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## 169. Formation and Properties of Losod, a New Sodium Zeolite

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(15. III. 74)

*Summary.* Losod, a new type of crystalline hydrated sodium aluminosilicate,  $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot q \text{H}_2\text{O}$ , has been prepared from reaction mixtures containing bulky quaternary alkylammonium ions, particularly azonia-spiro[4.4]nonane, besides sodium ions. Losod crystallizes from batches with a low sodium content ( $\text{Na}/\text{Al} \leq 1$  and  $\text{Si}/\text{Al} \approx 1$ ). The quaternary ammonium hydroxide primarily serves as a source of hydroxide ions and is not incorporated into the zeolite crystals. These bulky bases provide a useful means for controlling the alkalinity of the system independently of the concentration of the necessary cations built into the zeolite.

The crystals of Losod are hexagonal ( $a = 12.91$  and  $c = 10.54 \text{ \AA}$ ) and the proposed framework structure shows a polytypic relationship to sodalite and cancrinite. Losod has reversible

sorption and ion exchange properties typical of a small-pore zeolite and in essential agreement with the proposed structure.

**1. Introduction.** -- When aqueous solutions of alkali silicates and aluminates are mixed together, a voluminous precipitate is generally formed, or the entire mixture coagulates to form a 'gel'. These highly hydrated products have been examined by various methods [1]--[3] in the past. They are amorphous with respect to X-ray and electron diffraction. Because of their colloidal nature, any washing or drying is bound to change their structure and composition [4]. On heating the gel with the mother liquor or other alkaline fluids, crystalline products can be obtained. Some of these crystalline hydrated alkali aluminosilicates or synthetic zeolites have found wide application as molecular sieves [5].

Zeolites are distinguished on the basis of their structure type [6] defining the constitution or topology of the framework. The known parameters governing the formation of a particular type of zeolite include:

- a) bulk composition of the synthesis mixture,
- b) molecular state of aggregation of the starting materials,
- c) method of mixing the starting materials,
- d) temperature and time of ripening.

Crystallization from the reaction mixtures is normally considered to consist of two processes, nucleation and crystal growth. Nuclei are presumed to form through aggregation of precursors or finite groups of  $(\text{Si,Al})\text{O}_4$  tetrahedra [7], temporarily dissolved in the liquid phase. It is not unreasonable to relate the hypothetical precursor species to the secondary building units found in zeolite structures [8] [9].

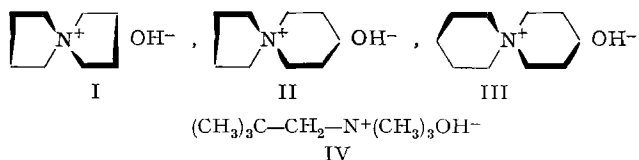
Other investigators tend to interpret the formation of zeolites as an ordering process within the 'solid phase' excluding dissolved aluminosilicate species from consideration [10] [11].

Alkyl amines and tetralkylammonium hydroxides were first used by *Barrer & Denny* [12] as bases in zeolite syntheses. These investigators obtained isotypes of known sodium zeolites with notably higher Si/Al ratios. Later data [13] indicated the requirement of a certain amount of sodium ions in the system if crystallization was to occur. *Kerr* [14] synthesized a new structure type using 1,4-dimethyl-diazonia-bicyclo[2.2.2]octane hydroxide besides sodium hydroxide. The only zeolites which have so far been obtained from reaction mixtures free of metal cations are the TMA-sodalite and TMA-gismondine-type species reported by *Baerlocher & Meier* [15].

The present work deals with the synthesis and properties of a new type of zeolite obtained in the presence of particular quaternary ammonium ions, larger than tetramethylammonium ions. The choice of the organic cations was governed by the following considerations and requirements [16]:

- a) good solubility and sufficient basicity of the hydroxide,
- b) high stability under the conditions of zeolite synthesis,
- c) well defined and rigid shape.

**2. Experimental Part.** -- 2.1 *Starting Materials.* The following quaternary ammonium hydroxides were used as components of synthesis mixtures:



The hydroxides of azonia-spiro[4.4]nonane I (Bispyrrolidinium, **BP**), azonia-spiro[4.5]decane II, and azonia-spiro[5.5]undecane III were prepared according to a general procedure derived from work of *von Braun* [17] and *Blicke & Hotelling* [18]. Most of the zeolite synthesis experiments were carried out with **BP** hydroxide (I), which proved to be quite stable at 100° as compared to tetramethylammonium hydroxide. Decomposition of **BP** hydroxide does not yield any small basic fragments [19].

Neopentyl-trimethyl-ammonium hydroxide IV was made in three steps [20] [21] from pivaloyl chloride. The final methylation was carried out in absolute ethanol with methyl iodide. The overall yield was 35%. This compound decomposes at 140° mainly into neopentyl-dimethyl-amine and methanol.

Sodium ions were introduced into the synthesis mixtures as the hydroxide, chloride or bromide. No specific influence of the anions on the products was noticed. Neither chloride nor bromide was found in the crystalline zeolites. Tetramethoxysilane was used throughout as a well defined silica source, and aluminum isopropylate supplied the necessary aluminate in solution [22]. The alcohols formed from the alkoxides were normally boiled off in an open container or by using rotatory evaporator.

**2.2 Synthesis Conditions.** Experiments with a set of different batch compositions were carried out in sealed polypropylene tubes (internal diameter 12 mm, volume 20–20 ml) [22].

Normally a solution of the quaternary ammonium base and sodium hydroxide was heated to 80° in a pyrex beaker. Aluminum isopropylate was then added under stirring till a clear solution was obtained. After cooling to 40–50° the calculated weight of tetramethoxysilane, diluted with an equal volume of methanol, was added under stirring. A precipitate or a gel of varying consistency is thereby formed. Adding the sodium ions last led to less reproducible results. The mixture was homogenized using a *Polytron* stirrer at 22000 rpm. The filled and sealed polypropylene tubes were rotated slowly in an oven at 100°. Products were filtered on G-4 sintered glass discs or centrifuged, washed with deionized water, and dried at 100°. Before examination the samples were stored at room temp. and 50% relative humidity for at least 24 h.

The procedure developed for the synthesis of Losod on a larger scale is based on the mole ratios Na : Al : Si : BP : H<sub>2</sub>O = 11 : 15 : 15 : 59 : 2000 and concentrations of [Na] = 0.252, [Al] = [Si] = 0.343 and [BP] = 1.35 mol/l. Solutions of **BP** aluminate and **BP** silicate are prepared independently. They are then mixed with sodium hydroxide solution, and the resulting gel is heated at 100° in a closed stainless steel vessel under stirring [16].

**Synthesis procedure:** The aluminate solution is prepared by heating 1 mol of approx. 2.5 M **BP** hydroxide in water to 80° and adding 69 g of aluminum isopropylate under stirring. The solution is heated until it is clear and then filtered through a sintered glass funnel. The 2-propanol is finally

distilled off using a rotatory evaporator. The silicate solution is prepared by heating 0.35 mol of approx. 1 M **BP** hydroxide in water to 45° and adding a solution of 51.5 g of tetramethoxysilane in 50 ml of methanol. The methanol is then boiled off. Thereafter 126 ml of 2M sodium hydroxide, the aluminate and the silicate solutions are mixed in this order, made up to one liter with water, and homogenized. The mixture is then transferred into a preheated reaction vessel and stirred. After 4 days at 100° about 40 g of pure Losod can be filtered off. The mother liquor can be re-used for the preparation of Losod by replenishing the consumed components.

2.3 *Methods of Characterization.* X-ray powder patterns (*Nonius Guinier* camera,  $\text{CuK}_\alpha$  radiation) were primarily used for the identification of all samples. The patterns were visually compared with a special reference collection of powder patterns of zeolites and related materials. In some cases an extensive data file containing *d*-values and intensities for nearly all aluminosilicates and silicates described in the literature was searched using a computer program [23]. X-ray intensities were recorded using a *Philips* powder diffractometer equipped with a *Geiger* counter. Precise *d*-values were determined using a *Jagodzinski* camera with  $\text{FeK}_\alpha$  radiation and silicon as an internal standard. No absorption correction was applied.

Samples were analyzed for sodium, aluminum and silicon by atomic absorption spectrophotometry (*Perkin Elmer* models 303 and 305).

The following methods were applied for detecting any incorporated organic bases in the zeolites:

- a) A sufficient amount of the zeolite sample was dissolved in hydrochloric acid and the concentrated solution tested with *Dragendorffs* reagent and ninhydrine;
- b) Another portion of the zeolite sample was dissolved in concentrated potassium hydroxide solution and the vapour of the heated solution tested for alkalinity and odour;
- c) A portion of the sample was slowly heated to about 900° in a thermogravimetric apparatus (see below) in a stream of argon which was then passed through dilute boric acid solution with methyl red serving as an indicator for trace amounts of base.

Densities were determined using a mixture of methyl iodide and carbon tetrachloride (buoyancy-method). Electron microscopic transmission and carbon replica photographs as well as electron diffraction patterns were recorded by Mr. A. *Portmann* (Anorganisch-chemisches Institut der Universität Zürich). Scanning electron micrographs were taken by Mr. R. *Wessicken* (Laboratorium für Elektronenmikroskopie II der ETHZ). Thermogravimetric and differential thermal analysis was performed on a *Du Pont* thermal analyzer. Argon, nitrogen, oxygen and dry air were used as sweeping gases in different runs. The sorption properties were qualitatively tested with the same apparatus. All sorbates except for carbon dioxide were introduced by the sweeping gas. Static water sorption isotherms were determined in a gravimetric apparatus described in [16]. The kinetics of sorption could be followed using the same setup. Equilibrium was attained within 0.01% of total sample weight in about 7 days at 25° and around 50 h at 49.5°. The sodium ions in the original zeolite were exchanged by silver, lithium, potassium, and ammonium ions by percolation with salt solutions. The samples were thereby placed on a sintered glass disc and a heating jacket allowed the exchange to proceed at elevated temperature (approx. 80°). Silver ion exchange isotherms were determined by potentiometric (at low silver concentration) and gravimetric methods.

**3. Results.** – 3.1 *Conditions for the Synthesis of Losod.* In exploratory synthesis experiments using **BP** and sodium hydroxides as bases the mole ratios of components were varied within the following limits:

$$0 \leq \text{Na/Al} \leq 2.5$$

$$0.5 \leq \text{Si/Al} \leq 12$$

$$0.21 \leq \text{BP}/(\text{Na} + \text{Al} + \text{Si} + \text{BP}) \leq 0.91$$

In addition to several zeolites which are known to grow from monocationic sodium systems a new product was thereby recorded. This latter product crystallized only from mixtures with low sodium contents ( $0.25 \leq \text{Na/Al} \leq 1.0$ ,  $\text{Si/Al} \leq 1$ ). It was therefore given the designation *Losod*. Table 1 gives examples of batch compositions and analyses of products. These syntheses yielded *Losod* as the only product, without any visible gel impurities. The  $\text{Si/Al}$  ratio of the new phase is constant within experimental error.

No crystalline product nor gel could be detected to form from sodium free batches, even after one month at 100 or 140°. A gel formed instantaneously on adding sodium ions to these mixtures.

*Losod* was also obtained when the **BP** hydroxide in the starting mixture was replaced by the quaternary ammonium hydroxides II, III or IV. On the other hand, batches with lithium, potassium, or tetramethyl ammonium ions replacing the sodium ions yielded crystalline phases bearing no resemblance to *Losod*. In most cases, identification with known silicates was possible [16]. *Nitrogen containing substances*, *i.e.* organic bases or fragments thereof, were *not* detected in any sample of *Losod*. This is in line with the  $\text{Na/Al}$  ratio of the zeolite which was found to be always close to 1. The yields of *Losod* obtained from batches with an initial ratio of  $\text{Na/Al} < 1$  turned out to be determined by the total amount of sodium ions available in the system.

Examination of the mother liquors from syntheses with **BP** or neopentyl-trimethyl-ammonium ions by ionophoresis [15] showed that the organic base was unchanged and free of decomposition products with different  $R_f$  values.

When sodium ions up to a  $\text{Na/Al}$  ratio of 0.7 are added to the mother liquor containing the remaining aluminium and silicon a further amount of *Losod* crystallizes on heating.

3.2 *Crystallization Fields of Losod in the Na, BP-System as a Function of Time.* In this series of synthesis experiments the variables and their range were

$$\begin{array}{ll} (n_{\text{Na}} + n_{\text{BP}}): & 40 \text{ to } 90 \text{ millimol} \\ n_{\text{Na}}/n_{\text{Al}}: & 0.25 \text{ to } 4.0 \\ \text{reaction time:} & 1.5 \text{ h to } 16 \text{ d} \end{array}$$

The variables were subject to the following constraints:

$$\left. \begin{array}{l} n_{\text{Al}} = n_{\text{Si}} \\ n_{\text{H}_2\text{O}} = 100 + 10 (n_{\text{Na}} + n_{\text{BP}}) \\ n_{\text{Na}} + n_{\text{Al}} + n_{\text{Si}} + n_{\text{BP}} = 100 \end{array} \right\} \text{ millimol per batch}$$

Table 1. *Some Examples of Losod Syntheses*

No.	Starting comp., mol percent			Time days	Crystallinity (powder lines)	Product analysis, wt. percent			Product, mol ratios			Yield percent <sup>a)</sup>				
	Na	Al	Si			BPOH	H <sub>2</sub> O	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	H <sub>2</sub> O		total	Na	Al	Si
19AR	5	10	10	75	2400	5	good	16.3	30.1	39.2	13.0	98.6	.94	1	1.11	1.22
40	4	8	8	80	2100	4	very good	15.8	29.8	36.9	15.1	97.6	.92	1	1.05	1.44
52	2.5	10	10	77.5	2000	4	sl. diffuse	14.6	29.5	36.6	16.1	96.8	.87	1	1.05	1.54
54	5	8	10	77	2000	4	good	16.1	31.1	36.6	15.5	99.3	.90	1	1.00	1.41
56	8	16	8	68	2000	4	good	17.5	30.4	35.6	13.8	97.3	1.01	1	.99	1.29
58A						7 hours	amorphous	16.1	29.9	34.7			.95	1	.99	
58B	5	10	10	75	2000	6	good	16.7	29.5	34.7			.95	1	1.08	
58C						20	good	16.9	29.0	37.4	15.7	97.6	.99	1	1.02	1.49
64	2	3.5	3.5	91	2500	3 <sup>b)</sup>	good	17.0	28.8	35.0	15.7	96.5	1.03	1	1.03	1.54
65	5	9	9	77	2100	3 <sup>b)</sup>	good	19.0	29.6	34.7	14.3	97.6	1.12	1	1.00	1.37
G1	5.3	10.6	10.6	73.5	2050	2 <sup>b)</sup>	good	15.3	30.6	37.4	16.0	99.3	.88	1	1.04	1.48
G2	5	9	9	77	2000	3.7 <sup>b)</sup>	good	18.0	29.3	35.8	15.6	98.7	1.07	1	1.04	1.50
G3	11	15	15	59	2000	4	good	18.2	28.5	36.2	17.1	100	1.05	1	1.08	1.74
TN6 <sup>c)</sup>	10	15	15	60	1670	4	sl. diffuse	17.2	29.3	35.8	16.2	98.5	1.03	1	1.04	1.56

a) Referring to the total amount of sodium ions in the starting solution.

b) Seeded with approx. 10 wt. percent of Losod from previous run.

c) Neopentyl-trimethyl-ammonium hydroxide as base.

All sodium and **BP** ions were added as the hydroxides. The total molality of hydroxide ions was kept between 1.6 and 2.6 mol per kg H<sub>2</sub>O. Results for reaction times of 6 h up to 16 days are shown in Figure 1. Reaction times of 1.5 h yielded no crystalline product in any of the samples. Each circle in Figure 1 represents an experimental point in terms of composition and time. The observed crystalline products comprise NaP [8] [24], sodalite hydrate [25], (Na, **BP**)X, NaA [26], and Losod. Mixtures of these phases were frequently encountered. The faujasite type zeolite X

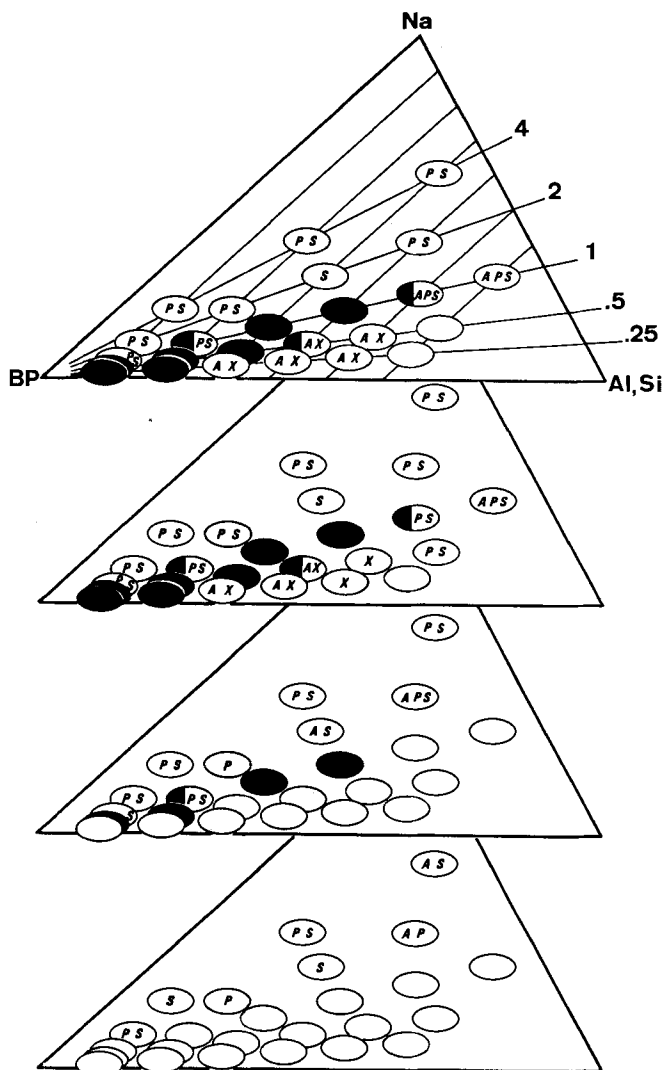


Fig. 1. Crystallization fields of Losod after reaction times of 6 hours (bottom), 50 hours, 10 days and 16 days (top). The numbers denote the ratios  $n_{\text{Na}}/n_{\text{Al}}$ , black fields: Losod, A: zeolite NaA, P: NaP, S: sodalite hydrate, X: (Na, BP) X

contained incorporated **BP** ions besides  $\text{Na}^+$  as demonstrated by the TGA-method and by paper electrophoresis of its solution in hydrofluoric acid.

Each batch was filled into two tubes and except for the experiments at the lowest (40%) base contents, the products in the corresponding tubes were found to be identical.

**3.3 Crystallization from Mother Liquor.** The mother liquor from a crystallization of Losod was concentrated to 0.15M Si and Al and 2.2M **BP**. Different quantities of 2M sodium hydroxide were then added to samples of 25 ml of concentrated mother liquor. Products were examined after 24 h at 100°.

At low Na/Al ratios Losod was obtained. Higher Na/Al ratios yielded various intermediate products approaching sodalite hydrate. In Figure 2 the X-ray powder patterns of some intermediate products are shown in comparison with those of the end members, Losod and sodalite hydrate.  $h k 0$  lines of the intermediate products were found to be sharper than the other lines. This means that these products cannot simply be mixtures of the end members.

**3.4 Phase Transformations.** Crystallization sequences were found to be a noteworthy feature of the Na, Li-system by *Borer & Meier* [22]. Such crystallization sequences are not so evident in the Na, **BP**-system as shown in Figure 1. It must be noted, however, that the range in composition and reaction time adopted in the present investigation is too limited for comparisons in this respect.

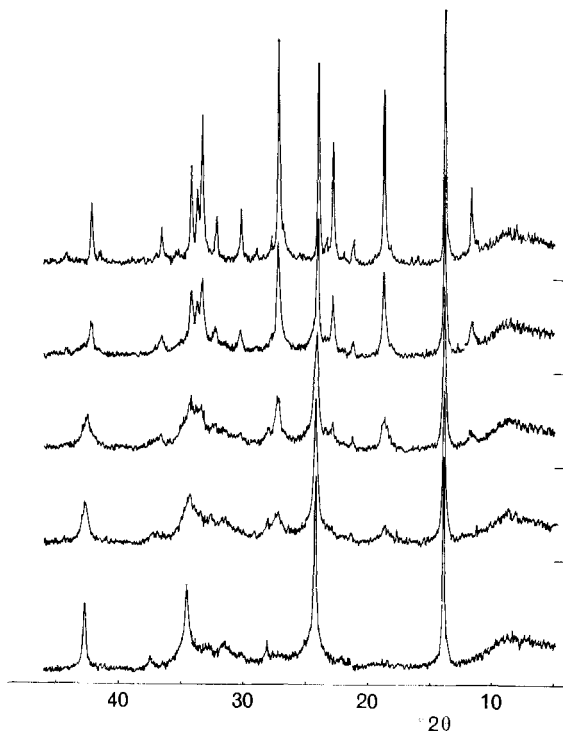


Fig. 2. Powder diffractograms of Losod (top), sodalite (bottom) and intermediate products



Losod did not form from other crystalline phases nor transform into such in the parent system.

On heating Losod with lithium chloride solution, ion exchange occurs accompanied by some contraction of the framework (see 3.5). When Losod is treated 3 days with a solution of 1M LiCl and 0.04M OH<sup>-</sup> at 100°, a transformation to cancrinite-type phase *C* [22] is observed. The same phase *C* can be obtained from Li-exchanged Losod by heating with **BP** hydroxide. In the presence of excess sodium ions the transformation does not occur. No cancrinite is obtained by direct synthesis in the Li-**BP** system. Further increase in alkalinity and time of the treatment lead to crystallization of phase *O* [22], and still more severe conditions (1.1M LiCl, 1.8M OH<sup>-</sup>, 17 days) yield LiK [27]. The structures of the two phases *O* and *K* are still unknown.

When heated in a dry atmosphere up to a temperature of 800° for 24 h, Losod remains crystalline. At 950° it transforms into low-carnegieite.

3.5 *Characterization of Losod.* Losod forms hexagonal platy crystals interpenetrating at an angle of about 60°. Electron micrographs of these rosette-like aggregates, which are remarkably uniform in size and shape, are shown in Figure 3. The larger

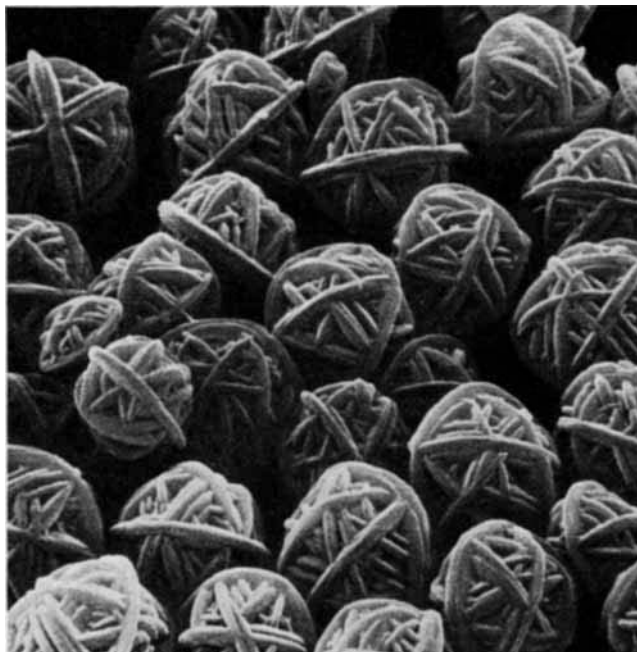


Fig. 3. Scanning electron micrographs of Losod crystals. Magnification 7350x.

the aggregates the more intricate appears the shape of the aggregates. Very thin, single platelets could be detected. Electron diffraction patterns (Fig. 4) confirm the hexagonal symmetry of the crystals.

The  $d$ -spacings and the relative intensities of the powder lines are given in Table 2. The indexing is based on a hexagonal unit cell with the dimensions:

$$a = 12.906 \pm .003 \text{ \AA}, \quad c = 10.541 \pm .003 \text{ \AA}.$$

Table 2. *Interplanar Spacings and Relative Intensities of Losod*

hkl	$d_{\text{obs}}$ \AA	$d_{\text{calc}}$ \AA	$I_{\text{obs}}$ (uncor- rected)	hkl	$d_{\text{obs}}$ \AA	$d_{\text{calc}}$ \AA	$I_{\text{obs}}$ (uncor- rected)
100	11.11	11.18	9	303	–	2.556	4
101	7.64	7.67	44	321	2.492	2.492	2
110	6.43	6.45	100	402	2.469	2.469	16
200	5.59	5.59	13	410	} 2.438	2.439	} 4
201	4.933	4.938	8	114		2.440	
102	4.750	4.767	72	411	–	2.376	2
210	4.221	4.225	11	313	2.328	2.325	1
112	4.077	4.082	3	500	} 2.237	2.235	} 1
211	3.916	3.921	52	214		2.236	
202	3.830	3.834	10	501	} 2.189	2.186	} 6
300	3.723	3.726	78	403		2.187	
301	3.519	3.514	2	330	} 2.150	2.151	} 33
103	3.344	3.352	14	304		2.151	
212	3.293	3.296	96	502	2.058	2.058	5
220	3.226	3.227	10	511	–	1.972	2
310	3.098	3.100	5	205	–	1.973	2
311	} 2.973	2.974	} 21	404	1.919	1.917	5
203		2.975					
400	2.793	2.794	20	503	} 1.888	1.886	} 6
222	–	2.752	5	215		1.886	
401	} 2.700	2.701	} 70	512	1.876	1.876	5
231		2.701					
312	2.673	2.672	29	430	} 1.838	1.838	} 2
004	2.634	2.635	42	324		1.838	
320	–	2.564	} 4	601	–	1.834	3
104	–	2.565		431	305	–	1.835
				423	1.811	1.810	3
						1.810	

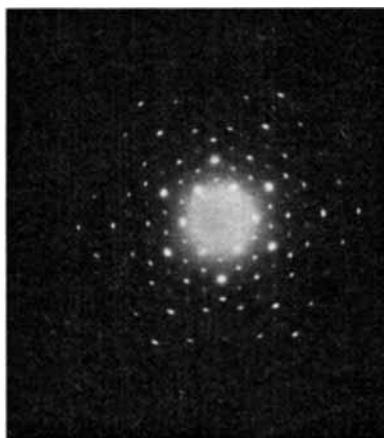
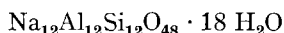


Fig. 4. *Electron diffraction pattern of Losod (125 kV)*

The density of the sample G3 used for structural investigation was  $2.15 \pm .01 \text{ gcm}^{-3}$ . The chemical composition (Table 1) corresponds to a cell contents of  $\text{Na}_{11.5}\text{Al}_{11}\text{Si}_{12}\text{O}_{46} \cdot 19 \text{ H}_2\text{O}$ . This is reasonably close to the idealized formula



(corresponding to a calculated density of  $2.21 \text{ gcm}^{-3}$ ) which was adopted in view of the hexagonal symmetry.

The powder pattern of Losod resembles that of cancrinite (Fig. 5). The lattice constants of cancrinite [28],  $a = 12.75$  and  $c = 5.14 \text{ \AA}$ , also appear to indicate a structural relationship. The  $c$  constant of Losod is about twice that of cancrinite while the  $a$  constants are quite similar. The aluminosilicate framework of cancrinite and related structures can be described in terms of parallel 6-membered rings which are stacked in a way analogous to close packed spheres. The cancrinite structure is thus characterized by a simple AB...stacking sequence, while the ABC...sequence of 6-membered rings is found in sodalite. In the case of Losod the cell dimensions would then indicate a 4-layer sequence ABAC. This leads unequivocally to a hexagonal structure with maximum symmetry  $P6_3/mmc$  and 24 Si + Al atoms per unit cell, in essential agreement with the observed cell contents. The observed cell constants are also in agreement with this proposed structure.

A *Patterson* map was calculated using the available powder data [29]. All T-T vectors of the proposed structure could be identified in this map. Ideal coordinates of the framework atoms were generated with the aid of DLS [30]. Initial refinement of the structure based on  $P6_3/mmc$  did not lead to an  $R(I)$ -value much below 40%. A likely reason for these difficulties is the high symmetry of the model. This would

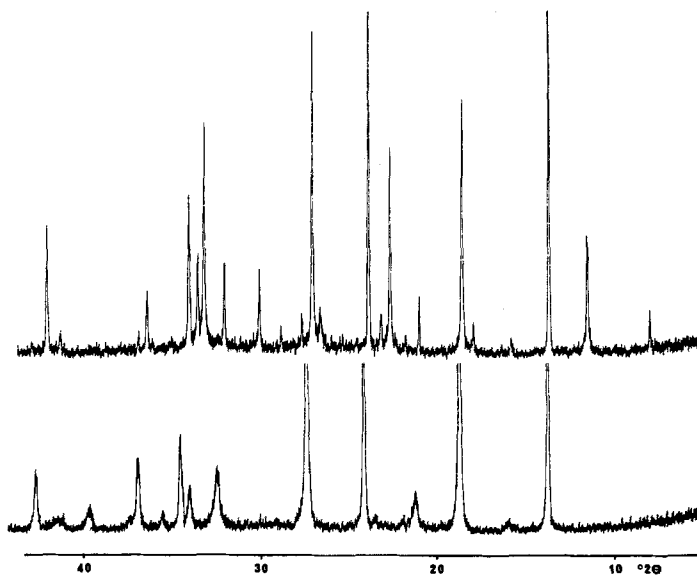


Fig. 5. Powder diffractograms of Losod (top) and phase C (bottom) obtained by transformation from Losod

require planar 6-rings and angles which appear highly improbable. However, the available powder data were insufficient for a structure analysis assuming lower symmetry<sup>1)</sup>.

The atomic coordinates of the model structure of the framework are listed in Table 3. The framework contains two types of cages illustrated in Figure 6. The

Table 3. *Coordinates of the Framework Atoms of Losod*. Model structure calculated by DLS  
Space group  $P6_3/mmc$  T = (Si, Al)

Atom	Position	x	y	z
T1	12i	.242	0	0
T2	12j	.426	.098	$\frac{1}{4}$
O1	12k	.224	.112	-.054
O2	24l	.340	.047	.120
O3	6h	.408	.249	$\frac{1}{4}$
O4	6h	.526	.052	$\frac{1}{4}$

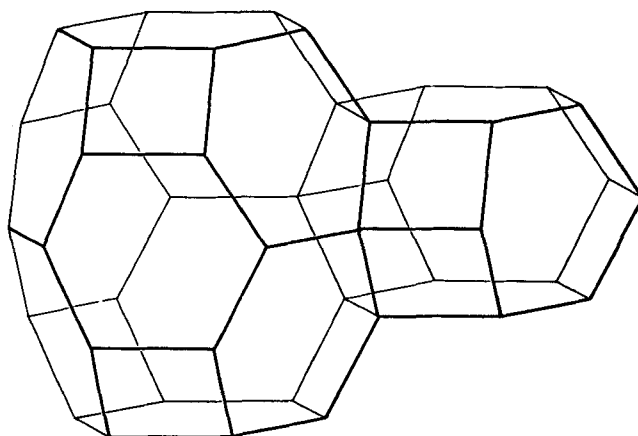


Fig. 6. *The cages in the framework of Losod (only T-atoms shown)*

smaller cancrinite cages consisting of 5 six-rings and 6 four-rings also occur in zeolites *L*, erionite and offretite. The other polyhedron, formed by 11 six-rings and 6 four-rings, has not been observed before. The unit cell of the new phase contains two cancrinite cages and one 17-hedron ('*Losod cage*'). The intracrystalline channels are thus restricted by six-rings as in sodalite and molecules larger than  $H_2O$  and  $CO_2$  are not expected to be sorbed by Losod. The larger volume of the Losod cages, on the other hand, would promise an increased sorption capacity.

Sorption experiments with *n*-hexane and *n*-pentane on dehydrated Losod confirmed the expected exclusion of these molecules. 7.5 wt. percent of carbon dioxide were sorbed at room temperature. The water sorption isotherms at 25 and 49.5° are shown in Figure 7. The samples were activated at about 370°. The shape of the isotherms and the observed hysteresis suggest the presence of non-equivalent water positions.

<sup>1)</sup> Further work on the structure of Losod is in progress.

Displacement of included ions upon dehydration is also a possibility. Although the sorption capacity was slightly lower after the second activation no loss in crystallinity could be observed.

Losod shows a strong selectivity for silver over sodium ions. The calculated selectivity coefficient,  $K = Z_{\text{Ag}} S_{\text{Na}} / S_{\text{Ag}} Z_{\text{Na}}$ , reaches a maximum value of about 2000 ( $Z_{\text{M}}$  and  $S_{\text{M}}$  denote the mol fractions of the ion in the zeolite and in the solution, respectively). Equilibrium was reached within 30 minutes. This high selectivity for silver ions has been observed with other zeolites before [31]. While the fully exchanged silver form showed only a slight contraction of the lattice with respect to the sodium form, a marked contraction was observed on lithium exchange with  $a = 12.39$  and  $c = 10.03 \text{ \AA}$  ( $\pm 0.1 \text{ \AA}$ ). This represents a decrease of  $a$  by 4 percent, of  $c$  by 5 percent, and of the cell volume by 12.5 percent.

The crystallinity of the lithium, silver, and ammonium forms is lost on dehydration at  $350^\circ$ . The reversibility of the lithium exchange has been demonstrated by back-exchange with sodium.

**4. Discussion.** – 4.1 *General.* Reaction mixtures containing bulky quaternary ammonium ions besides sodium have led to the synthesis of a zeolitic species representing a new structure type. The free openings in the aluminosilicate framework of Losod are comparatively small (less than  $3 \text{ \AA}$ ) and yet the sorption capacity for small molecules is relatively large.

It is worth noting that the different organic cations (I–IV) used for Losod syntheses are of such a size as to fill the larger cage of the structure (Fig. 6). However, the organic cations are not incorporated into the zeolite phase. They act as counterions of the hydroxyl ions keeping the aluminate and silicate in solution, *i.e.* in a reactive state. With the aid of these organic bases the ratio of alkali ions to aluminum or silicon can be reduced to any desired level. If the Na/Al ratio is above 1 only previously established phases typical of the Na-system are formed. At Na/Al ratios below 1 crystallization of Losod occurs. The yield of Losod is determined by the total amount of sodium present in the reaction mixture. 98 percent of the sodium ions are thereby used up. The essentially catalytic role of the organic base is further substantiated by the demonstrated re-use of the mother liquor for Losod syntheses after replenishing the consumed inorganic components.

Neither gel nor crystals are formed in these systems in the absence of alkali ions. Systems with organic bases of the type reported here make it possible to control the hydroxide ion concentration independently of the concentration of the cations which are incorporated in the zeolite.

The observations described are not in contradiction to the results obtained using tetramethylammonium [15] and dimethyl-diazonia-bicyclooctane [14]. The charge of the latter cations is much less screened than that of the bases used in the present investigation. The azonia-spiro compounds and neopentyl-trimethyl-ammonium exert a weaker coordinating force, and they are not able to displace water from the hydration sphere of the aluminosilicate anions. Presumably, the aluminosilicates of these cations are soluble because their size is obviously too large in comparison to the density of negative charges in a zeolite framework containing equal amounts of

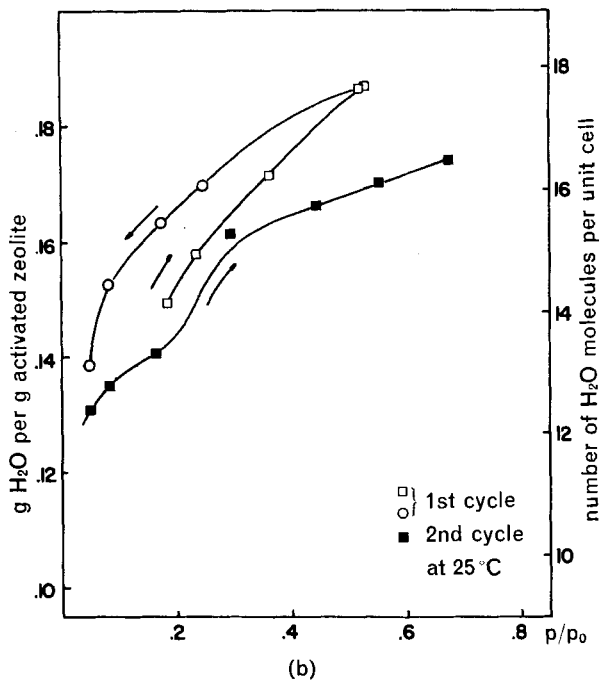
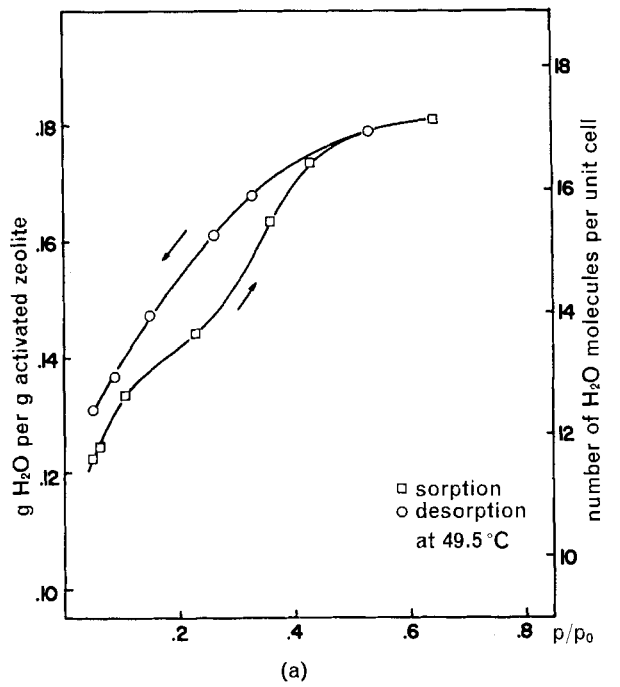


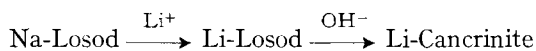
Fig. 7. Water sorption isotherms of Losod at 49.5° (a) and 25° (b)

silicon and aluminum. Silicates of quaternary ammonium ions tend to be much more soluble than the corresponding alkali compounds [32].

Products of high Si/Al ratio have not been observed in the present investigation. The tendency of silicate ions towards polycondensation is very small at the hydroxyl ion concentration examined. The formation of high-silica TMA species reported by *Baerlocher & Meier* [15] appear to have been linked with a decrease of pH caused by partial decomposition of the tetramethylammonium hydroxide at the reaction temperature of 130–180°.

**4.2 Structure and Mechanism of Formation.** The sole crystallization of a particular zeolite type is at least in part controlled by kinetic factors and not so much by free energy differences which are bound to be very small in the case of different but related framework types.

The closely related structures of Losod, sodalite and cancrinite (representing polytypes), the neighbouring crystallization fields of Losod and sodalite (Fig. 1), the occurrence of 'intermediate phases', and the transformation



may indicate the existence of a common precursor species. The 6-membered ring is obviously a possible building unit common to Losod, sodalite and cancrinite. However, many other zeolite frameworks can also be built from 6-membered rings which cannot be specifically associated with the zeolites under consideration. No larger finite units, such as polyhedral cages, can be found which are common to the frameworks of Losod, sodalite and cancrinite. These frameworks can, on the other hand, be thought to consist of infinite sheets. The puckered hexagonal sheets, shown in Figure 8, consist of two layers of 6-membered rings in AB sequence. These sheets can be stacked in many possible ways and the relative orientation of a particular sheet in such a polytypic structure can be readily described in terms of the customary letter symbols, *i.e.* (AB), (BA), (AC), (CA), (BC), or (CB). Of particular interest are the simplest stacking sequences involving 1, 2 and 3 sheets, *i.e.*:

(AB)	cancrinite
(AB) (AC)	Losod (Fig. 8)
(AB) (CA) (BC)	sodalite

(AB) is converted to (BC) by simple translation, to (AC) by rotation in the plane.

The following hypothesis concerning a mechanism of formation of Losod and related phases is based on these sheets and also to some extent on the electron microscopical observations by *Aiello, Barrer & Kerr* [33] of the formation of lamellae during the initial stages of zeolite growth from highly alkaline media. The sheets with adhering cations could be imagined to form quite rapidly upon combining alkali aluminate and silicate solutions. Charges on the sheet originate from tetrahedral aluminum and terminal oxygens. The latter could well be transiently compensated by alkylammonium ions which may stabilize these puckered sheets. These primary polycondensates could form gel-like phases or colloidal solutions which would be amorphous to X-rays. These sheet-like precursors would then condense to three-

dimensional crystallites. Small differences in the conditions could well determine the particular stacking sequence of the sheets. The hypothesis could also serve to explain the observed transformation of Losod to cancrinite under mild conditions, only part of the bonds being broken hydrolytically. Observed pseudomorphs of cancrinite formed from Losod provide evidence in support of this.

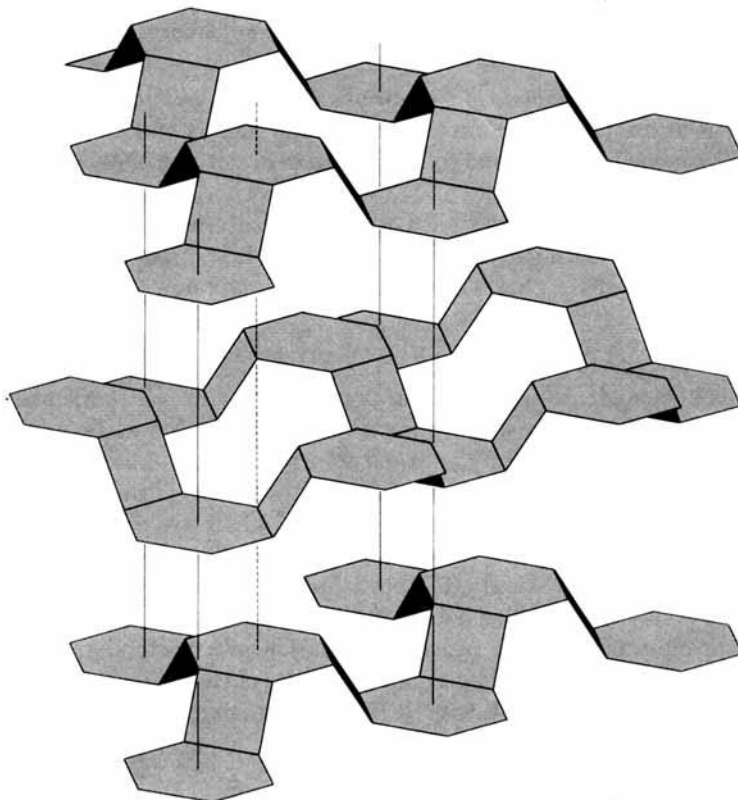


Fig. 8. Stacking of puckered sheets in Losod

We are indebted to Mr. *A. Portmann* and to Mr. *R. Wessicken* for supplying numerous electron micrographs. We also wish to thank Dr. *W. Thoeni* for advance information on the structure. Financial support of this investigation by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* is gratefully acknowledged.

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## 170. Substituent Increments for the $^1\text{H}$ -NMR. Chemical Shifts of the 18- and 19-Methyl Protons of Steroids. Part I: $9\beta$ , $10\alpha$ (*Retro*)-Steroids

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Dedicated to Professor *Pl. A. Plattner* on his 70th birthday

(22. V. 74)

*Summary.* This paper reports 261 substituent increments for the  $^1\text{H}$ -NMR. chemical shifts (solvent:  $\text{CDCl}_3$ ) of the 18- and 19-methyl protons of  $9\beta$ ,  $10\alpha$ (*retro*)-steroids relative to  $5\beta$ ,  $9\beta$ ,  $10\alpha$ ,-androstane. The increments were calculated by a least-squares procedure from 1334 spectra of 759 different steroids.

**1. Introduction.** – Since *Shoolery & Rogers* [1] reported on the application of  $^1\text{H}$ -NMR. spectroscopy to the study of steroids, this technique has proved extremely useful for the elucidation of unknown structures. Especially the fact that the chemical shifts of the angular methyl protons can in many cases be calculated from additive shift increments of the substituents (or of suitably chosen combinations thereof)