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The structure of the inclusion complex of sodium nitrate in zeolite *A*

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Auszug

Die Kristallstruktur der Einschlußverbindung von Zeolith Na-*A* mit $NaNO_3$ wurde aus Pulveraufnahmen bestimmt und nach der Fourier-Methode und der Methode der kleinsten Quadrate bis zu $R_I = 0{,}17$ verfeinert. Die kubische Pseudozelle mit der Gitterkonstanten $a = 12{,}39 \pm 0{,}02$ Å enthält 12 $NaAlSiO_4 \cdot 9{,}3\,NaNO_3 \cdot 6{,}7\,H_2O$. Raumgruppe ist *Pm3m*.

Die 3-zähligen Achsen aller Nitratanionen sind auch 3-zählige Achsen der Wirtstruktur. Zwei Nitratgruppen befinden sich innerhalb der Sodalith-Käfige. Die meisten Nitratanionen und die beim Waschen eingefügten Wassermoleküle besetzen Lagen im großen Hohlraum. Die unmittelbar an den Hohlraumwänden haftenden Nitratanionen liegen in Ebenen durch die nächsten drei Kationen. Aus Atomabstandsbetrachtungen folgt, daß es nicht möglich ist, zwischen Kationen, die ganz dem Gerüst angehören, und solchen, die mit den eingeschlossenen Nitratanionen eingewandert sind, zu unterscheiden.

Abstract

The crystal structure of the inclusion complex of zeolite Na-*A* with $NaNO_3$ has been determined from powder data. The refinement in space group *Pm3m* was carried out by means of Fourier and least-squares methods, and led to an *R* value based on intensities of 0.17. The cubic pseudo-cell content was $12Na[12AlO_2, 12SiO_2], 9.3NaNO_3, 6.7H_2O$ with a cell constant of 12.39 ± 0.02 Å.

All nitrate anions have their threefold axis in common with the similar axis present in the host structure. Two nitrates appear to be located inside the sodalite cage. Most of the nitrates, and also the water molecules incorporated during washing, occupy positions in the large cavity. The nitrate anions attached directly to the wall of the cavity lie in the plane formed by the nearest three

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cations. Consideration of the interatomic distances shows that one cannot strictly distinguish between cations belonging entirely to the framework and those entering with the included nitrate anions.

Introduction

The structures of sorbate phases and inclusion complexes within porous host crystals have attracted considerable attention during the last decade (*e.g.* FANG and SMITH, 1964; MEIER and SHOEMAKER, 1966; SEFF and SHOEMAKER, 1967; SMITH, 1968; AMARO and SEFF, 1973). The occlusion of various nitrates in zeolite *A* and proposals for the structures of the inclusion complexes have been the subject of two papers (BARRER and MEIER, 1958; LIQUORNIK and MARCUS, 1968). The first two authors based their proposed structure of silver nitrate in zeolite *A* on the observed superstructure lines, which were indexed on the basis of a tetragonal unit cell. The second two authors argued on grounds of an assumed charge distribution. This work is an attempt to clarify further the structure of the nitrate inclusion complexes of zeolite *A*.

Experimental

Salt inclusions from melts

Basic cancrinite, Na chabazite, zeolites Na-*A*, Na-*X* and Na-*Y*, and mordenite, were each subjected to treatment with molten $NaNO_2$ and $NaNO_3$. Sodium nitrite and nitrate were found to be stable at the temperatures employed which were 290 °C and 330 °C respectively. However, the presence of certain molecular sieves caused some reaction with evolution of nitrous gases and oxygen. $NaNO_2$ tended to decompose to Na_2O (as indicated by an alkaline reaction with water) when contacted with various sieves. The reaction became more marked along the series Na-*A*, cancrinite, mordenite and chabazite. $NaNO_3$ tended to be decomposed to $NaNO_2$ in the presence of cancrinite and mordenite, but with chabazite the reaction also gave some Na_2O. Thus cancrinite, mordenite and in particular chabazite catalysed both decompositions while Na-*A* decomposed only sodium nitrite. Na-*X* and Na-*Y* did not produce appreciable decomposition of either nitrate or nitrite.

The presence of nitrite as a decomposition product of nitrate was established by the reaction of nitrite with urea in acid solution:

$$2NO_2^- + CO(NH_2)_2 + 2H^+ \rightarrow 2N_2 + CO_2 + 3H_2O.$$

From the changes of powder line intensities and qualitative chemical analyses, it could be seen that mordenite and chabazite contained salt after washing. It was not possible to incorporate any salt into basic cancrinite, a behaviour attributed to prior blockage of channels due either to stacking faults in the aluminosilicate framework or to the intercalation of other species during synthesis (Barrer, Cole and Villiger, 1970). Occlusion of $NaClO_3$ from melts was also obtained with all sieves, except cancrinite.

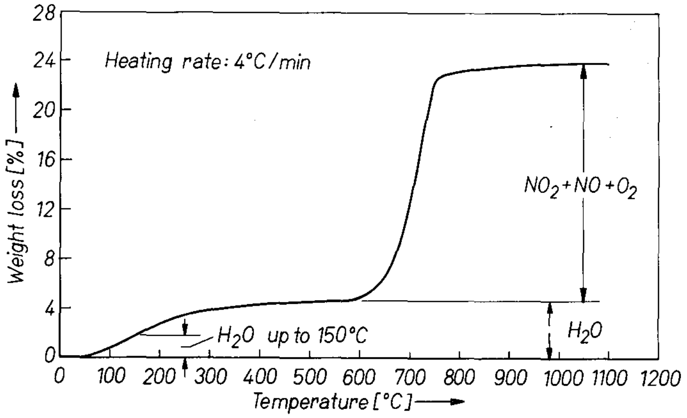

Fig. 1. Weight loss of Na-*A*,$NaNO_3$ complex as a function of temperature

Due to their very open channel system, Na-*X* and Na-*Y* could not be washed free of adherent salt without extracting large amounts of included salt. Also in view of the more favourable crystal symmetry and the ease of preparation of the salt inclusion complex, Na-*A* was preferred for a structural investigation. As reported by Meier (1957) the sodium nitrate inclusion complex in zeolite *A* showed hardly any additional powder lines due to a specific arrangement, in contrast with $LiNO_3$ and $AgNO_3$ complexes. All samples of Na-*A* filled with salt had very weak 100, 110 and 200 lines compared with the hydrated sample, and the lattice was slightly expanded. $NaClO_3$ in Na-*A* showed many additional lines which, in general, were rather broad and diffuse.

A sample of the Na-*A*, $NaNO_3$ inclusion compound was analyzed for nitrate and water only, since many previous analyses of the parent Na-*A* had demonstrated its fairly consistent composition. Nitrate was determined gravimetrically by precipitation with nitron reagent.

Combined determination of water and nitrate (Cole, 1969) was achieved with thermogravimetric measurements as shown by the TGA trace in Fig. 1.

X-ray measurements

Unit-cell dimensions were determined from Guinier photographs using Cu$K\alpha$ radiation and sodium chloride as internal standard. The x-ray powder patterns were obtained with a General Electric XRD6 diffractometer using a flat sample, Cu$K\alpha$ radiation and a proportional counter. Integrated intensities of powder lines below the angle of $2\theta = 80°$ were measured with a planimeter. Due to the experimental conditions chosen, corrections for absorption were not necessary. No systematic absence were encountered in the powder pattern and only two relatively weak lines in the nitrate complex could not be indexed. These had 2θ values of 21.3° and 24.3° respectively.

Composition and unit cell

Zeolite *A* has been extensively investigated (*e.g.* Reed and Breck, 1956; Barrer and Meier, 1958; Broussard and Shoemaker, 1960; Gramlich and Meier, 1971) and the unit-cell content has been given as

$$12Na\,[12AlO_2,\ 12SiO_2],\ 27H_2O$$

with the cell constant of 12.3 Å for the cubic pseudo cell. The bulk sample of Na-*A* which was supplied by Union Carbide was found to have

$$a = 12.29 \pm 0.02\ \text{Å}.$$

The unit cell of the sieve filled with sodium nitrate and washed free of adherent salt was determined as

$$a = 12.39 \pm 0.02\ \text{Å}.$$

The filled and carefully washed sample after equilibration with 14 Torr water vapour pressure had the pseudo-unit cell content

$$12Na\,[12AlO_2,\ 12SiO_2],\ 9.3\ NaNO_3,\ 6.7H_2O.$$

Thus, one $NaNO_3$ is the equivalent of about 2.2 water molecules in filling the intracrystalline free volume, and the ideal salt-filled Na-*A* would have $12NaNO_3$ per unit cell.

Crystal structure of Na-*A*, $NaNO_3$ complex

The structure of Na-*A* was refined by Broussard and Shoemaker (1960) and Gramlich and Meier (1971). The aluminosilicate framework can be built from 14-hedral sodalite cages the faces of which are six and four-membered rings. The cages are connected by oxygen bridges and in sixfold coordination through their square faces. Thereby a large 26-hedral cavity, is formed which is seen in Fig. 2. These large cavities are accessible through their eight-ring windows which have a free diameter of ~ 4.2 Å. Table 1 contains the atom coordinates based on *Pm*3*m* quoted by Broussard and Shoemaker for hydrated Na-*A* and those given by Meier and Shoemaker for the bromine complex of Na-*A*. Due to the ordered distribution of silicon and aluminium, the symmetry can be approximated as *Fm*3 with a doubled cubic unit-cell edge of ~ 24.6 Å.

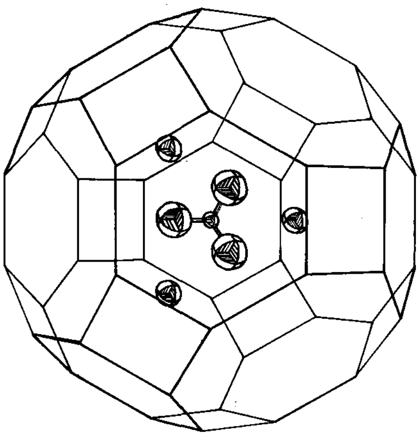

Fig. 2. Arrangement of sodium nitrate inside the large cavity of sieve *A*. The view is taken along the [111] axis and all details obscuring the drawing have been omitted. If the nitrate positions were fully occupied, there would be a nitrate anion in front of each six-ring. An aluminium or silicon atom is centred at each apex and the centres of oxygen atoms lie about halfway between the apices, near, but in general not on the lines connecting pairs of apices

On the basis of the true unit cell, the stronger of the two additional lines found in the pattern of the nitrate complex could then be indexed as 531. The super-lattice for Ag-*A* containing $AgNO_3$ was reported (Meier, 1957) to be tetragonal with $a' = 2a$ and $c' = a$, where $a = 12.3$ Å, the value of the cubic pseudo cell. The very weak line

Table 1. *Coordinates of* Na-*A based on Pm3m*

Atom	Position	Hydrated Na-*A* (BROUSSARD and SHOEMAKER)			Bromine complex of Na-*A* (MEIER and SHOEMAKER)		
		x	y	z	x	y	z
Si, Al	24*k*	0	0.1822	0.3713	0	0.185	0.3735
O(1)	12*h*	0	0.2229	0.5	0	0.232	0.5
O(2)	12*i*	0	0.2937	0.2937	0	0.294	0.294
O(3)	24*m*	0.1117	0.1117	0.3407	0.115	0.115	0.339
Na	8*g*	0.2082	0.2082	0.2082	0.214	0.214	0.214

at $2\theta = 24.3°$ would correspond with 303 on the basis of this cell, but 531 would not fit. Hence, it is not possible to fit all the spacings *d* to either of these two cells. Assuming similarity between the inclusion structures of $AgNO_3$ and $NaNO_3$ the above observations would imply that the actual structures are very complex. However, it seemed justifiable to neglect these two comparatively weak lines, since the limited number of powder lines would not permit one to lower the symmetry in any case.

Refinement

The initial R values of the data from the filled species were $R_I = 1.04$ and $R_F = 0.33$, where $R_I = \Sigma\,(I_{\text{obs}} - I_{\text{calc}})/\Sigma\,I_{\text{obs}}$ and $R_F = \Sigma\,(F_{\text{obs}} - sF_{\text{calc}})/\Sigma F_{\text{obs}}$.

I_{obs} = *uncorrected* observed relative intensity

$$I_{\text{calc}} = \sum_{i=1}^{n} M_i \cdot (Lp)_i \cdot [s\,(F_i)_{\text{calc}}]^2$$

n = number of non-equivalent reflections contributing to a powder line.

$(Lp)_i$ = Lorentz and polarization correction factor for each reflection

M_i = multiplicity factor for each reflection

$s(F_i)_{\text{calc}}$ = scaled calculated structure amplitude.

Reasons for abandoning the use of conventional R values common in single-crystal work have been discussed earlier (BARRER and VILLIGER, 1969).

The structure factors were calculated using the atom coordinates given by BROUSSARD and SHOEMAKER (1960) and their overall temperature factor of $B_0 = 1.4$ Å^2. An attempt was made to estimate

B_0 from a plot of $\ln(|F|^2/f^2)$ versus $(\sin^2\theta)/\lambda^2$. The value found was $B_0 = -0.1$ Å^2, which did not have physical reality and was probably due to the lack of high-angle reflections which are those mainly affected by thermal motion. The first set of Fourier maps was calculated using the parameters previously mentioned and an overall temperature factor of 4.0 Å^2. Evaluation of these maps immediately revealed the positions later called O(4), O(5), N and Na(2) as listed in Table 2. From the interatomic distance of 1.2 Å for N—O(4) it was concluded that one nitrate anion was lying on the threefold axis. Shifts of framework atoms were rather small but Na(1) moved 0.2 Å towards the centre of the sodalite cage. Insertion of the newly found peaks and the shifts of atoms already present lowered the R values to 0.60 and 0.24 respectively. Four additional sets of Fourier maps were calculated and carefully evaluated. After that, the refinement ceased to be effective and the corresponding R values were 0.40 and 0.17 for R_I and R_F respectively.

The least-squares refinement was carried out in the usual way, using first unit and then individual weights. In the last few least-squares cycles the restriction of a planar nitrate anion was removed but the final coordinates in Table 2 show that the planarity was retained within the limits of error. The R values obtained were $R_I = 0.18$ and $R_F = 0.14$. The coordinates after completion of the Fourier refinement were for most of the atoms not very different from the final ones. This implies that the further lowering of the R values during the least-squares refinement was mainly due to improvement of occupational and thermal parameters.

An attempt was made to exclude some of the positions of low occupancy [in particular O(7)] but every move in this direction led to divergence of the least-squares calculations.

Observed and calculated intensities listed in Table 3 show a very satisfactory correspondence. Interatomic distances involving framework atoms are given in Table 4. The ordering of Si and Al, which was not taken into account in the present analysis causes every oxygen position to be an average of two different ones. The mean value of 1.67 Å for the (Si,Al)—O bond length agrees well with the expected value of 1.68 Å. It is of interest to compare the free volumes of sodalite cages in different structures. The estimation, based on parameters of framework oxygen atoms O(2) and O(3) using an oxygen radius of 1.4 Å, gives the results assembled in Table 5. This table shows how the sodalite cage adjusts itself to different environments.

Table 2. *Parameters of the* Na-*A*, $NaNO_3$ *inclusion complex* (standard deviations given in brackets)

Atom	Position based on *Pm*3*m*	Fractional occupancy	*x*	*y*	*z*	*B*
Si, Al	24*k*	1	0	0.1839 (0.0010)	0.3721 (0.0010)	0.3 Å^2 (0.3)
O(1)	12*h*	1	0	0.235 (0.004)	0	3.1 (1.1)
O(2)	12*i*	1	0	0.284 (0.002)	0.2842	4.8 (1.2)
O(3)	24*m*	1	0.1075 (0.0018)	0.1075	0.348 (0.002)	3.5 (0.8)
O(4)	24*m*	0.81 (0.08)	0.360 (0.005)	0.3602	0.234 (0.009)	18 (3)
O(5)	12*i*	0.56 (0.04)	0	0.112 (0.003)	0.1118	3 (2)
O(6)	24*m*	0.46 (0.05)	0.429 (0.005)	0.4289	0.063 (0.009)	19 (6)
O(7)	12*j*	0.18 (0.09)	0.370 (0.015)	0.370	0.5	10 (11)
Na(3)	6*f*	0.73 (0.15)	0.22 (0.02)	0.5	0.5	21 (9)
O(8)	8*g*	0.53 (0.18)	0.38 (0.02)	0.377	0.377	16 (8)
N	8*g*	0.9 (0.2)	0.313 (0.007)	0.3127	0.3127	4 (3)
Na(1)	8*g*	0.84 (0.08)	0.186 (0.003)	0.1864	0.1864	6 (2)
Na(2)	12*j*	0.84 (0.05)	0.230 (0.003)	0.2302	0.5	7.4 (1.4)
Na(4)	1*b*	1	0.5	0.5	0.5	4 (3)

Table 3. *Calculated and observed intensities of the inclusion complex of sodium nitrate in* Na-*A*

h k l	d_{calc}	I_{calc}	I_{obs}
1 0 0	12.39 Å	148	133
1 1 0	8.76	233	225
1 1 1	7.15	416	396
2 0 0	6.20	13	11
2 1 0	5.54	48	43
2 1 1	5.06	37	33
2 2 0	4.38	142	129
2 2 1 3 0 0	4.13	300	258
3 1 0	3.92	2	11
3 1 1	3.74	764	593
2 2 2	3.58	24	20
3 2 0	3.44	324	313
3 2 1	3.31	803	978
4 0 0	3.10	2	2
4 1 0 3 2 2	3.00	760	953
3 3 0 4 1 1	2.920	137	140
3 3 1	2.842	2	2
4 2 0	2.770	76	87
4 2 1	2.704	38	33
3 3 2	2.642	672	723
4 2 2	2.529	0	1
4 3 0 5 0 0	2.478	179	143
4 3 1 5 1 0	2.430	22	37
3 3 3 5 1 1	2.384	152	140
4 3 2 5 2 0	2.300	30	24
5 2 1	2.262	76	77
4 4 0	2.190	235	243
4 4 1 5 2 2	2.157	1	15
4 3 3 5 3 0	2.125	204	173
5 3 1	2.094	91	82
4 4 2 6 0 0	2.065	176	147
6 1 0	2.036	19	10
5 3 2 6 1 1	2.009	6	4
6 2 0	1.959	80	64
4 4 3 5 4 0 6 2 1	1.935	43	37
5 4 1	1.912 Å	179	170
5 3 3	1.889	0	2
6 2 2	1.868	4	2
5 4 2 6 3 0	1.847	3	5
6 3 1	1.827	0	2
4 4 4	1.788	44	41
6 3 2 7 0 0	1.770	21	9
5 4 3 5 5 0 7 1 0	1.752	172	224
5 5 1 7 1 1	1.735	35	56
6 4 0	1.718	1	11
6 4 1 7 2 0	1.701	148	136
5 5 2 6 3 3 7 2 1	1.686	54	28
6 4 2	1.655	24	25
5 4 4 7 2 2	1.641	58	80
7 3 0	1.627	7	2
5 5 3 7 3 1	1.613	89	103
6 4 3 6 5 0	1.586	112	112
6 5 1 7 3 2	1.573	5	2
8 0 0	1.549	57	43
6 5 2 7 4 0 8 1 0	1.537	25	35
5 5 4 7 4 1 8 1 1	1.525	34	43
7 3 3	1.514	0	4
6 4 4 8 2 0	1.503	9	4
7 4 2 8 2 1	1.492	39	56
6 5 3	1.481	41	26
6 6 0 8 2 2	1.460	27	21
6 6 1 8 3 0	1.450	39	27
7 4 3 7 5 0 8 3 1	1.441 Å	70	68
5 5 5 7 5 1	1.431	42	31
6 6 2	1.422	4	4
6 5 4 8 3 2	1.411	111	121
7 5 2	1.402	2	2
8 4 0	1.385	2	1
6 6 3 7 4 4 8 4 1 9 0 0	1.376	30	23
8 3 3 9 1 0	1.368	185	183
7 5 3 9 1 1	1.360	4	5
8 4 2	1.351	6	2
7 6 0 9 2 0	1.344	6	22
6 5 5 7 6 1 9 2 1	1.336	164	125
6 6 4	1.320	6	2
7 6 2 8 4 3 8 5 0 9 2 2	1.313	14	4
7 5 4 8 5 1 9 3 0	1.306	57	67
9 3 1	1.299	4	10
8 5 2	1.285	2	1
7 6 3 9 3 2	1.278	4	6
8 4 4	1.264	59	58
6 6 5 9 4 0	1.258	54	47
7 7 0 8 5 3 9 4 1	1.252	18	18
7 5 5 7 7 1 9 3 3	1.245	23	28
8 6 0 10 0 0	1.239 Å	30	35
7 6 4 8 6 1 9 4 2 10 1 0	1.233	57	56
7 7 2 10 1 1	1.227	16	12
8 6 2 10 2 0	1.215	2	4
8 5 4 10 2 1	1.209	2	2
9 4 3 9 5 0	1.204	25	27
7 7 3 9 5 1	1.198	32	32
6 6 6 10 2 2	1.192	1	2
8 6 3 10 3 0	1.187	11	24
7 6 5 9 5 2 10 3 1	1.182	33	36
8 7 0 9 4 4 10 3 2	1.166	21	22
7 7 4 8 5 5 8 7 1	1.161	21	28
9 5 3	1.156	13	16
10 4 0	1.151	2	4
8 7 2 9 6 0 10 4 1	1.146	8	2
9 6 1 10 3 3	1.141	0	2
10 4 2	1.131	0	2
7 6 6 9 6 2 11 0 0	1.127	33	33
8 7 3 9 5 4 11 1 0	1.122	15	22
7 7 5 11 1 1	1.118	7	9

Table 4. *Interatomic distances between framework atoms of zeolite A filled with sodium nitrate*

In the brackets are estimated standard deviations in units of the last figure

Si,Al—O(1)	1.70(2) Å	O(1)—O(2)	2.74(3) Å
—O(2)	1.65(1)	—O(3)	2.79(3)
—O(3)	1.66(1)	O(2)—O(3)	2.68(2)
		O(3)—O(3)	2.66(4)
Mean	1.67	Mean	2.72

Cations and inclusion complex

The number of sodium ions calculated from their respective occupancy factors adds up to 22 ± 2 Na^+ per unit cell, a figure near the 21 found by chemical analysis. Na(1) lies in the planes formed by (Si,Al), O(2) and O(3) within the limits of error. This is not the case in hydrated Na-*A* and in the bromine complex of Na-*A*. In these structures Na(1) lies nearer to the centre of the large cavity and its mean distance from the planes formed by the aforementioned atoms is about 0.5 Å. The relevant numerical data are given in Table 6. From these, one can conclude that in the inclusion structure Na(1)

Table 5. *Free volumes of sodalite cages in several structures*

Structure and reference	per cage	per *N* cages*	coordination of cages
Sodalite (Löns and Schulz, 1967)	113 Å^3	68 cm^3	8, (6-rings) 6, (4-rings)
Faujasite (Baur, 1964)	144	87	4, (6-rings)
(Na,Ca)-*A* with I_2-inclusion (Seff and Shoemaker, 1967)	147	88	6, (4-rings)
dehydrated (Na,Ca)-*A* (Seff and Shoemaker, 1967)	155	94	6, (4-rings)
Na-*A* with $NaNO_3$-inclusion (This work)	160	96	6, (4-rings)
Na-*A* with Br_2-inclusion (Meier and Shoemaker, 1966)	163	98	6, (4-rings)
hydrated Na-*A* (Broussard and Shoemaker, 1960)	163	98	6, (4-rings)

* $N = 6.02 \times 10^{23}$

also partly serves to offset the ionic charge of the NO_3^- located inside the sodalite cage. This might be a reason for its different position as compared with Na-*A* and with Na-*A* containing bromine.

Na(2) is associated primarily with the nitrate anions which are lying on the threefold axes near to the wall of the main cage (Fig. 2). However, some interaction with framework oxygen atom cannot be excluded. Na(3) and Na(4) are completely surrounded by inclusion atoms.

Pictorial illustration of the whole complex is difficult due to the high degree of filling and the many positions which are only partially occupied. However, starting from the centre of the sodalite cavity (000) it is possible to describe the actual arrangement by moving along one threefold axis. All nitrate ions lie on the threefold axes, and Table 7 contains numerical values of interest.

The bulk of the nitrates [O(4).N] are situated at the opposite side of the aforementioned six rings. The corresponding cations, Na(2),

Table 6. *Interatomic distances between cations and oxygen atoms for zeolite A with included sodium nitrate*

In brackets are given the estimated standard deviations in units of the last figure

Na(1)—O(3)	2.42(3) Å	threefold	framework
—O(5)	2.65(6)	threefold (1.7)*	nitrate in sodalite cage
—O(2)	2.87(3)	threefold	framework
Na(2)—O(4)	2.36(2)	fourfold (3.2)*	nitrate in main cage
—O(7)	2.4(2)	onefold (0.2)*	nitrate at centre of main cage
—O(1)	2.85(3)	twofold	framework
—O(3)	2.86(4)	twofold	framework
—O(8)	3.0(4)	twofold (1.0)*	water
Na(3)—O(6)	2.4(3)	fourfold (1.8)*	water
—O(7)	2.4(3)	fourfold (0.7)*	nitrate at centre of main cage
—O(4)	2.4(3)	fourfold (3.2)*	nitrate in main cage
—O(8)	2.9(4)	fourfold (2.1)*	water
Na(4)—O(7)	2.3(2)	twelvefold (2.0)*	nitrate at centre of main cage
—O(8)	2.6(4)	eightfold (3.2)*	water

* coordinations taking the fractional occupancy of the ligand atom into account.

Table 7

Positions of atoms and planes formed by atoms with respect to the threefold axis

Figures in brackets are standard deviations in units of the last figure quoted

Atom	Origin or nearest neighbours of cations	$x,x,x;$		
		$x =$ nitrate complex of Na-*A*	$x =$ bromine complex of Na-*A*	$x =$ hydrated Na-*A*
O(5)	nitrate inside the sodalite cage	0.075(2)	—	—
Si, Al	framework	0.1853(6)	0.186	0.1845
Na(1)	framework: O(2), O(3); nitrate: O(5)	0.186(3)	0.214	0.2082
O(3)	framework	0.188(2)	0.183	0.1880
O(2)	framework	0.1895(16)	0.196	0.1958
N	nitrate at the wall of the main cage	0.313(7)	—	—
O(4)	nitrate at the wall of the main cage	0.318(5)	—	—
Na(2)	nitrate ion : O(4), O(7), framework: O(1), O(3), water: O(8)	0.320(2)	—	—
O(8)	water molecule on the threefold axis	0.38(2)	—	—
O(7)	nitrate near the centre of the main cage	0.413(10)	—	—
Na(4)	nitrate: O(7); water: O(8)	0.5	—	—

Table 8. *Sodium nitrate inclusion in Linde sieve A*

Smallest interatomic distances between nitrate oxygen atoms and other atoms (Designations: f = framework; c = cation; w = water; n = nitrate)

O(4) n—N	1.28 Å	O(5) n—O(5) n	1.95 Å	O(7) n—O(8) w	1.5 Å*
—O (8) w	1.8*	—Na(1) c	2.65	—Na(4) c	2.3
—Na(2) c	2.36	—O(5) n	2.76	—O(7) n	2.3
—O (7) n	2.4*	—O(2) f	3.01	—Na(3) c	2.4
—O (6) w	2.4*	—O (3) f	3.21	—O(4) n	2.4
—Na(3) c	2.5	—Si, Al f	3.34	—Na(2) c	2.4
—Na(1) c	3.09			—N	2.5
—O(2) f	3.18			—O(7) w	3.2
—O(7) n	3.3			—O(4) n	3.3

* low fractional occupancy factors together with their large standard deviations (Table 2) permit these short distances.

lie in the same plane as the nitrate anion within the limits of error (Table 7 and Fig. 2). Finally, O(7) is thought to belong to a third kind of nitrate mainly because of the distance O(7)—O(7) which is 2.3 ± 0.2 Å and therefore close to the oxygen-oxygen distance of 2.12 Å in a nitrate anion. The number of nitrates calculated from the occupancy factors of O(4), O(5) and O(7) is 9.4 ± 1.1, in accord with the chemical analysis. The number of atoms assumed to be water molecules is 15 ± 4 and does not fit with the analytical value of 6.7. However the quoted figures, in particular those for water molecules, are of limited reliability due to the high temperature coefficients and the close correlation of occupancy factors and temperature coefficients. The shortest interatomic distances between the nitrate oxygen atoms O(4), O(5) and O(7) and other atoms are summarized in Table 8. These distances are reasonable; where short distances occur, as indicated in the table, these are permitted by low fractional occupancy factors.

Oxygen O(5) has a fractional occupancy of 0.54 and its nearest distance to a neighbour is O(5)—O(5) = 1.96 ± 0.06 Å. Since three- and fourfold axes are present, half occupancy will always leave this short distance between two atoms. Therefore it is not possible that position O(5) is occupied by a water molecule and so these oxygen atoms belong to nitrate anions. The N—O distance in solid sodium nitrate is given as 1.22 to 1.24 Å (STURM and LODDING, 1968). This leads to an oxygen-oxygen distance of 2.11 to 2.14 Å which is almost within the range of 1.96 Å plus doubled standard deviation. The fractional occupancy of 0.54 would therefore correspond with two nitrates—O(5)—

per cage which are easily accomodated since no other short distances can be detected. The central nitrogen would be in an eightfold position and could hardly be seen in a Fourier map. Also, any corresponding cations would occupy manyfold sites since there are no twofold positions available. The arrangement of the nitrate anions in the sodalite cage, relative to each other and to nitrate outside this cage is shown in Fig. 3.

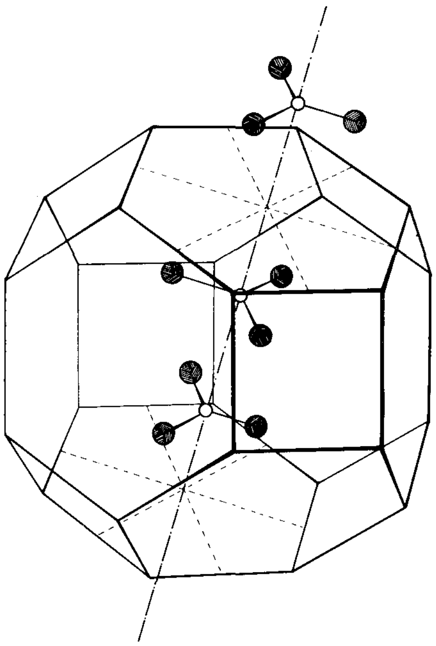

Fig. 3. Arrangement of the two nitrate anions in the sodalite cage, showing also their relation with the nitrate anions outside the sodalite cage in the large cavity

These nitrate anions have to pass through a six-membered ring with an approximate free diameter of 2.6 Å. The critical dimensions of a nitrate anion are 2.8 × 4.6 Å based on a van der Waals radius of 1.4 Å for oxygen. Although such a process seems unlikely, one has to take into account the high temperature of 330 °C. At such temperatures Kr (diameter ~ 4 Å) enters outgassed sodalite hydrate (Barrer and Vaughan, 1971). Another alternative would be that some of the nitrate ions were decomposed to smaller nitrite ions able to pass through a six-membered ring more readily. A qualitative chemical test for nitrite using urea proved negative, and indeed if there is nitrite in the sodalite cage, the occupancy factor of O(5) would correspond to the improbable content of three nitrite ions per cage.

Extraction of all nitrate from the large cavity would prove the existence of two nitrate ions inside the sodalite cage since these two would not be able to escape at the moderate temperatures of 80°—100°C which were employed. However, the escape rate of nitrate through the eight-rings of the large cage decreased strongly as one approached lower loadings of nitrate. Since zeolite *X* also contains sodalite cages and the large channels are circumscribed by twelve-rings, the aforementioned experiment could be carried out more readily. Na-*X* was subjected to an analogous treatment with molten sodium nitrate. Extraction of nitrate from the large cavity was then achieved with three washing steps using warm water, after which even extended extraction in a Soxhlet apparatus did not further lower the nitrate content of the sieve. Full analysis of the extracted product showed that 6.9 ± 0.4 NO_3^- were retained per unit cell corresponding to about 0.9 NO_3^- per sodalite cage. Tests for the presence of nitrite again proved negative. Hence molten sodium nitrate can penetrate through

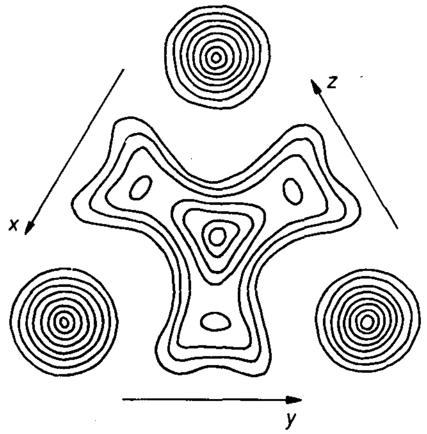

Fig. 4. Fourier section taken in the plane of the nitrate anion in front of the six-ring. The view is along the [111] axis. This Fourier section, calculated on the basis of the final F_{obs} values, indicates that the nitrate oxygen atoms do not lie exactly on the mirror planes as was assumed during the refinement. The appearance of the nitrate oxygen peaks suggests considerable positional and perhaps thermal disorder. The sodium positions are well defined

the small six-ring openings of the sodalite cages. The lower occupancy as compared with the x-ray results in Na-*A* might be due to the smaller volume of the sodalite cage in Na-*X* and the fact that only four six-ring openings are available in *X* whereas eight of them are present in *A*.

Two thirds of the total number of nitrates included are located in front of the six-ring openings to the interior of the sodalite cages as depicted in Fig. 2. The temperature factor of 17.5 Å^2 for O(4) seemed to be fairly high compared with 7.4 Å^2 for Na(2). A Fourier map, calculated with the final structure parameters showed that O(4) did not lie exactly on the 110 mirror plane. Figure 4 also indicates thermal and positional disorder perpendicular to the threefold axis. Therefore, it was not considered justifiable to split O(4) into half-atoms located on each side of the 110 plane. The interatomic distance of 1.28 ± 0.11 Å does not differ significantly from 1.24 Å, although it might indicate some translational movement of the whole nitrate anion perpendicular to the threefold axis. The relatively small temperature factor for nitrogen could be caused by a water molecule occupying nearly the same position as atom N when NO_3^- is absent (occupancy factor of 0.8). It would therefore rather indicate higher occupancy than reduced thermal motion.

Discussion

This structure determination establishes the arrangement of the bulk of the nitrate anions and Na cations in the unit cell. The main part of the sodium, namely Na(1) and Na(2), is shared between framework and included nitrate ions. The rest of the included species however do not interact directly with the framework. Neither of the models proposed earlier for the Ag-*A*, $AgNO_3$ complex matches completely with the Na-*A*, $NaNO_3$ complex. The silver nitrate complex (Barrer and Meier, 1958) might give a different arrangement compared with the present inclusion complex since there the tetragonal geometry of the super cell, which is probably due to the particular distribution of the silver cations, was clearly established.

The structural model proposed by Liquornik and Marcus (1968) does not correspond with our results. Their products were reported as anhydrous with a correspondingly higher nitrate content. Since their analysis was carried out by measuring the weight difference with respect to the initial product after washing with water and drying at 150 °C they could hardly distinguish whether there was any water present or not. From the thermogravimetric curve at 150 °C (Fig. 1) the loss of water at this stage corresponds almost exactly with the weight of the 10.1—9.3 = 0.8 $NaNO_3$. Therefore, it is possible that the complex prepared by LIQUORNIK and MARCUS had nearly the same composition as that in the present work.

LIQUORNIK and MARCUS based their model of $[Na—NO_3—Na]^+$ clusters on the net charge distribution of the O_6 and O_8 rings. Following their assumption that every oxygen atom carries a charge of $-\frac{1}{4}e$ one finds the following relationships:

a) eight O_6-rings with one half of the oxygen atoms shared between adjacent cells and O_8 rings.

$$24\,(-e/4) + 24\,[-(e/4)\cdot\tfrac{1}{2}\cdot\tfrac{1}{2}] = -\tfrac{15}{2}\,e\,.$$

which corresponds with $-\frac{15}{16}\,e$ per O_6-ring.

b) six O_8-rings with one half of the oxygen atoms shared between adjacent cells and the other half shared between adjacent cells *and* O_6-rings.

$$24\,(-e/4)\,\tfrac{1}{2} + 24\,(-e/4)\,\tfrac{1}{2}\cdot\tfrac{1}{2}$$

which corresponds with $-\frac{3}{4}\,e$ per O_8-ring.

Adding up the contributions a) and b) one finds 12, the number of units of electric charge required. On the other hand with the figures of LIQUORNIK and MARCUS ($-\frac{3}{2}\,e$ per O_6-ring and $-\frac{2}{3}\,e$ per O_8-ring) there is no way to obtain the required total of 12.

Using the corrected figures of the calculations a) and b) one finds that the relations in salt-free Na-*A* agree in the anhydrous zeolite with nearly one Na^+ per O_6-ring, the rest of the cations being distributed near the O_8-rings. In the inclusion complex of $NaNO_3$ in Na-*A* the assumption of distinct $[Na—NO_3—Na]^+$ clusters cannot be correct since we have shown that eight of the nitrates form a layer on the interior surface of the large cavity. In this layer each nitrate lies in the plane of three sodium cations and each sodium has four oxygen atoms stemming from two different nitrate ions as nearest neighbours.

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References

A. A. Amaro and K. Seff (1973), Crystal structure of an acetylene sorption complex of zeolite 4*A*. J. Physic. Chem. **77**, 906—910.

R. M. Barrer, J. F. Cole and H. Villiger (1970), Chemistry of soil minerals. Part VII. Synthesis, properties, and crystal structures of salt-filled cancrinites. J. Chem. Soc. [London] (A), 1523—1531.

R. M. Barrer and W. M. Meier (1958), Salt-inclusion complexes of zeolites. J. Chem. Soc. [London], 299—304.

R. M. Barrer and D. E. W. Vaughan (1971), Trapping of inert gases in sodalite and cancrinite crystals. J. Physics and Chem. Solids **32**, 731—743.

R. M. Barrer and H. Villiger (1969), The crystal structure of the synthetic zeolite *L*. Z. Kristallogr. **128**, 352—370.

W. H. Baur (1964), On the cation and water positions in faujasite. Amer. Mineral. **49**, 697—704.

L. Broussard and D. P. Shoemaker (1960), The structures of synthetic molecular sieves. J. Amer. Chem. Soc. **82**, 1041—1051.

J. F. Cole (1969), Anion entrainment during hydrothermal crystallization. Ph. D. Thesis, University of London.

J. H. Fang and J. V. Smith (1964), Crystal structures with a chabazite framework. Part IV. Reconnaissance of the chlorine complex. J. Chem. Soc. [London], 3749—3758.

V. Gramlich and W. M. Meier (1971), The crystal structure of hydrated Na-*A*. A detailed refinement of a pseudo-symmetric structure. Z. Kristallogr. **133**, 134—149.

M. Liquornik and Y. Marcus (1968), Ion exchange in molten salts. II: The Occlusion of lithium, sodium, potassium and silver nitrates in the respective forms of zeolite *A*. Israel J. Chem. **6**, 115—121.

J. Löns and H. Schulz (1967), Strukturverfeinerung von Sodalith, $Na_8Si_6Al_6O_{24}Cl_2$. Acta Crystallogr. **23**, 434—436.

W. M. Meier (1957), Ion exchange, salt inclusion and ion sieve properties of synthetic zeolites. Ph. D. Thesis, University of London.

W. M. Meier and D. P. Shoemaker (1966), The structure of a bromine sorption complex in synthetic zeolite sodium-*A*. Z. Kristallogr. **123**, 357—364.

T. B. Reed and D. W. Breck (1956), Crystalline zeolites. II. Crystal structure of synthetic zeolite, Type *A*. J. Amer. Chem. Soc. **78**, 5972—5977.

K. Seff and D. P. Shoemaker (1967), The structures of zeolite sorption complexes. I. The structures of dehydrated zeolite 5A and its iodine sorption complex. Acta Crystallogr. **22**, 162—170.

J. V. Smith (1968), Structure of sorption complexes in zeolites, in *Molecular sieves*, Soc. Chem. Ind. [London], p. 28—33.

E. Sturm and W. Lodding (1968), Correction for preferred orientation of platelike particles in diffractometer powder analysis. Acta Crystallogr. A **24**, 650—653.

H. Villiger (1969), Structural aspects of some porous crystals and their inclusion complexes. Ph. D. Thesis, University of London.