Rho samples is entirely due to the difference in data-collection temperature. At 11 K the cell constants are 0.1 Å smaller than at room temperature. In the case

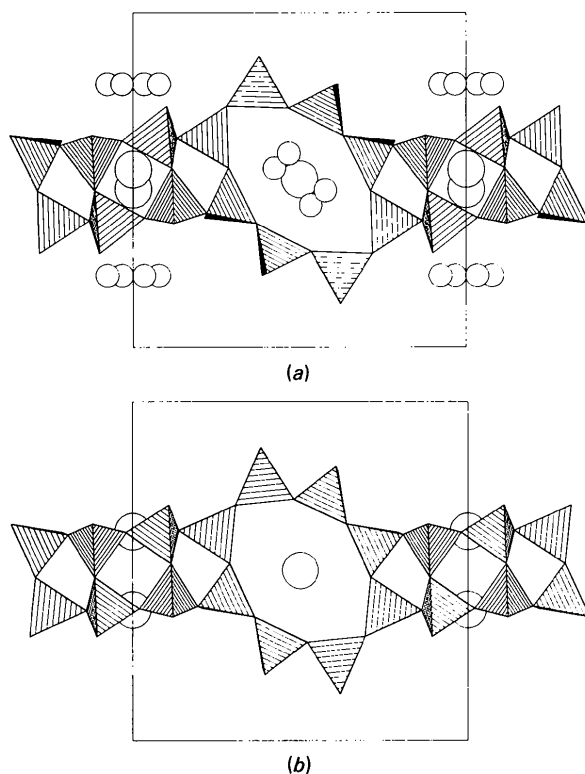


Fig. 2. Projection of parts of the crystal structures of ND_4^* -Rho-S873/RT and NH_4 -Rho in polyhedral representation illustrating the different ammonium ion positions and the different degrees of distortion of the eight-rings in the two structures: (a) this work; (b) McCusker (1984).

of Cs,D-Rho this difference was 0.12 Å at the same two data-collection temperatures (Parise, Abrams, Gier, Corbin, Jorgensen & Prince, 1984).

In ND₄*-Rho there are the same number or slightly fewer Al atoms per unit cell available in the framework than in NH₄-Rho, but there are fewer ammonium ions in the unit cell. The refined occupancies of N(2) plus the fixed number of N(1) yielded more ammonium ions than expected from the chemical analyses in both ND₄*-Rho-S873/RT and ND₄*-Rho-D633/11. However, the refined and analyzed ammonium content in ND₄*-Rho-D633/11 may be made to agree by assuming an error of just half an ammonium ion in both chemical analysis and structure refinement. The discrepancy between 12.7 ND₄⁺ ions in the refinement of ND₄*-Rho-S873/RT and 7.4 in the chemical analysis reflects experimental errors. In NH₄-Rho twelve NH₄⁺ are present in the unit cell and they occupy Wyckoff position 12(e) with an *x* parameter of about 0.38, thus accommodating all the available ammonium groups. When there are fewer ND₄⁺ groups per unit cell, the 12(e) position with an *x* parameter of about 0.52 becomes obviously energetically more favorable; however, only six ammonium groups can be placed there.

We can calculate the number of aluminium atoms per unit cell in the framework of ND₄*-Rho (Baur *et al.*, 1987; Baur, 1978; Baur & Ohta, 1982) from the mean *T*-O distances. From this we find that there are approximately eight Al atoms per 48 *T* positions, as opposed to 10.9 from the chemical analysis in ND₄*-Rho-S873/RT, and twelve Al atoms in ND₄*-Rho-D633/11. This is not unreasonable when we consider the e.s.d.'s of the mean *T*-O bond lengths.

So far the crystal structures of 16 zeolites Rho that crystallize in the noncentrosymmetric space group *I*43*m* have been determined. These are the two ND₄*-Rho described in this work, NH₄-Rho (McCusker, 1984), four Cs-exchanged Rho measured at various temperatures by Parise, Abrams, Gier, Corbin, Jorgensen & Prince (1984), three Cs,D-Rho zeolites (Parise & Prince, 1983), one D,Cs-Rho (Parise, Gier, Corbin & Cox, 1984), one D-Rho deep-bed calcined in steam at 773 K (Fischer *et al.*, 1986*a*), one D-Rho shallow-bed calcined in steam at 773 K (Fischer, Baur, Shannon, Staley, Abrams, Vega & Jorgensen, 1988), Ag-Rho and Li-Rho (Stucky *et al.*, 1986), and finally an Na,Cs-Rho (Baur, Bieniok, Shannon & Prince, 1988). For these sixteen refinements we find a reasonable agreement between observed mean *T*-O distances and chemical compositions.

We define the ellipticity, EL, of the distorted eight-ring in noncentrosymmetric zeolite Rho as the ratio of the *x* parameters of atoms O(2) and O(3). This is identical to the ratio of the main axes of the ellipse outlined by the eight-ring. This definition, which is different from the parameter used by Parise, Gier,

Corbin & Cox (1984), has the advantage of not being dependent on the absolute size of the unit cell of zeolite Rho. For these structure determinations, EL varies from 1.39 (Cs-Rho; Parise, Abrams, Gier, Corbin, Jorgensen & Prince, 1984) to 1.93 (Ag-Rho). The corresponding unit-cell constants range from 14.880 Å for a D-Rho (Fischer *et al.*, 1988) to 14.225 Å for Ag-Rho (Stucky *et al.*, 1986).

The relationship between ellipticity and cell constants of zeolite Rho as shown by Parise, Abrams, Gier, Corbin, Jorgensen & Prince (1984) is fully confirmed by the new more extensive data. The ellipticity EL can be estimated with confidence from a linear relationship between EL and the observed cell constant *a*:

$$EL = 13.866 - 0.839a.$$

This regression equation explains 99% of the variation in EL in terms of its dependence on the cell constant of Rho, the root mean square deviation between observed and estimated EL is 0.007. A measurement of *a* is thus sufficient to estimate the distortion of the elliptical eight-rings without a structure determination. For further details see Baur, Fischer & Shannon (1988).

Parise, Abrams, Gier, Corbin, Jorgensen & Prince (1984) demonstrated the change in unit-cell constants of noncentrosymmetric Rho upon heating from 11 to 573 K. The case of ND₄*-Rho is an even more extreme example of this flexibility of Rho, and one where for the first time a change in unit-cell constants can be clearly tied to changes in the location of nonframework species. The presence of deuterium instead of hydrogen in ND₄*-Rho should not make a difference as far as the crystal structure is concerned. The partially deammoniated and the reammoniated forms of zeolite H-Rho (ND₄*-Rho) are clearly different from its precursor ammonium Rho, since they have a significantly smaller unit cell and a different location for ammonium.

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Structure of a Diphosphate of Trivalent Molybdenum, RbMoP_2O_7

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Abstract. Molybdenum rubidium diphosphate, MoRbP_2O_7 , $M_r = 355.35$, monoclinic, $P2_1/c$, $a = 7.5237$ (6), $b = 10.3537$ (8), $c = 8.3998$ (8) Å, $\beta = 105.8321$ (69)°, $V = 629.51$ Å³, $Z = 4$, $D_x = 3.749$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 106$ cm⁻¹, $F(000) = 660$, $T = 298$ K, $R = 0.039$, $wR = 0.054$ for 2792 independent reflections with $\sigma(I)/I \leq 0.333$. The framework is built up from corner-sharing $\text{MoP}_2\text{O}_{11}$ units which delimit cages where Rb atoms are located. These cavities are

interconnected, leading to an intersecting tunnel structure.

Introduction. The investigation of the systems $A\text{—Mo—P—O}$ ($A = \text{Na, K, Rb, Cs}$) allowed several alkaline molybdenum diphosphates with the general formulation $A\text{MoP}_2\text{O}_7$ to be isolated, in which molybdenum exhibits the trivalent oxidation state. The diphosphates KMoP_2O_7 (Leclaire, Borel, Grandin & Raveau, 1989) and CsMoP_2O_7 (Lii & Haushalter, 1987) are isotopic