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Intercalation of Primary Diamines and Amino Acid in the Layer Structure Oxide $HTiNbO_5$

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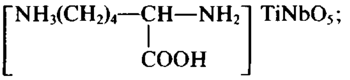
The intercalation of primary diamines in the layer structure $HTiNbO_5$ has been studied. This intercalation is quantitative and reversible: ten compounds have been synthesized corresponding to the general formula $NH_3(CH_2)_nNH_3(TiNbO_5)_2$ with $n = 2$–10 and 12. For each composition, two forms have been observed according to the temperature of synthesis, called low temperature (l.t.) and high temperature (h.t.), respectively. The X-ray diffraction study of these compounds shows that they are orthorhombic, with *a* and *b* parameters close to those of $HTiNbO_5$. The l.t. and h.t. forms differ one from another by the value of the *c* parameter which characterizes the spacing between the $(TiNbO_5)$ layers. The values of the *c* parameters are interpreted in terms of a transversal orientation of the diamine chains with respect to the $(TiNbO_5)$ layers. The transition l.t. $\leftrightarrows$ h.t. is explained by a conformational change of the diamine involving the formation either of gauche bonds or of kinks. The intercalation of an amino acid, lysine, is also quantitative and characterized by the intercalation of one mole per proton leading to the formulation



$$\left[\begin{array}{c} NH_3(CH_2)_4\text{—}\underset{\displaystyle COOH}{\underset{|}{CH}}\text{—}NH_2 \end{array}\right] TiNbO_5;$$

the greater value of the *c* parameter observed for this compound results from the formation of hydrogen bonds between the lysine molecules, which ensure the cohesion of the structure.

Introduction

Intercalation of organic compounds and especially of alkylammonium ions in oxides with a layer structure has been the purpose of several studies these last years in order to understand the structure of monomolecular and bimolecular films involved in biological membranes. In the same way, accurate data can be obtained from the study of such solids in the practical problems of dispersions and emulsions. Most of the intercalation studies of alkylammonium ions have been focused on oxides built up from tetrahedral layers, i.e., silicates (*1–4*) and phosphates (*5–7*). On the contrary, little is known about intercalation of alkylammines in oxides built up from octahedral layers. In this respect titanates and titanoniobates with a layer structure (*8–12*) are interesting candidates since they are easily synthesized and exhibit a rather simple structure for the interpretation of the models. In order to intercalate amines, the best method consists in using the protonic oxide as a starting material. Our attention was re-

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cently focused on the oxide $HTiNbO_5$ (*13*) synthesized by ion exchange in acidic medium on $KTiNbO_5$. The structure of this compound (*14*) is built up from octahedral layers whose cohesion is ensured by short hydrogen bonds (Fig. 1). In spite of these rather strong hydrogen bonds, $HTiNbO_5$ can be considered as the best titanoniobate for intercalation since it can intercalate one molecule of monoalkylamine per proton (*15*), whatever the size of the amine may be and in a wide range of pK_A down to 6, whereas other titanates do not intercalate amines with pK_A smaller than 9. Moreover the knowledge of the intercalation of diamines in layer oxides is rather poor although it could yield information about the orientation of the alkyl chains in those compounds. Thus, the present work deals with the intercalation of diamines in the oxide $HTiNbO_5$.

Experimental Methods

The compound $HTiNbO_5$ whose preparation has already been described (*13*) was placed in an appropriate diamine solution and stirred for about 20 hr. The exchange reaction was carried out with diluted diamine either in water or in a mixture—50% water and 50% ethanol. The synthesis is similar to that described for monoamine intercalation (*15–16*).

The intercalation compounds were generally obtained in the form of a very thin powder and were sometimes difficult to recover. In order to separate the solid from the liquid phase, it was necessary to centri-

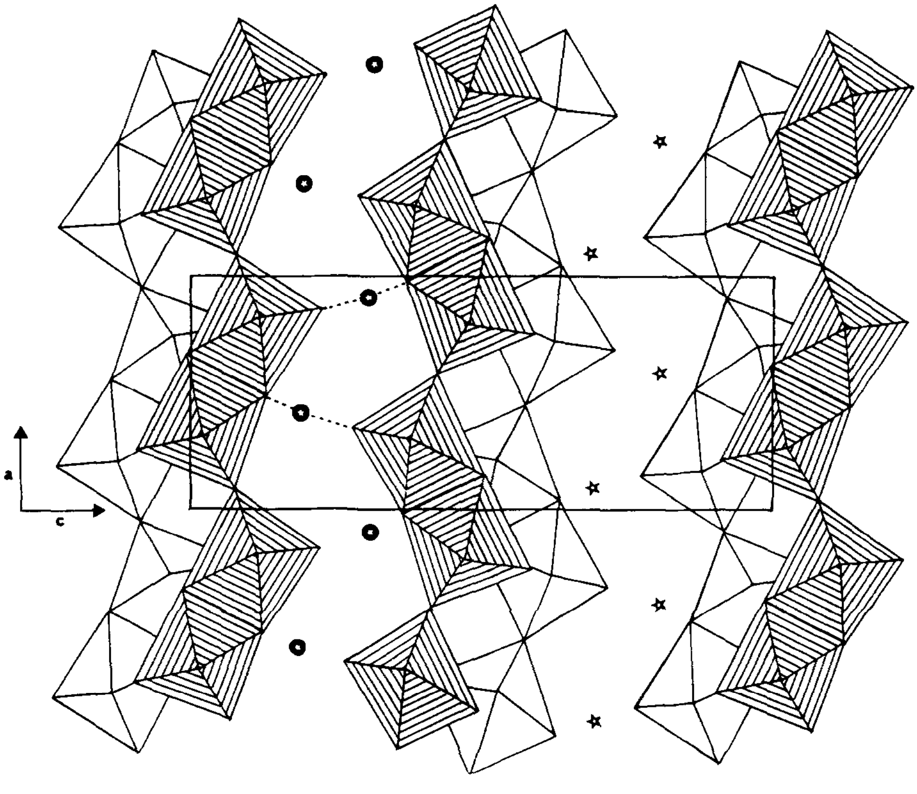


FIG. 1. Projection of $HTiNbO_5$ structure on to (010).

fuge the mixture. The resulting compounds were washed with a mixture of water and ethanol and dried in air.

The compounds were identified by X-ray diffraction using a Guinier–De Wolff camera; the cell parameters were determined from the patterns taken with an X-ray powder diffractometer using Cu$K\alpha$ radiation. The cell parameters were refined using a least-squares method on a total number of observed reflexions ranging from 13 to 27 according to the nature of the product. The composition of the final products was determined by microanalyses of N, C, and H and was confirmed. These results were confirmed by thermogravimetric measurements, using a Setaram microbalance with a temperature climbing speed of 150°C hr^{-1}; one must point out that for these conditions the decomposition appears to take place in only one step.

Results and Discussion

The intercalation of primary diamines $NH_2(CH_2)_nNH_2$ was investigated for the members ranging from $n = 2$ to $n = 12$, except the member $n = 11$ which was not available. Whatever the nature of the amine may be, one always observes the same amount of intercalated amine, i.e., half a mole per mole of $HTiNbO_5$. This is in agreement with the complete neutralization of the protonic function of $HTiNbO_5$ according to the reaction:

$$2HTiNbO_5 + NH_2(CH_2)_nNH_2 \rightarrow NH_3(CH_2)_nNH_3(TiNbO_5)_2$$

It must be pointed out that the presence of water is necessary for intercalation, owing to the acido-basic character of the reaction. Moreover the reaction is reversible: action of an acid on the intercalated compound leads again to $HTiNbO_5$.

The X-ray diffraction study of the intercalated compounds shows an original feature: for the same diamine two forms can be obtained at room temperature, either as pure phases or as mixtures depending on the temperature of preparation. A study with a Guinier–Lenne camera allowed us to isolate these two forms, called low temperature (l.t.) and high temperature (h.t.) forms. Table I, which describes the conditions of preparation of these compounds and their stability, shows that most of the l.t. forms can be isolated by intercalation at 4°C and that these forms are stable at room temperature. In return, only four l.t. forms could be isolated (n = 3, 5, 7, 8) by intercalating the amines at room temperature. The temperature corresponding to the transition l.t. $\rightleftarrows$ h.t. ranges from 45 to 110°C. This transition is reversible. However some h.t. forms can be isolated by cooling the compounds to room temperature. This phenomenon has been observed for n = 3–5. It should be pointed out that the h.t. form is metastable at room temperature: for instance, for n = 5, the h.t. form is easily

TABLE I

SYNTHESIS TEMPERATURE OF LOW- AND HIGH-TEMPERATURE FORMS

Synthesis temperature (°C)	$H_3N(CH_2)_nNH_3(TiNbO_5)_2$									
	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$	$n = 9$	$n = 10$	$n = 12$
l.t. form	4	r.t.[a]	4	r.t.	4	r.t.	r.t.	4	4 Mixture	4
h.t. form	70	60	80	65	85	70	110	80	80	Mixture

[a] r.t. = room temperature.

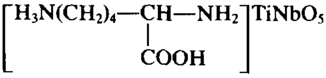
isolated at room temperature by cooling the compound from 65 to 20°C, but then it transforms slowly into the l.t. form by aging and finally disappears after 1 month at room temperature.

Both forms are orthorhombic (Table II). The *a* and *b* parameters which characterize the $(TiNbO_5)$ layers are very similar for both forms, whereas the *c* parameters which correspond to the spacing of the layers are very different for the two forms: the l.t. forms exhibit a much higher *c* parameter than the h.t. forms. It must be noticed that the intercalation of diamine is sometimes accompanied by a change of space group (Table II); this is easily explained by a gliding of the $(TiNbO_5)$ layer with respect to the *Pnma* group of $HTiNbO_5$.

The drastic contraction of the *c* parameter obtained by raising the temperature suggests that this transition, which is reversible, corresponds to a change of conformation of the diamine, as already observed for intercalation of monoamines in different silicates (*4*). This point of view will be discussed further. In this respect the *trans*-conformation of the chains should be favored at low temperature. Figure 2 presents the evolution of the *c* parameter of the l.t. form versus the chain length of the all-*trans* diamine, compared to the results obtained for the monoalkylamines (*15*).

TABLE II

CRYSTALLOGRAPHIC DATA OF $[H_2N(CH_2)_nNH_2]_{0.5}HTiNbO_5$ AND [lysine H]TiNbO₅

		a	*b*	*c*	
$[H_2NNH_2]_{0.5}HTiNbO_5$ (*16*)		6.491(6)	3.768(7)	21.30(2)	*Pnma*
$[H_2N(CH_2)_2NH_2]_{0.5}HTiNbO_5$ (*16*)	l.t.			23.60	M[a]
	h.t.	6.534(4)	3.777(3)	20.80(1)	*Pnma*
$[H_2N(CH_2)_3NH_2]_{0.5}HTiNbO_5$	l.t.	6.466(10)	3.782(6)	25.57(51)	[b]
	h.t.	6.444(20)	3.802(6)	22.67(13)	[b]
$[H_2N(CH_2)_4NH_2]_{0.5}HTiNbO_5$	l.t.	6.458(14)	3.801(6)	27.39(5)	*Pnma*
	h.t.	6.433(8)	3.804(4)	24.40(2)	*Pnma*
$[H_2N(CH_2)_5NH_2]_{0.5}HTiNbO_5$	l.t.	6.435(9)	3.806(9)	29.37(7)	[b]
	h.t.	6.424(4)	3.816(2)	26.97(2)	*Pnma*
$[H_2N(CH_2)_6NH_2]_{0.5}HTiNbO_5$	l.t.	6.472(4)	3.819(3)	32.10(6)	*Pnma*
				28.21	M
$[H_2N(CH_2)_7NH_2]_{0.5}HTiNbO_5$	l.t.	6.436(7)	3.805(5)	34.41(3)	[c]
	h.t.			32.00	
$[H_2N(CH_2)_8NH_2]_{0.5}HTiNbO_5$	l.t.	6.453(5)	3.784(5)	35.12(6)	*Pnma*
	h.t.			31.64	
$[H_2N(CH_2)_9NH_2]_{0.5}HTiNbO_5$	l.t.	6.483(33)	3.808(7)	38.50(13)	[b]
	h.t.			34.40	M
$[H_2N(CH_2)_{10}NH_2]_{0.5}HTiNbO_5$	l.t.			40.30	
	h.t.			35.60	
$[H_2N(CH_2)_{12}NH_2]_{0.5}HTiNbO_5$	l.t.	6.445(17)	3.799(5)	47.80(24)	[b]
	h.t.			38.60	M
 $\left[H_3N(CH_2)_4{-}\underset{\displaystyle COOH}{\underset{\mid}{CH}}{-}NH_2\right]TiNbO_5$		6.487(34)	3.804(6)	47.32(11)	[b]

[a] M—the mixtures of l.t. and h.t. forms.

[b] Extra lines with respect to *Pnma*, corresponding to $0kl$, $k + 1 = 2n + 1$.

[c] Extra lines with respect to *Pnma*, corresponding to $kh0$, $h = 2n + 1$.

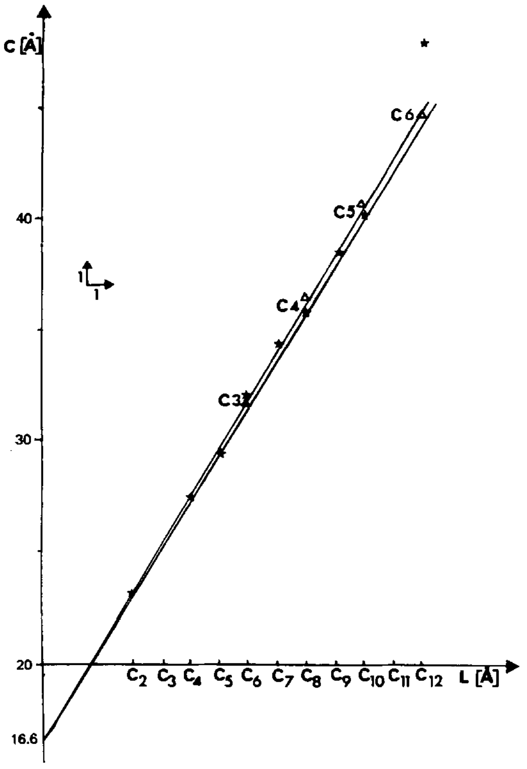


FIG. 2. Evolution of the *c* parameter of the oxides $[NH_3(CH_2)_nNH_3]_{0.5}TiNbO_5$ (l.t. form ★) as a function of the mean lengths of the *n* chains. Comparison with the evolution of the *c* parameter of the oxides ($NH_3C_nH_{2n+1}$)$TiNbO_5$ (△) (*15*).

One can see that the intercalation for monoalkylamines involves a drastic expansion of the *c* parameter as the chain length increases. It should be pointed out that the *c* values of the l.t. forms are close to those of monoamine intercalates whose length corresponds to a half the number of carbon atoms. This is easily explained by a transversal orientation of the diamine chains in the intercalated oxides as shown for example by comparing the hypothetical structure of the hexyldiammonium l.t. form (see Fig. 3a) to that of the propylmonoammonium oxide (see Fig. 3b). Moreover, if it is supposed that the NH_3^+ ends are located at the same distance from the oxide layer, in the same positions as NH_4^+ or Rb^+ in NH_4TiNbO_5 or $RbTiNbO_5$ (*16*), one observes that the ($TiNbO_5$) layer spacing observed for $n = 5$–7 and 12 fits exactly with the length of the *trans* diamine chain (see Fig. 3a). In return the layer spacings observed for the other members do not coincide so accurately with such a position of the NH_3^+ end: the low *n* members ($n = 2$–4) exhibit an interlayer spacing greater than that required by placing the NH_3^+ ends of the $NH_3^+(CH_2)_nNH_3^+$ ions in the positions previously observed for Rb^+ or NH_4^+, whereas the contrary is observed for high *n* members ($n = 8$–10). This cannot be only explained by a translation of the ($TiNbO_5$) layer with respect one to the other, since some members ($n = 4, 8$) do not exhibit a change of space group with respect to $HTiNbO_5$ or $RbTiNbO_5$. Thus, it appears that the ends of the $NH_3^+(CH_2)_nNH_3^+$ ions are not exactly located at the Rb^+ or NH_4^+ positions; the result is that the small diamine chains ($n = 2$–4) may tend to be oriented in a direction almost perpendicular to the plane of the ($TiNbO_5$) layers as shown for $n = 4$ (see Fig. 4), whereas the longer diamine chains ($n = 8$–10) would tend to present one or several gauche bonds, leading to a slightly oblique orientation of the chain with respect to the oxide layers as shown for $n = 8$ (see Fig. 5). The presence of a gauche bond, stable at room temperature, has indeed been observed for alkylammonium ions in the cadmium layer chloride structure $(C_{10}H_{21}NH_3)_2CdCl_4$ (*17*).

In order to explain the contraction of the *c* parameters observed for the h.t. forms three hypotheses need to be considered successively:

(i) translation of one layer out of two along *a* or *b* in order to accommodate to the smaller spacing of the ($TiNbO_5$) layers;

(ii) tilting of the diamine chain with respect to the plane of the ($TiNbO_5$) layers; and

(iii) conformational changes of the diamine chain involving either isolated

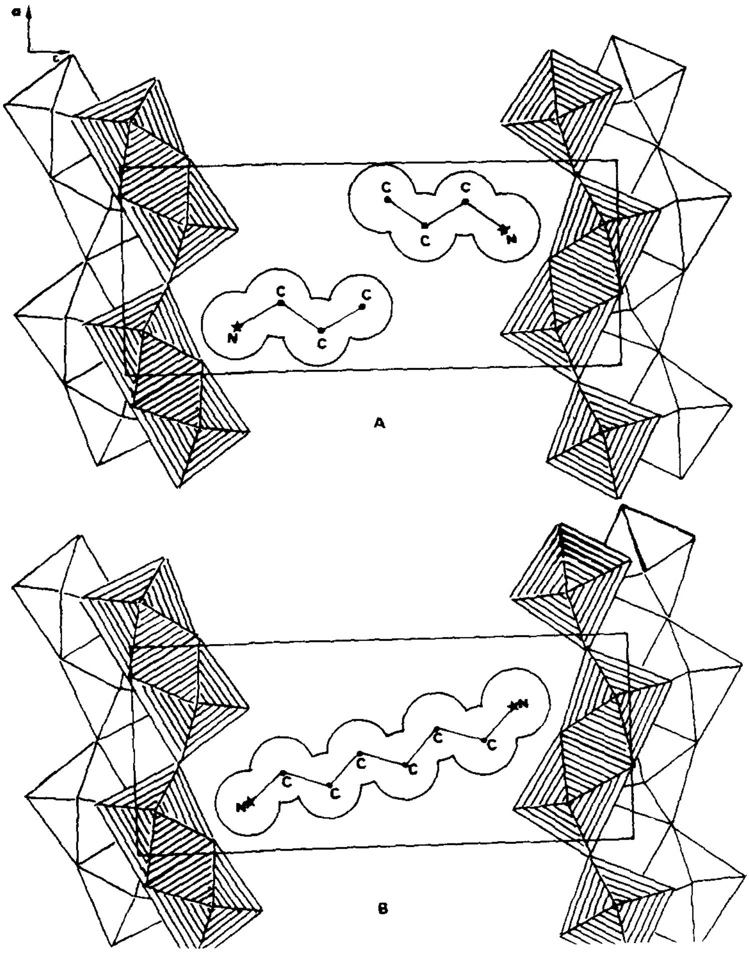


FIG. 3. Hypothetical structure of the hexyldiammonium (l.t. form) and propyl monoammonium oxides (b). The position of the NH_3^+ ends coincide exactly with the Rb^+ or NH_4^+ positions (★) in $RbTiNbO_5$ or NH_4TiNbO_5.

gauche bonds or regular sequences of *trans* and gauche bonds called kinks (*18*).

The first hypothesis which would involve a change of the space group can be ruled out. For some intercalated oxides ($n = 4$) no change of the *Pnma* space group is observed in spite of the contraction of *c*. The reversibility of the transformation l.t. ⇄ h.t. at rather low temperatures 60–100°C mitigates against the second hypothesis which would involve more energy due to the migration of the NH_3^+ ends. Thus a conformational change for the diamine chain, involving a change of the *c* parameter, appears as the most probable. The endothermic peaks observed by the thermodifferential analysis are in agreement with this point of view. Moreover it must be pointed out that the difference between the spacings of the layers corresponding to the l.t.–h.t. transformation (Table II) is 1.2 Å (for $n = 5$, 7), 1.9–2.35 (for $n = 6$, 9, 10), and 4.6 (for $n = 12$). This is in agreement with the formation of one kink, or two kinks, or four

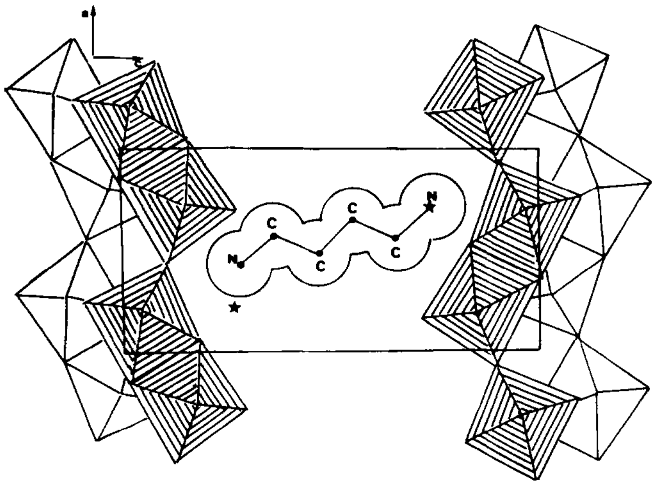


FIG. 4. Possible orientation for the l.t. form of butyldiammonium oxide. The position of the NH_3^+ ends does not coincide with Rb^+ or NH_4^+ positions (★).

kinks in the diamine chain, respectively; it has indeed previously been observed (*19*) that the formation of a kink in an alkyl chain shortens it by 0.9 to 1.2 Å. Figure 6 shows as an example the hypothetical structure of the h.t. form of the C_5 diammonium oxide characterized by a kink. The fact that the difference between $c_{h.t.}$ and $c_{l.t.}$ is not always a multiple of 0.9–1.2 Å (for instance for $n = 4$) lead us to believe that the formation of kinks is not a rule in these compounds but that several gauche bonds may happen in the diamine chains which will more or less shorten the diamine chain according to their relative positions in the chain.

Particular attention must be drawn on the h.t. form of ethylene diamine compound (*n*

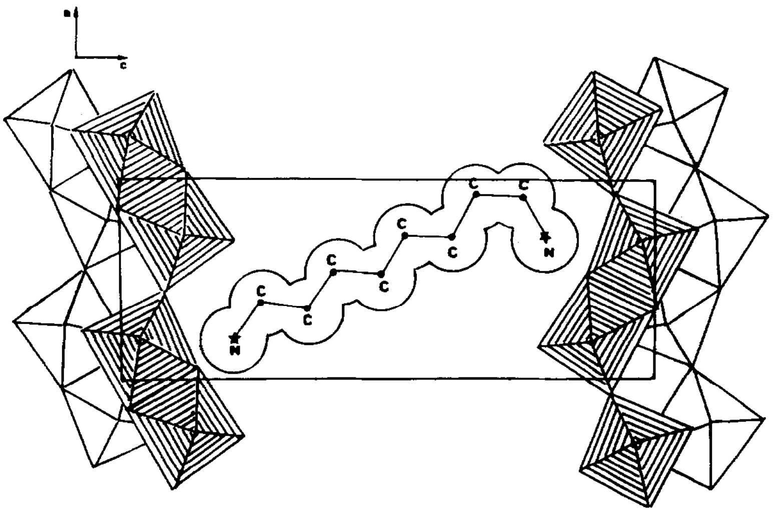


FIG. 5. Possible orientation for the l.t. form of octyldiammonium oxide with a gauche bond. The position of the NH_3^+ ends coincide exactly with the Rb^+ or NH_4^+ positions (★).

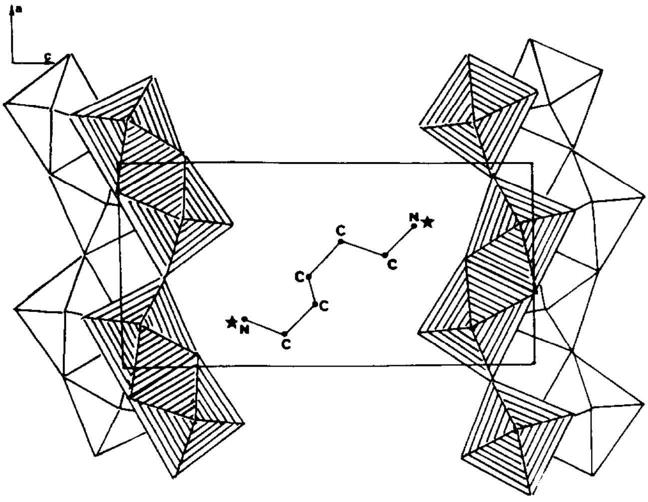
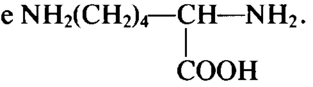


FIG. 6. Hypothetical orientation for the h.t. form of pentyldiammonium oxide.

= 2) whose *c* parameter (20.8 Å) is greater than that expected by considering the length of the diamine chain (3.8 Å). Thus it appears that in the case of ethylene diamine the NH_3^+ ends are displaced with respect to the positions of Rb^+ or NH_4^+ in the l.t. form (see Fig. 7a) as well as in the h.t. form (Fig. 7b).

The intercalation of amino acids in $HTiNbO_5$ seems to be more difficult owing to the low pK_A values of these compounds. However, an interesting result has been obtained for lysine



$$NH_2(CH_2)_4\text{—}\underset{\displaystyle COOH}{\underset{|}{CH}}\text{—}NH_2.$$

The intercalation of this compound at room temperature is similar to that observed for monoamines: an intercalation of 1 mole per proton is observed. The *c* parameter of the lysine compound (c = 47.3 Å) is much greater than that of the C_6 diammonium compound (c = 32.1 Å) although the two alkyl chains exhibit rather similar lengths. From a comparison with the monoalkylammonium compounds it appears that the spacing of the $TiNbO_5$ layers is closer to that observed for the C_6 monoammonium oxide (c = 44.8 Å). Nevertheless, the lysine compound *c* parameter is greater than that

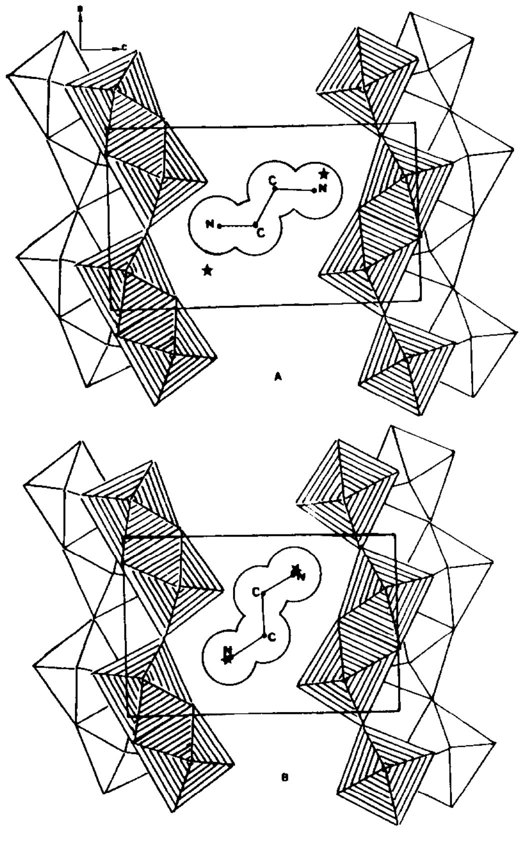


FIG. 7. Possible orientation for the h.t. (a) and l.t. (b) forms of ethylene diammonium oxide (★ Rb^+ or NH_4^+ positions in $RbTiNbO_5$ or NH_4TiNbO_5).

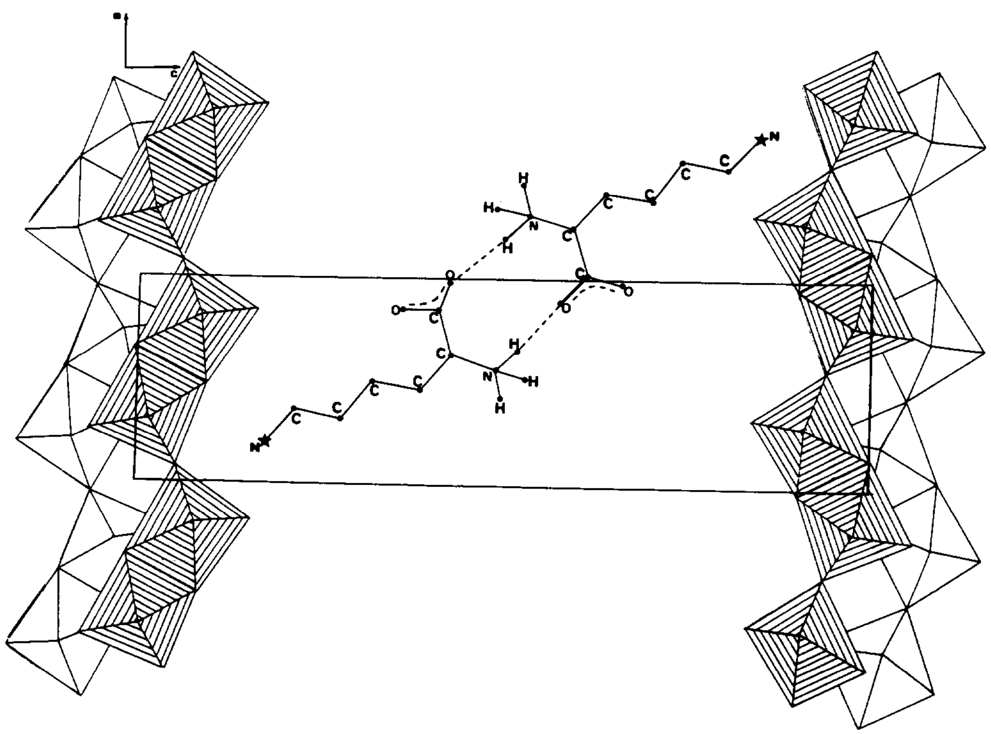
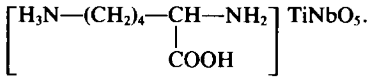


FIG. 8. The possible orientation of lysine in the oxide



$$\left[\begin{array}{c}H_3N{-}(CH_2)_4{-}\underset{\displaystyle COOH}{\underset{|}{CH}}{-}NH_2\end{array}\right]TiNbO_5.$$

of the C_6 monoammonium compound. As a consequence, the structural behavior of lysine can also be explained by a transversal orientation of the amino acid chain with respect to the $TiNbO_5$ layers; but only one end of the chain forms a cation NH_3^+— while the other end involving the carboxylic function would form hydrogen bonds with another lysine chain (see Fig. 8). Thus it appears that the cohesion of the lysine structure would be ensured by hydrogen bond explaining the greater *c* parameter observed for this compound.

Finally, a particular property of some diamines ($n = 3, 4$) and of lysine must be emphasized: their ability to form gels during their synthesis. This can be compared to the behavior of the zirconium phosphate system (*20*). Moreover by drying these gels, compounds are be obtained in the form of foils which look like polymers. Further investigation will be necessary to understand this phenomenon. A detailed infrared spectroscopic study will be necessary to understand the conformational problems of diamines in those oxides. The intercalation of branched primary diamines and of secondary and tertiary diamines will be carried out in order to understand the interaction of the diamines with the ($TiNbO_5$) layers.

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