

## Inclusion Complexes of Zeolites

### Part 1.—Inclusion Complexes of Zeolite 4A with Silver Nitrate and Alkali Nitrates

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The structural properties of inclusion complexes of zeolite 4A with alkali nitrates and silver nitrate have been investigated from the point of view of the state and position of the included component. The crystal structures of alkali nitrate complexes,  $\text{Li}_{12}\text{A} \cdot 9.8\text{LiNO}_3 \cdot 9.3\text{H}_2\text{O}$  and  $\text{Na}_{12}\text{A} \cdot 10\text{NaNO}_3 \cdot 6.6\text{H}_2\text{O}$ , have been solved and refined in the cubic space-group  $Pm\bar{3}m$ ; at 24 °C the unit-cell constants are:  $a_0 = 12.075(1)$  Å and  $a_0 = 12.295(1)$  Å, respectively. For  $\text{Ag}_{12}\text{A} \cdot 9.5\text{AgNO}_3 \cdot 5.9\text{H}_2\text{O}$  complex the unit-cell constant is  $a_0 = 12.340(1)$  Å. On the basis of i.r. and X-ray structure analyses it is found that the included nitrate in zeolite cages exists partially as a nitrate ion and partially as a nitrate complex. The nitrate ions, situated near the S6R, are in coordination with the zeolite counter-ion and also with the closest included cations. The nitrate ions, situated near the S8R, are in coordination with included cations only.

Channels and cages in a zeolite structure are filled with water molecules, but these may be replaced by other molecules. Using a melt as the reaction medium, with the zeolite in contact with the molten salt, the salt is absorbed into the zeolite and water molecules are replaced by salt molecules. In this way inclusion complexes are formed. The first zeolite inclusion complexes were prepared by Barrer and Meier,<sup>1</sup> and subsequently by Marcus and Liquornik.<sup>2,3</sup> Marcus and Liquornik were more engaged in the study of the phenomenon of the inclusion process and ion exchange from a melt, whereas Barrer and his workers have investigated the structure of inclusion complexes.<sup>4</sup> We have investigated the inclusion of cobalt nitrate,<sup>5</sup> alkali nitrates, sulphates and halides,<sup>6,7</sup> as well as modification of the sodium nitrate inclusion complex by ion exchange from a molten salt.<sup>8</sup>

The present work is the continuation of an investigation and definition of nitrate inclusion complexes with special reference to the mutual relationship of the included component and the zeolite framework.

## EXPERIMENTAL

The preparation of nitrate inclusion complexes has been described earlier.<sup>6</sup> The chemical composition and formulae of unit cells of the complexes are given below.

formulae of unit cell	symbol
$\text{Ag}_{12}\text{A} \cdot 9.5\text{AgNO}_3 \cdot 5.9\text{H}_2\text{O}$	$\text{AgA} \cdot \text{AgNO}_3$
$\text{Li}_{12}\text{A} \cdot 9.8\text{LiNO}_3 \cdot 9.3\text{H}_2\text{O}$	$\text{LiA} \cdot \text{LiNO}_3$
$\text{Na}_{12}\text{A} \cdot 10\text{NaNO}_3 \cdot 6.6\text{H}_2\text{O}$	$\text{NaA} \cdot \text{NaNO}_3$

I.r. spectra were recorded on a Perkin-Elmer grating spectrophotometer type 457 in the region 4000-250  $\text{cm}^{-1}$ . The KBr technique was used.

Crystals of  $\text{NaA} \cdot \text{NaNO}_3$ ,  $\text{LiA} \cdot \text{LiNO}_3$  and  $\text{AgA} \cdot \text{AgNO}_3$  with edges *ca.* 0.07 mm were mounted on a Syntex P1 four-circle computer-controlled diffractometer. Cell constants were determined for each of the crystals by least-squares treatment of 15 reflections of the largest intensities. In all of our experiments molybdenum radiation ( $K\alpha, \lambda = 0.71069 \text{ \AA}$ ) was used.

Intensity data were collected using an  $\omega$  scan, with a scan rate of  $1/2^\circ \text{ min}^{-1}$ , up to  $2\theta = 60^\circ$ . Only those reflections whose intensity exceeded 3 times their corresponding estimated standard deviations (191 for  $\text{NaA} \cdot \text{NaNO}_3$ , 132 for  $\text{LiA} \cdot \text{LiNO}_3$  and 175 for  $\text{AgA} \cdot \text{AgNO}_3$ ) were included in the refinement process.

A Robert L. Stone differential analyser (model 12) was employed for d.t.a. investigations. Sample sizes ranged from 100 to 150 mg. The samples were heated to  $900^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$ .

## RESULTS

## D.T.A. INVESTIGATIONS

The thermochemical behaviour of the inclusion complexes and their structural stability were defined using d.t.a. curves. In the d.t.a. diagrams (fig. 1) one notices the presence of the included component through the thermal effects associated with the nitrate component present: endothermic peaks at  $285$  and  $505^\circ\text{C}$  in  $\text{NaA} \cdot \text{NaNO}_3$ ,

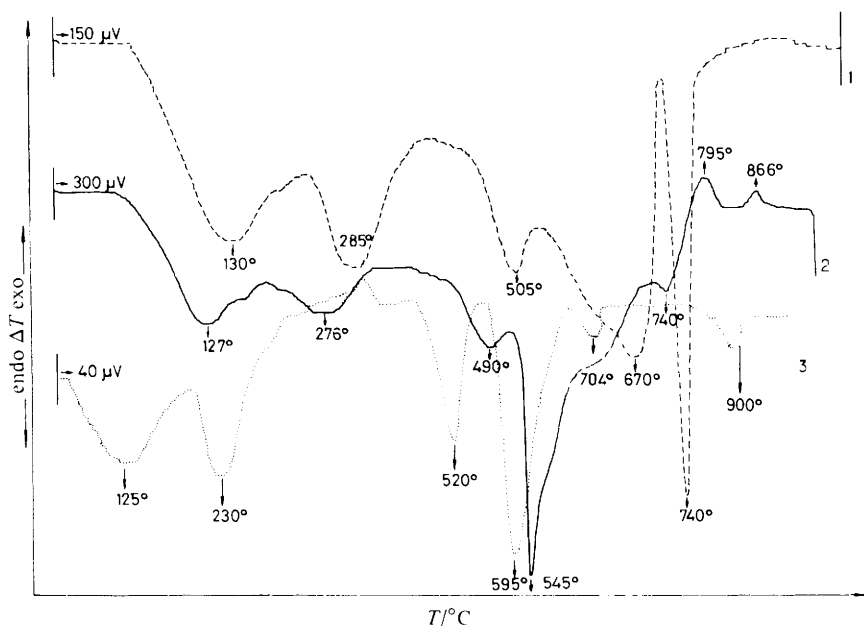


Fig. 1.—D.t.a. curves for: (1)  $\text{NaA} \cdot \text{NaNO}_3$ , (2)  $\text{AgA} \cdot \text{AgNO}_3$  and (3)  $\text{LiA} \cdot \text{LiNO}_3$ .

at 520 and 595 °C in  $\text{LiA} \cdot \text{LiNO}_3$  and at 490 and 545 °C in  $\text{AgA} \cdot \text{AgNO}_3$ . The identification of the peaks was made on the basis of the literature data on the pure zeolite, NaA, and on the pure nitrate salts.

The endothermic peaks at 130 °C for  $\text{NaA} \cdot \text{NaNO}_3$ , at 125 and 230 °C for  $\text{LiA} \cdot \text{LiNO}_3$  and at 127 and 276 °C for  $\text{AgA} \cdot \text{AgNO}_3$  were identified as water peaks because they disappear on dehydration of the complexes. This is the water that remains after the process of salt inclusion and its content is considerably smaller than that contained in the basic forms of the zeolites. The process of dehydration of inclusion complexes is reversible, as in a pure zeolite, up to the temperature of structural stability. In this work we do not comment in detail on water in the inclusion complexes because water, its location and its manner of bonding are the subject of another work.<sup>9</sup>

The thermal stability of inclusion complexes was determined by the presence of the nitrate component. The upper limit of thermal stability for the investigated inclusion complexes is 450 °C. Above this temperature the nitrate gradually decomposes to give a denitrated zeolite. The structural stability is also determined by the presence of nitrate. The limit of structural stability is *ca.* 600 °C, which is considerably lower than the upper limit for the structural stability of pure zeolites, which ranges from 750 to

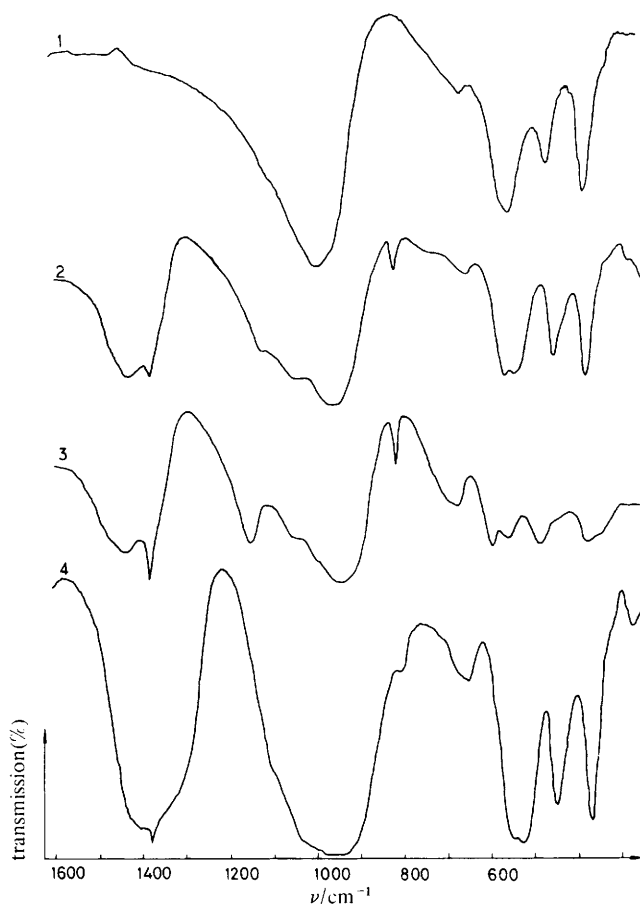


FIG. 2.—Infrared spectra of inclusion complexes: (1) NaA, (2)  $\text{NaA} \cdot \text{NaNO}_3$ , (3)  $\text{LiA} \cdot \text{LiNO}_3$  and (4)  $\text{AgA} \cdot \text{AgNO}_3$ .

800 °C. In the structural transformations, new phases appear,<sup>10</sup> accompanied by definite thermal effects at temperatures above 600 °C.

#### I.R. INVESTIGATIONS

The i.r. spectra of inclusion complexes of zeolites in the range 4000-250 cm<sup>-1</sup> contain bands characteristic of both the zeolite and the included salt. We paid special attention to the changes which appear in i.r. spectra in the range 2500-250 cm<sup>-1</sup>, since in this range there are bands characteristic of the nitrate component. At higher wavenumbers we mainly find bands characteristic of water and OH groups on zeolites.

The i.r. spectra of inclusion complexes are compared on the one hand with the spectra of the salts, *i.e.* with the spectra of nitrates in the melt, and on the other hand with the spectra of the zeolite itself.

I.r. spectra of inclusion complexes show that the nitrate ion in zeolite cages exists to a greater extent as a coordinated ion, the nitrato complex, with a pronounced metal-nitrate interaction, and to a lesser extent as a free nitrate ion. Metal-nitrate interaction is manifested in the spectra by a complex structure of nitrate bands at *ca.* 1400 and 1050 cm<sup>-1</sup> (fig. 2 and table 1). The nitrate ion in the coordinated complex belongs to the C<sub>2v</sub> symmetry group.<sup>11</sup> The lowering of the symmetry of the nitrate ion leads to the loss of degeneration of the  $\nu_3$  band of the nitrate ion, to its splitting, to the appearance of a  $\nu_1$  band and to the appearance of complex combination bands at *ca.* 2440 and 1750 cm<sup>-1</sup>.

The inclusion complex AgA·AgNO<sub>3</sub> is in a certain sense distinguished from inclusion complexes of zeolite A with alkali nitrates, since in the complex structure of the  $\nu_3$  band of the nitrate ion a relatively intense band appears at 1330 cm<sup>-1</sup>. This band is characteristic of the unidentate coordination of the nitrate group. On the basis of this it could be concluded that in the AgA·AgNO<sub>3</sub> complex unidentate coordination of the nitrate group with cation is more pronounced.

Definite changes are also noticed in the basic bands of zeolite A. In the i.r. spectra of all the inclusion complexes one notices a shift of the characteristic bands with respect to the spectrum of the pure zeolite, which indicates that the oxygen atoms in the lattice take part in coordination with the included cation (fig. 2 and table 1). The changes are most pronounced in the band at *ca.* 550 cm<sup>-1</sup> (double four ring, D4R), where the band is split and also some splitting of the band at *ca.* 990 cm<sup>-1</sup> is observed.

#### STRUCTURE DETERMINATION

Structural investigation of the NaA·NaNO<sub>3</sub> [*a*<sub>0</sub> = 12.295(1) Å], LiA·LiNO<sub>3</sub> [*a*<sub>0</sub> = 12.075(1) Å] and AgA·AgNO<sub>3</sub> [*a*<sub>0</sub> = 12.340(1) Å] complexes was started using the atomic parameters of the framework atoms.<sup>4</sup> Although on long-exposure oscillation photographs a small number of weak reflections were recorded, indicating a superstructure with 24 Å cubic axes (due to the Si-Al order), all the present investigations were carried out in the space group *Pm3m*.

Evaluation of the first Fourier map revealed the positions of counter-ions near the centre of S6R and included cations near the D4R. Several additional Fourier and difference Fourier maps were calculated and the positions of other cations and oxygens were located. Least-squares refinement of all the atoms and fractional occupancies followed and an *R* factor of 9.50% for the NaA·NaNO<sub>3</sub> complex and 9.90% for the LiA·LiNO<sub>3</sub> complex was obtained. Corresponding positional parameters and selected interatomic distances and angles for NaA·NaNO<sub>3</sub> and LiA·LiNO<sub>3</sub> complexes are given in tables 2-5.

The refinement process for the AgA·AgNO<sub>3</sub> complex did not proceed in a satisfactory manner. However, a high degree of disorder of Ag cations was evident. The refinement of this structure is in progress.

TABLE 1.—OBSERVED FREQUENCIES (IN  $\text{cm}^{-1}$ ) AND BAND ASSIGNMENTS OF ZEOLITE NaA AND NITRATE INCLUSION COMPLEXES (OH VIBRATIONS OMITTED)

samples					assignments		
NaA	NaA • NaNO <sub>3</sub>	LiA • LiNO <sub>3</sub>	AgA • AgNO <sub>3</sub>		nitrate NO <sub>3</sub> <sup>-</sup>	nitrate (NO <sub>3</sub> ) complexes	zeolite
—	2485 sh	—	—		$\nu_3 + \nu_1$	—	—
—	2460 vw	2475 vw	2425 vw				
—	2420 vw	2425 vw	2395 w				
—	—	2120 sh	1775 sh		$\nu_1 + \nu_4$	—	—
—	1785 vw	1780 vw	1762 w				
—	1772 vw	—	1470 sh			$\nu_1(A_1)$ biden. or bridg.	—
—	1470 sh	1470 sh	1420 s		$\nu_3(E')$	—	—
—	1440 s	1440 s	1380 m			$\nu_1(A_1)$ uniden.	—
—	1380 s	1380 s	1330 mb			$\nu_2(A)$ biden. or bridg.	—
—	1130 w	1150 s	1120 sh		$\nu_1(A_1')^a$		$\nu_{\text{T-O,asym}}$ stretch
—	1050 m	1050 m	1050 w				—
990 sb	970 s	990 sh	990 s				—
—	—	950 s	—				—
—	820 w	815 w	818 w		$\nu_2(A_2')$		—
—	—	690 sh	720 sh		$\nu_4(E')$		—
—	660 w	675 m	653 w				—
550 m	570 m	595 m	553 s				double
—	545 m	560 m	530 s				four ring
460 m	453 m	490 m	452 m				$\delta_{\text{T-O}}$ bend
370 m	382 m	380 m	373 s				pore opening
—	—	340 sh	275 w			$\nu_{\text{M-O}}$	—

Key: s, strong; m, medium; w, weak; b, broad; v, very; uniden., unidentate; biden., bidentate; bridg., bridging; <sup>a</sup> infrared inactive.

TABLE 2.—POSITIONAL, THERMAL AND OCCUPANCY PARAMETERS<sup>a</sup> FOR NaA · NaNO<sub>3</sub> INCLUSION COMPLEX

atom	Wyckoff position	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>	s.o.f.
Si, Al	24(k)	0	1837(4)	3734(4)	69(21)	116(34)	106(30)	102(26)	0	0	24
O(1)	12(h)	0	2323(16)	1/2	484(130)	274(117)	165(107)	0	0	0	12
O(2)	12(i)	0	2863(12)	2863(12)	299(120)	203(71)	203(71)	236(94)	0	0	12
O(3)	24(m)	1106(8)	1106(8)	3488(11)	261(60)	261(60)	434(96)	116(48)	116(48)	122(59)	24
O(4)	24(m)	3715(24)	3715(24)	2365(28)	655(146)	655(146)	263(142)	-96(109)	-96(109)	-14(143)	5/12
O(5)	24(m)	3421(53)	3421(53)	3986(56)	690(170)	690(170)	426(151)	471(142)	471(142)	370(152)	1/6
O(6)	24(m)	4390(34)	4390(34)	1553(45)	846(153)	846(153)	524(163)	-91(131)	-91(131)	-67(148)	1/4
O(7)	6(e)	0	0	1208(96)	494(159)	933(195)	933(195)	0	0	0	1/3
O(8)	1(a)	0	0	0	694(165)	694(165)	694(165)	0	0	0	1
O(9)	8(g)	804(37)	804(37)	804(37)	873(140)	873(140)	873(140)	-128(144)	-128(144)	-128(144)	1/4
O(10)	6(f)	1/2	1/2	741(162)	1139(187)	1620(185)	1620(185)	0	0	0	1/6
O(11)	24(l)	723(82)	4098(77)	1/2	424(159)	469(154)	536(170)	513(156)	0	0	1/8
O(12)	8(g)	4420(50)	4420(50)	4420(50)	406(177)	406(177)	406(177)	-92(146)	-92(146)	-92(146)	1/4
Na(1)	8(g)	1827(17)	1827(17)	1827(17)	496(104)	496(104)	496(104)	-75(80)	-75(80)	-75(80)	1/2
Na(2)	8(g)	2165(17)	2165(17)	2165(17)	310(87)	310(87)	310(87)	-28(81)	-28(81)	-28(81)	3/8
Na(3)	12(j)	2263(20)	2263(20)	1/2	578(181)	828(131)	828(131)	497(142)	0	0	7/12
Na(4)	6(e)	0	0	1948(124)	1338(207)	1506(202)	1506(202)	0	0	0	1/3
Na(5)	6(f)	1/2	1/2	2185(64)	490(175)	866(163)	866(163)	0	0	0	1/2
Na(6)	8(g)	1637(58)	1637(58)	1637(58)	455(149)	455(149)	455(149)	389(153)	389(153)	389(153)	1/8
Na(7)	1(b)	1/2	1/2	1/2	746(152)	746(152)	746(152)	0	0	0	1
Na(8)	24(l)	1602(86)	2777(86)	1/2	459(159)	512(159)	452(159)	446(157)	0	0	1/24
N	8(g)	3150(26)	3150(26)	3150(26)	863(142)	863(142)	863(142)	-114(124)	-114(124)	-114(124)	5/8

<sup>a</sup> All positional and thermal parameters are given  $\times 10^4$ ; standard deviations are in units of the least significant digit given for the corresponding parameter.

TABLE 3.—SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°)<sup>a</sup> FOR NaA·NaNO<sub>3</sub> INCLUSION COMPLEX

(Si, Al)—O(1)	1.668(8)		
(Si, Al)—O(2)	1.655(5)	O(1)—(Si, Al)—O(2)	109(1)
(Si, Al)—O(3)	1.658(5)	O(1)—(Si, Al)—O(3)	111.4(6)
O(1)—O(2)	2.71(1)	O(2)—(Si, Al)—O(3)	107.2(6)
O(2)—O(3)	2.666(9)	O(3)—(Si, Al)—O(3)	110(1)
O(1)—O(3)	2.75(1)		
O(3)—O(3)	2.72(2)		
Na(1)—O(2)	2.88(1)	O(4)—N	1.37(4)
Na(1)—O(3)	2.40(1)	O(4)—O(4)	2.34(7)
Na(1)—O(9)	2.18(9)	O(5)—O(6)	2.60(9)
Na(2)—O(2)	2.926(11)	O(5)—O(12)	2.62(6)
Na(2)—O(3)	2.46(1)	O(6)—O(6)	2.12(9)
Na(2)—O(4)	2.71(5)	O(4)—N—O(4)	117(4)
Na(2)—O(9)	2.90(9)		
Na(2)—N	2.10(6)		
Na(3)—O(1)	2.78(2)		
Na(3)—O(3)	2.74(3)		
Na(3)—O(4)	2.39(6)		
Na(3)—O(5)	2.37(8)		
Na(3)—O(6)	2.86(8)		
Na(4)—O(3)	2.7(1)		
Na(5)—O(4)	2.24(4)		
Na(5)—O(12)	2.93(8)		
Na(5)—O(5)	2.76(5)		

<sup>a</sup> Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

## DISCUSSION

These results show that the incorporation of the included component into a zeolite cage leads to a larger or smaller interaction of the included component with the zeolite framework. This interaction may be established *via* the counter-ion of the zeolite or *via* the included cation and this determines the orientation and arrangement inside the cage.

The i.r. spectra of inclusion complexes unambiguously show that in the inclusion complexes part of the included nitrate exists as a nitrate ion with characteristic vibrations  $\nu_3$  at 1380 cm<sup>-1</sup> and  $\nu_2$  at 820 cm<sup>-1</sup>, while another part exists as a nitrato complex with a pronounced metal–nitrate interaction.

In a nitrate salt melt, from which zeolite inclusion complexes are formed, stable ion pairs, nitrato complexes, are formed due to metal–nitrate interaction.<sup>12, 13</sup> The strength of this interaction is associated with the strength of the action of the electrostatic field of the cation on the nitrate ion. The interaction leads to a definite coordination of the anion and cation and this coordination may be in a unidentate or bidentate fashion or may be bridging. In all these cases a distortion of the nitrate ion and a lowering of the symmetry occur. The nitrate ion belongs to the  $D_{3h}$  symmetry group, while the coordinated nitrate ion belongs to the  $C_{2v}$  or  $C_s$  symmetry group.

TABLE 4.—POSITIONAL, THERMAL AND OCCUPANCY PARAMETERS<sup>a</sup> FOR LiA · LiNO<sub>3</sub> INCLUSION COMPLEX

atom	Wyckoff position	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>	s.o.f.
Si, Al	24(k)	0	1830(6)	3679(5)	135(38)	62(34)	101(35)	109(32)	0	0	24
O(1)	12(h)	0	2109(24)	1/2	1248(194)	126(137)	508(149)	0	0	0	12
O(2)	12(i)	0	3011(20)	3011(20)	534(155)	506(115)	506(115)	462(137)	0	0	12
O(3)	24(m)	1138(11)	1138(11)	3368(20)	242(68)	242(68)	1044(146)	-265(80)	-265(80)	173(87)	24
O(4)	24(m)	3761(40)	3761(40)	2509(57)	699(177)	699(177)	1325(216)	-440(190)	-440(190)	499(206)	5/12
O(5)	24(m)	3294(54)	3294(54)	2584(68)	495(159)	495(159)	312(190)	-184(147)	-184(147)	-169(177)	1/6
O(6)	24(m)	4239(91)	4239(91)	602(90)	644(212)	644(212)	437(241)	-137(207)	-137(207)	-84(132)	1/4
O(7)	1(a)	0	0	0	624(184)	624(184)	624(184)	0	0	0	1
O(8)	8(g)	4065(195)	4065(195)	4065(195)	545(226)	545(226)	545(226)	35(227)	35(227)	35(227)	3/8
O(9)	8(g)	1443(98)	1443(98)	1443(98)	442(191)	442(191)	442(191)	359(203)	359(203)	359(203)	1/4
O(10)	6(f)	1/2	1/2	606(41)	1364(210)	816(164)	864(164)	0	0	0	2/3
O(11)	3(c)	1/2	1/2	0	530(194)	298(184)	298(184)	0	0	0	1/3
O(12)	6(f)	1/2	1/2	3447(69)	221(206)	311(177)	311(177)	0	0	0	1/3
Li(1)	8(g)	1908(187)	1908(187)	1908(187)	274(181)	274(181)	274(181)	111(211)	111(211)	111(211)	1/2
Li(2)	8(g)	2090(156)	2090(156)	2090(156)	330(183)	330(183)	330(183)	181(193)	181(193)	181(193)	1/2
Li(3)	12(j)	2995(95)	2995(95)	1/2	760(216)	1296(211)	1296(211)	459(220)	0	0	2/3
Li(4)	6(e)	0	0	2050(138)	248(180)	1120(221)	1120(221)	0	0	0	2/3
Li(5)	6(f)	1/2	1/2	2412(100)	517(215)	585(202)	585(202)	0	0	0	1/3
Li(6)	1(b)	1/2	1/2	1/2	256(119)	256(119)	256(119)	0	0	0	1
N	8(g)	3253(37)	3253(37)	3253(37)	530(145)	530(145)	530(145)	-169(148)	-169(148)	-169(148)	3/4

<sup>a</sup> All positional and thermal parameters are given  $\times 10^4$ ; standard deviations are in units of the least significant digit given for the corresponding parameter.



TABLE 5.—SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR  $\text{LiA} \cdot \text{LiNO}_3$  INCLUSION COMPLEX

(Si, Al)—O(1)	1.630(9)		
(Si, Al)—O(2)	1.638(12)	O(1)—(Si, Al)—O(2)	108(2)
(Si, Al)—O(3)	1.652(10)	O(1)—(Si, Al)—O(3)	109(1)
O(1)—O(2)	2.64(2)	O(2)—(Si, Al)—O(3)	109(2)
O(2)—O(3)	2.68(2)	O(3)—(Si, Al)—O(3)	113(1)
O(1)—O(3)	2.67(2)		
O(3)—O(3)	2.75(2)		
Li(1)—O(2)	2.98(2)		
Li(1)—O(3)	2.20(6)	O(4)—N	1.25(7)
Li(2)—O(2)	2.97(2)	O(4)—O(4)	2.1(1)
Li(2)—O(3)	2.24(6)	O(5)—O(6)	2.8(1)
Li(2)—O(4)	2.8(2)	O(6)—O(6)	2.3(2)
Li(2)—N	2.4(2)	O(4)—N—O(4)	118(6)
Li(3)—O(4)	1.85(3)		
Li(3)—O(5)	2.42(9)		
Li(4)—O(3)	2.51(9)		
Li(5)—O(4)	2.1(1)		

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

Nitrato complex formation is evident due to the complex bands at *ca.* 2400, 1700, 1400 and 1300  $\text{cm}^{-1}$ , as well as a band at *ca.* 1050  $\text{cm}^{-1}$  with the  $\nu_1$  ( $A_1$ ) band which is now active in the i.r. spectra. The nitrato complex also exhibits an M—O stretching band in the 350–250  $\text{cm}^{-1}$  region.

Since in the i.r. spectra of all the inclusion complexes there appears a band at *ca.* 1450  $\text{cm}^{-1}$ , which we have identified as  $\nu_1(A_1)$  of the bridging nitrate group, as well as the splitting of the band at *ca.* 1000  $\text{cm}^{-1}$  (table 1 and fig. 2), we conclude that in the inclusion complexes bridging coordination of the nitrate groups is the main component.

The position of nitrate groups in an  $\alpha$  cage was obtained from the results of X-ray structure analysis. Three nitrate groups are at the threefold axis facing the inlet into the  $\beta$  cages, S6R. They are coordinated with cations Na(3) in the position 12(*j*) and also with Na(2) in the position of counter-ion 8(*g*). These nitrate groups in the i.r. spectrum of the inclusion complex exhibit the characteristics of a nitrate ion ( $D_{3h}$  symmetry) with the band  $\nu_1$  at *ca.* 1380  $\text{cm}^{-1}$  and  $\nu_2$  at *ca.* 820  $\text{cm}^{-1}$ . This points to the fact that a nitrate ion in this position is 'liberated' and the structure of the nitrato complex from the melt is disturbed.

The counter-cations Na(1) and Na(2) are found on the threefold axes, at S6R.

The Na(2) counter-ion forms an octahedral coordination with the nitrate group and three oxygens O(3) from the S6R ring. Coordination polyhedron around the Na(2) cation has the form of flattened trigonal prism of  $\bar{3}$  symmetry. Interatomic distances and angles are given in table 4. The Na(2) cation is displaced by 0.5 Å from the plane formed by the O(3) oxygens from the S6R ring toward the centre of an  $\alpha$  cage. This may be attributed to the effect of the nitrate group, although the interaction may be mutual. The evidence of this is the position of the N atom which is 0.2 Å out of the plane formed by oxygen atoms of the nitrate group. Corresponding distances N—O(4)

and O(4)—O(4) in the nitrate group (given in table 4) are larger in comparison with those found in solid  $\text{NaNO}_3$ .

Counter-cation Na(1) in position 8(g) is in trigonal, almost planar, coordination with three oxygens O(3) from the S6R ring. Na(1) is displaced from the plane formed by O(3) oxygens toward the centre of a  $\beta$  cage by 0.15 Å. The length of the bond Na(1)—O(3) is 2.399(16) Å and represents the shortest approach of a Na cation to the oxygens of the framework. As O(3) atoms also form a D4R ring the interaction with the framework is directly manifested in the i.r. spectra by the splitting of the bands which are characteristic of zeolite structure,  $\text{TO}_4$  and D4R, *i.e.* the bands at 990 and 550  $\text{cm}^{-1}$ , respectively (table 1 and fig. 2). On the basis of the i.r. spectra it may also be concluded that this interaction is most pronounced in the  $\text{LiA} \cdot \text{LiNO}_3$  complex, then in the  $\text{NaA} \cdot \text{NaNO}_3$  complex and least in the  $\text{AgA} \cdot \text{AgNO}_3$  complex. This is certainly associated with the nature of the cation, *i.e.* with its size. Lithium is a small cation and it may approach the oxygens of the framework very closely, whereas  $\text{Ag}^+$  as a larger cation is more distant from the walls of the cage.

Going further from the position of Na(1), toward the centre of an  $\alpha$  cage, we have O(5) in positions 24(m). This oxygen is a part of one nitrate group; the remaining two oxygens are close to an S8R ring, with the distance O(5)—O(6) = 2.60(9) Å. The remaining relevant distances are given in table 4. This nitrate group in the i.r. spectrum of the inclusion complex exhibits the characteristics of a nitrate group with lowered symmetry,  $C_{2v}$ . That means that this is a species manifested as a nitrate complex with a pronounced metal–nitrate interaction with bands at *ca.* 2440, 1770, 1450 and 1050  $\text{cm}^{-1}$ , and by the appearance of a new metal–oxygen band  $\nu_{\text{M-O}}$  at *ca.* 300  $\text{cm}^{-1}$  in the i.r. spectra (table 1 and fig. 2). The position and geometry of the remaining nitrate groups could not be located with certainty. We have assumed that one of the nitrate groups is situated close to the centre of an  $\alpha$  cage and the remaining one in the S8R ring between two neighbouring  $\alpha$  cages.

A cation designated as Na(4) is found in the  $\beta$  cage. This cation, with the oxygens from the framework, has the same coordination as an Na(3) cation in an  $\alpha$  cage. It is found on the apex of a pyramid whose base is formed by oxygens O(3) from D4R ring. The cation density at a D4R ring in  $\alpha$  and  $\beta$  cages is high bearing in mind the coordination of Na(1) with O(3) from D4R and S6R rings; this is manifested by the splitting of the  $\text{TO}_4$  and D4R bands in the i.r. spectra as we have mentioned above.

In and near the centre of a  $\beta$  cage we have found electron density concentrations designated as O(7), O(8) and O(9). These positions are statistically occupied and give the values of the interatomic distances. We have assumed that in these positions we have three to four water molecules which are bonded to a Na(4) cation.

The same distribution of cations and nitrate groups is found in the structure of the  $\text{LiA} \cdot \text{LiNO}_3$  complex, tables 3 and 5.

Because of the large number of positions and their statistical occupancy it is difficult to give a clear schematic presentation of the inclusion complex in  $\alpha$  and  $\beta$  cages. This model can be generally described as follows. Most of the cations in  $\alpha$  cages are situated towards the walls of the cage forming a 'monolayer'. These cations are in coordination with nitrate and nitrate groups situated towards the centre of the  $\alpha$  cage. Going closer to the centre of the  $\alpha$  cage, the nitrate groups are bridged by cations Na(5) in the position 6(f). These cations are possibly bonded to a nitrate group in the vicinity of the centre of the  $\alpha$  cage.

From the interatomic distances it is evident that the bonds of the counter-ions Na(2) [and also Li(2)] are weakened, as well as the bonds within the included ion pairs. In this way a very mobile cation phase is formed which is identified in these inclusion complexes by other methods.<sup>14, 15</sup>

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(PAPER 9/845)