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Intercalation of Primary Diamines in the Lamellar Niobate $HNb_3O_8 \cdot H_2O$

R. NEDJAR, M. M. BOREL, AND B. RAVEAU

Laboratoire CRISMAT, U.A. 251 associé au CNRS, ISMRa-Université, Bd du Maréchal Juin, 14032 Caen Cedex, France

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The intercalation of alkyl diamines in the protonic oxide $HNb_3O_8 \cdot H_2O$ is quantitative for the diamines $H_2N-(CH_2)_n-NH_2$ with n ranging from 2 to 10. All the intercalated oxides $[H_3N-(CH_2)_n-NH_3]_{0.5}Nb_3O_8 \cdot yH_2O$ are hydrated at room temperature; they can be easily and reversibly dehydrated to the oxides $[H_3N-(CH_2)_n-NH_3]_{0.5}Nb_3O_8$. The structural behavior of those compounds is compared to that of the alkyldiammonium titanoniobates $[H_3N-(CH_2)_n-NH_3]_{0.5}TiNbO_5$. An interpretation of their structural properties is given which takes into account the tendency of amines to assume an orientation transverse to oxide layers, the conformation of the amine chains, and the tendency to form dense organic layers. © 1987 Academic Press, Inc.

Introduction

Intercalation of monoalkyl amines in lamellar oxides has been the subject of several publications dealing with tetrahedral layers (*1–7*) and octahedral layers (*8–12*). It was recently shown that the protonic titanates and titanoniobates are potential materials for amine intercalation. However, those oxides exhibit many differences which are not yet well understood. For instance it is worth pointing out that the amount of intercalated amine increases with niobium content: $H_2Ti_4O_9 \cdot nH_2O$ (*8*) and $H_3Ti_5NbO_{14} \cdot H_2O$ (*9*) are characterized by a partial neutralization of their protonic functions by amine, whereas a quantitative intercalation of monoalkyl amines has been observed for $HTi_2NbO_7 \cdot H_2O$ (*10*), $HTiNbO_5$ (*11*) and $HNb_3O_8 \cdot H_2O$ (*12*). Moreover, the niobates form hydrates $RNH_3Nb_3O_8 \cdot yH_2O$ at room temperature, whereas only anhydrous phases RNH_3TiNbO_5 are synthesized for the titanoniobates. Comparison of the anhydrous phases $RNH_3Nb_3O_8$ and RNH_3TiNbO_5 shows that both exhibit a transverse orientation of the amine chains with respect to their octahedral layers but that they differ by the fact the chains are interpenetrated in $RNH_3Nb_3O_8$ and not in RNH_3TiNbO_5. Few results have been obtained for the intercalation of diamines in those compounds except for $HTiNbO_5$ (*13*). Thus the present work deals with the intercalation of primary diamines in the niobate $HNb_3O_8 \cdot H_2O$ and compares it to that observed in $HTiNbO_5$.

Experimental

The method of intercalation of diamines in the oxide $HNb_3O_8 \cdot H_2O$ is similar to that

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described previously for monoamines (*12*): 1.5 g of $HNb_3O_8 \cdot H_2O$ was suspended in the form of thin solid particles in 100 ml of a diamine solution stirred for 1 hr and then left in contact for 3 days. It was necessary, however, to use a different solution for diamine in order to avoid the formation of gels: ethanol was added to the diamine aqueous solution, and the concentration of diamines was much smaller than in solutions of monoamines: 10 ml of diamine was added to 100 ml of a mixture of 50% water and 50% ethanol. After filtration all the intercalated oxides were washed with a mixture of water and ethanol at 50% water and then dried in air at room temperature.

Initial characterization was by X-ray powder diffraction recorded with a Philips powder diffractometer using CuK_α radiation.

Chemical analysis was performed on carbon, hydrogen, and nitrogen by the method of Dumas.

The composition was also confirmed by thermogravimetric analysis by means of a Setaram microbalance.

Results and Discussion

Intercalation of diamines $H_2N(CH_2)_nNH_2$ was carried out for *n* ranging from 2 to 10. Whatever the *n* value, a quantitative intercalation was observed according to the equation

$$H_2N(CH_2)_nNH_2 + 2HNb_3O_8 \cdot H_2O \xrightarrow[C_2H_5OH]{H_2O} 2[H_3N\text{-}(CH_2)_n\text{-}NH_3]_{0.5}Nb_3O_8 \cdot yH_2O$$

This reaction is reversible: $HNb_3O_8 \cdot H_2O$ was obtained by action of an acid solution on the intercalated oxides.

$HNb_3O_8 \cdot H_2O$ differs from $HTiNbO_5$ in that all the intercalated oxides are hydrated at room temperature with a variable number of H_2O molecules ranging from 1 to 2 per formula $[H_3N(CH_2)_nNH_3]_{0.5}Nb_3O_8$. Moreover, three of them, *n* = 7, 9, 10, exhibit two hydrates. This peculiar ten-

TABLE I

SYNTHESIS TEMPERATURES OF THE DIFFERENT HYDRATES FROM SPECTRA OF THE GUINIER LENNE CAMERA $[H_3N(CH_2)_nNH_3]_{0.5}Nb_3O_8 \cdot yH_2O$

yH_2O	*n* = 2	*n* = 3	*n* = 4	*n* = 5	*n* = 6	*n* = 7	*n* = 8	*n* = 9	*n* = 10
$2H_2O$				*RT* → 60°C Isolated		*RT* → 60°C Isolated	*RT* → 50°C Isolated	*RT* Not isolated Mixture	
$1.5H_2O$		*RT* → 50°C Isolated	*RT* → 50°C Isolated		*RT* → 80°C Isolated				*RT* → 60°C Isolated
$1H_2O$	*RT* → 80°C Isolated Not indexed					60°C → 140°C Isolated	50°C → 70°C Not isolated	30°C → 80°C Isolated	60°C → 100°C Isolated
Anhydrous	80°C → 240°C Isolated	50°C → 240°C Isolated	50°C → 250°C Isolated	60°C → 240°C Isolated	80°C → 200°C Not isolated	140°C → 270°C Not isolated	50°C → 200°C Isolated	80°C → 190°C Not isolated	100°C → 200°C Not isolated

dency to hydration of those niobates, as well as of monoammonium oxides and of diammonium compounds, with respect to other titanoniobates and especially with respect to $H_3NRTiNbO_5$ and $[H_3N(CH_2)_nNH_3]_{0.5}TiNbO_5$, could be due to their greater *a* parameter (~9 Å versus ~6.5 Å in $ATiNbO_5$ oxides), which induces a greater spacing of the amine chains along *a*.

The thermolysis of those intercalated oxides was controlled by thermogravimetric and thermodifferential analysis to isolate the anhydrous phases. All the hydrates decompose into anhydrous oxides $[H_3N(CH_2)_nNH_3]_{0.5}Nb_3O_8$ without any destruction of the structure.

The dehydration starts around 60°C for all members of the series except for $n = 3$ and $n = 9$. These latter oxides exhibit unstable hydrates at room temperature whose water content close to $y = 2$ could not be well established owing to their decomposition into the monohydrates. In all cases the final dehydration is characterized by an endothermic peak at temperatures ranging from 100 to 225°C (Table I). It is worth pointing out that the anhydrous phases corresponding to $n = 3$, 4, 5, 7, 8 are stable at room temperature and are only very slowly rehydrated by atmospheric moisture. In contrast, the anhydrous phases corresponding to $n = 6$, 9, 10 are unstable at room temperature: they absorb atmospheric water, giving the initial hydrates (Table II).

All the intercalated oxides have been indexed in an orthorhombic cell (Table II) with *a* and *c* parameters close to those of $HNb_3O_8 \cdot H_2O$, in agreement with the fact that the $[Nb_3O_8]$ layers have not been destroyed during the reaction. The measured

TABLE II

CRYSTALLOGRAPHIC DATA OF COMPOUNDS $[H_3N(CH_2)_nNH_3]_{0.5}Nb_3O_8 \cdot yH_2O$

	a (Å)	*b* (Å)	*c* (Å)	d_{calc}	d_{obs}	Δm (calc %)	Δm (obs %)
$[NH_3(CH_2)_2NH_3]_{0.5}Nb_3O_8 \cdot 1H_2O$		~27.00			3.43	12.50	12.01
$[NH_3(CH_2)_3NH_3]_{0.5}Nb_3O_8 \cdot 1.5H_2O$	8.945(15)	30.428(54)	3.798(4)	3.01	2.94	15.47	15.20
$[NH_3(CH_2)_4NH_3]_{0.5}Nb_3O_8 \cdot 1.5H_2O$	8.942(13)	30.776(43)	3.817(3)	3.03	3.27	16.70	17.20
$[NH_3(CH_2)_5NH_3]_{0.5}Nb_3O_8 \cdot 2H_2O$	8.928(19)	33.538(58)	3.804(6)	2.88	2.92	19.40	19.22
$[NH_3(CH_2)_6NH_3]_{0.5}Nb_3O_8 \cdot 1.5H_2O$	8.975(15)	34.231(53)	3.804(4)	2.80	2.75	19.08	19.46
$[NH_3(CH_2)_7NH_3]_{0.5}Nb_3O_8 \cdot 2H_2O$	9.000(32)	37.686(50)	3.788(4)	2.63	2.72	21.63	21.74
$[NH_3(CH_2)_7NH_3]_{0.5}Nb_3O_8 \cdot 1H_2O$	8.886(11)	33.261(60)	3.811(4)	2.89	2.94	18.74	16.70
$[NH_3(CH_2)_8NH_3]_{0.5}Nb_3O_8 \cdot 2H_2O$	9.034(15)	39.843(46)	3.793(5)	2.50	2.33	22.68	23.25
$[NH_3(CH_2)_9NH_3]_{0.5}Nb_3O_8 \cdot 2H_2O$		~44.					
$[NH_3(CH_2)_9NH_3]_{0.5}Nb_3O_8 \cdot 1H_2O$	9.054(13)	37.016(59)	3.790(3)	2.64	2.64	21.00	21.42
$[NH_3(CH_2)_{10}NH_3]_{0.5}Nb_3O_8 \cdot 1.5H_2O$	8.967(12)	40.410(87)	3.801(4)	2.51	2.632	22.76	22.76
$[NH_3(CH_2)_{10}NH_3]_{0.5}Nb_3O_8 \cdot 1H_2O$	8.976(8)	37.483(36)	3.792(3)				
$[NH_3(CH_2)_2NH_3]_{0.5}Nb_3O_8$	9.26(2)	23.202(20)	3.784(9)	3.57	3.51	8.91	8.95
$[NH_3(CH_2)_3NH_3]_{0.5}Nb_3O_8$	8.974(12)	26.011(32)	3.796(3)	3.33	3.42	10.34	13.30
$[NH_3(CH_2)_4NH_3]_{0.5}Nb_3O_8$	9.055(5)	26.175(15)	3.806(1)	3.33	3.39	11.73	11.9
$[NH_3(CH_2)_5NH_3]_{0.5}Nb_3O_8$	9.000(3)	27.143(38)	3.806(4)	3.28	3.38	13.07	14.22
$[NH_3(CH_2)_6NH_{30.5}Nb_3O_8$	9.000	28.40	3.800				
$[NH_3(CH_2)_7NH_3]_{0.5}Nb_3O_8$		~30.					
$[NH_3(CH_2)_8NH_3]_{0.5}Nb_3O_8$	9.099(19)	30.612(44)	3.803(6)	3.01	3.04	16.88	21.6
$[NH_3(CH_2)_9NH_3]_{0.5}Nb_3O_8$	9.00	34.00	3.80				
$[NH_3(CH_2)_{10}NH_3]_{0.5}Nb_3O_8$	9.00	35.1	3.80				

Note. d = density; Δm = loss of weight.

densities as well as the loss in weight confirm the composition deduced from the chemical analysis. The *b* parameter which characterizes the spacing of the $[Nb_3O_8]$ layers exhibits a behavior different from that observed for *c* in the case of the diammonium titanoniobates $[H_3N(CH_2)_nNH_3]_{0.5}TiNbO_5$.

The comparison of those *b* and *c* parameters as a function of length *L* of the diamine chain, assuming an all *trans* configuration, is shown in Fig. 1. Contrary to the two forms of $[H_3N(CH_2)_nNH_3]_{0.5}TiNbO_5$ (low and high temperature), the oxides $[H_3N(CH_2)_nNH_3]_{0.5}Nb_3O_8$ and $[H_3N(CH_2)_nNH_3]_{0.5}Nb_3O_8 \cdot yH_2O$ do not exhibit a regular linear increase of the spacing with *n*. For the hydrates, the *b* parameter increases as the length of the diamine chain increases from $n = 2$ to $n = 8$, but in a rather irregular way; curiously, the *b* parameter of the monohydrate corresponding to $n = 10$ is smaller than that of $n = 8$. Nevertheless, this seems to be correlated with water content since the members $n = 9, 10$, which contain more water, exhibit a much greater parameter. In the same way, the *b* parameter of the anhydrous oxides does not vary in a continuous manner.

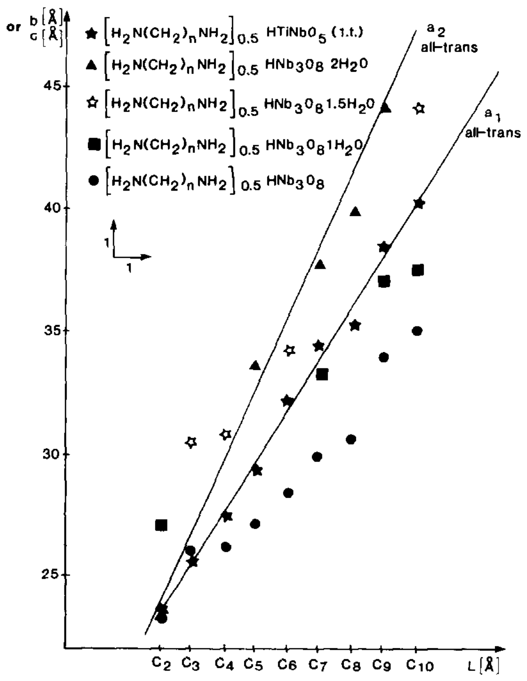

FIG. 1. Comparison of parameters as a function of length *L* of the diamine chain: *c* for low-temperature form of $[NH_3(CH_2)_nNH_3]_{0.5}TiNbO_5$ (all-*trans*); *b* for the oxide $[NH_3(CH_2)_nNH_3]_{0.5}Nb_3O_8 \cdot yH_2O$.

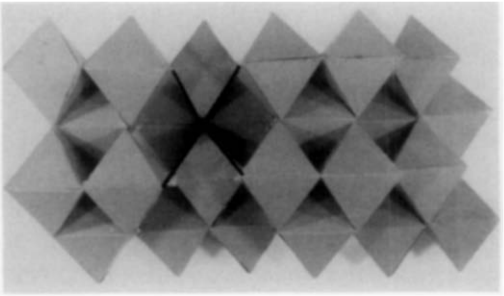

FIG. 2. The NH_3^+ ends of the diamine chain take the places of K^+ in KNb_3O_8.

Thus it appears that the intercalation of the diamines in $HNb_3O_8 \cdot H_2O$ cannot be explained by a simple transverse orientation of the diamines with an all-*trans* configuration. In order to interpret the spacing of the layers we will take into consideration the following points:

(i) The NH_3^+ ends of the diamine chain will tend to take the place of K^+ in KNb_3O_8 and thus will form four $H_3N^+–O$ distances close to 2.6 Å with the oxygen atoms belonging to the same octahedral layer as depicted in Fig. 2. The transverse orientation of the monoamines previously observed for the oxides $H_3NRNb_3O_8$ support this hypothesis.

(ii) The diamine chain tends to assume an all-*trans* configuration at low temperature. This tendency decreases as the length of the chain and the temperature increases, leading to the formation of kinks.

(iii) The diamine chain tends to assume a transverse orientation with respect to the oxide layers at least at low temperature.

The hydrated compounds will be examined first. If one takes into consideration the above hypotheses (i) and (ii), one observes that the hydrated members with low n (n = 2–4) exhibit an interlayer spacing much greater than that required by placing the NH_3^+ ends in the positions previously observed for K^+ in KNb_3O_8 (Fig.

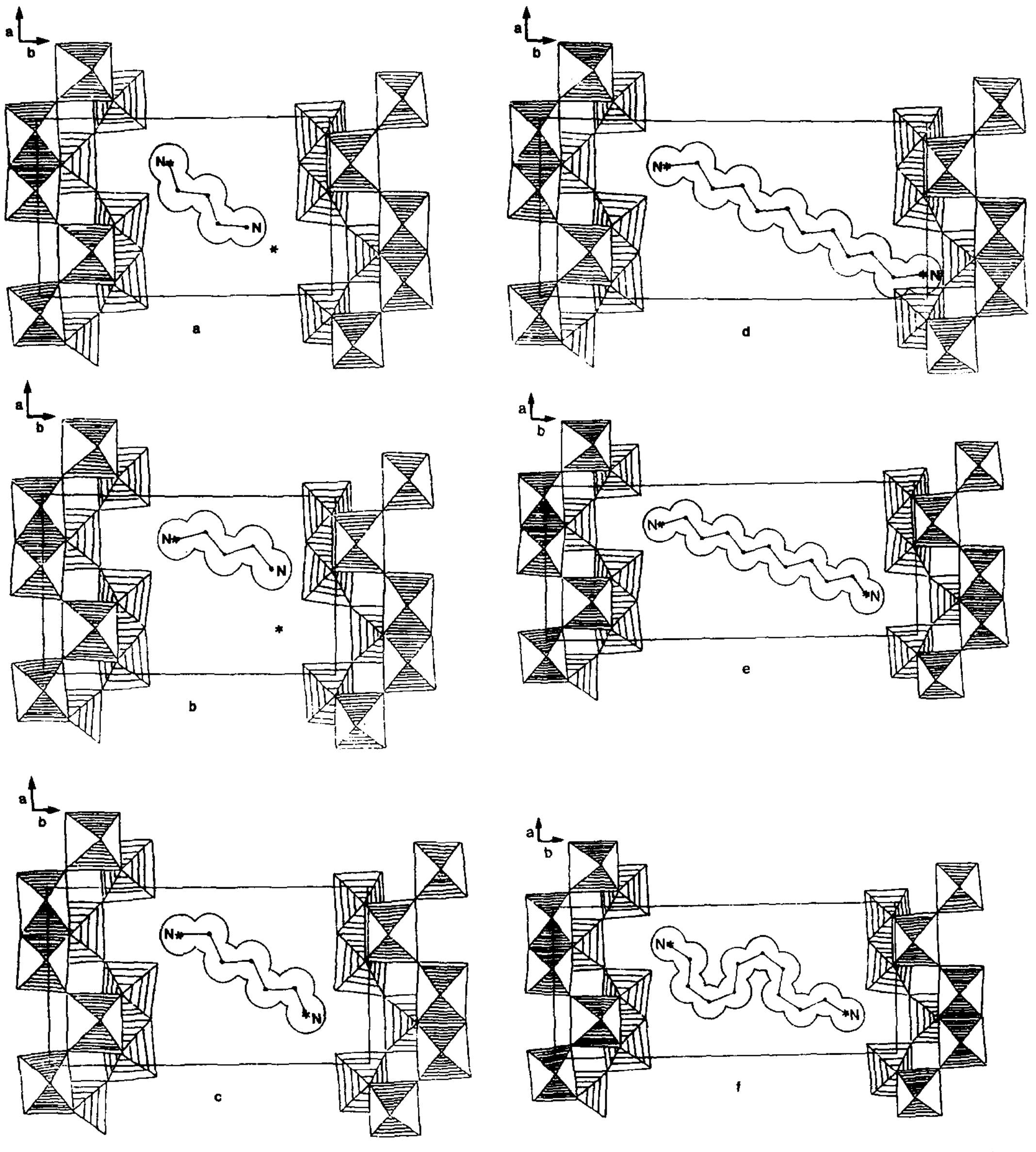

FIG. 3. Hypothetical structure of (a) $[H_3N(CH_2)_3NH_3]_{0.5}Nb_3O_8 \cdot 1.5H_2O$. NH_3^+ ends in the observed positions for K^+ (★) in KNb_3O_8 ($d_{N\text{-}N} < d_{K\text{-}K}$). (b) $[H_3N(CH_2)_3NH_3]_{0.5}Nb_3O_8 \cdot 1.5H_2O$ with a transverse orientation of the diamine chain. (c) $[H_3N(CH_2)_5NH_3]_{0.5}Nb_3O_8 \cdot 2H_2O$. NH_3^+ ends in the positions of K^+ (★) in KNb_3O_8 ($d_{N\text{-}N} = d_{K\text{-}K}$). (d) $[H_3N(CH_2)_{10}NH_3]_{0.5}Nb_3O_8 \cdot 1.5H_2O$. NH_3^+ ends in the positions of K^+ (★) in KNb_3O_8 ($d_{N\text{-}N} > d_{K\text{-}K}$). (e) $[H_3N(CH_2)_9NH_3]_{0.5}Nb_3O_8 \cdot 2H_2O$. NH_3^+ ends in the positions of K^+ (★) in KNb_3O_8 ($d_{N\text{-}N} = d_{K\text{-}K}$). (f) $[H_3N(CH_2)_{10}NH_3]_{0.5}Nb_3O_8 \cdot 2H_2O$. Formation of kinks.

3a). This phenomenon has already been observed for anhydrous oxides $[NH_3(CH_2)_n NH_3]_{0.5}TiNbO_5$ (*13*) and has been attributed to the tendency of the diamine chain to assume a transverse orientation with respect to the oxide layers according to (iii). Thus it is likely that for those low *n* values the NH_3^+ ends are displaced from their ideal positions, as shown for instance for $n = 3$ (Fig. 3b), leaving much space for the water molecules. The intermediate member $n = 5$ fits exactly with the all-*trans* configuration of the diamine chain (Fig. 3c), whereas the high *n* members ($n = 6$–10) have their interlayer spacing smaller than that required by an all-*trans* configuration of the diamine chain (Fig. 3d) except for the dihydrate corresponding to $n = 9$, which fits exactly (Fig. 3e) but is in fact unstable at room temperature. This smaller *b* parameter results from the formation of gauche bonds and kinks as shown, for instance, for the model proposed for $n = 10$ (Fig. 3f).

As the temperature increases, the tendency to form kinks increases as stated in (ii), at least for members with rather high values of *n*. This is confirmed by the behavior of the anhydrous oxides corresponding to $n \geq 4$, whose parameters can be explained only by the presence of kinks. Moreover the number of kinks generally increases as *n* increases, as shown, for instance, by a comparison of the models corresponding to the two anhydrous oxides, $n = 4$ (Fig. 4a) and $n = 9$ (Fig. 4b). This phenomenon is easily understood by

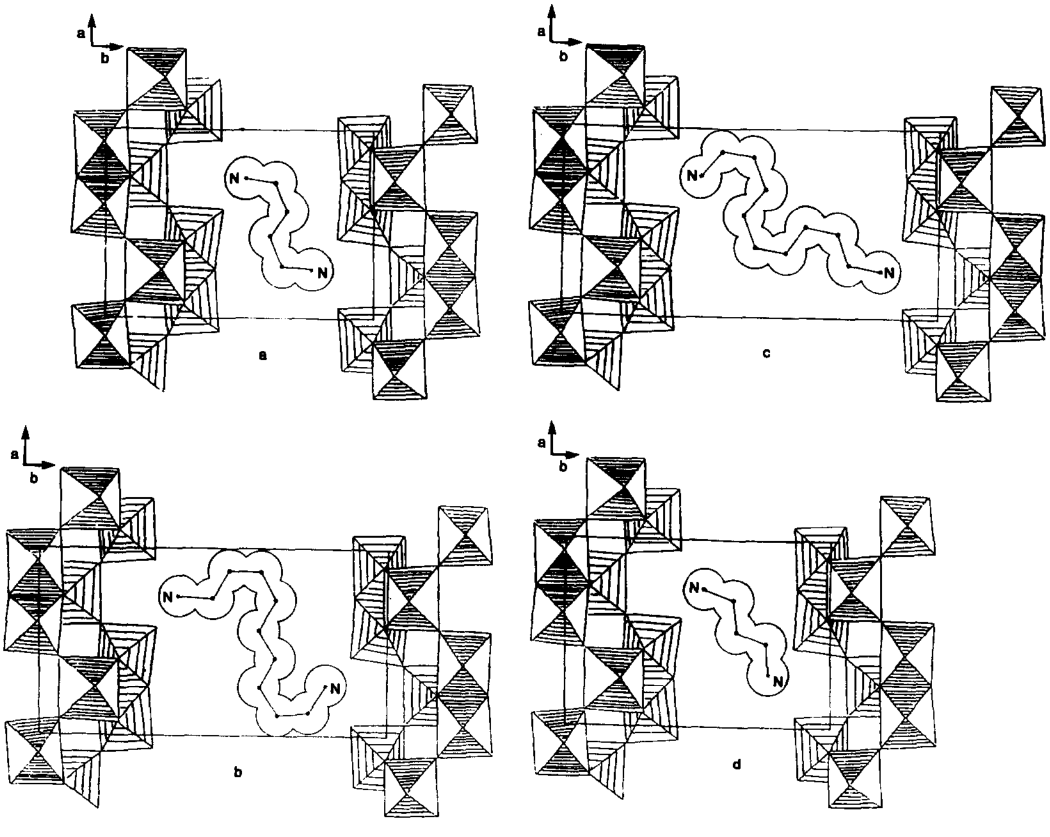

FIG. 4. Models of the structure of (a) $[NH_3(CH_2)_4NH_3]_{0.5}Nb_3O_8$; (b) $[NH_3(CH_2)_9NH_3]_{0.5}Nb_3O_8$; (c) $[NH_3(CH_2)_3NH_3]_{0.5}Nb_3O_8$; (d) $[NH_3(CH_2)_3NH_3]_{0.5}Nb_3O_8$. (★), Positions of K^+ in KNb_3O_8.

considering that the diamine chains are rather far from each other along *a* in the hydrated forms. After having lost their water molecules, the diamine chains tend to fill all the space available and form a more dense organic slab. The parameters of the intermediate hydrates are in agreement with such a hypothesis: for instance, the intermediate monohydrate of the member $n = 9$ (Fig. 4c) is characterized by a smaller number of kinks than the anhydrous phase (Fig. 4b), which leaves more place for one water molecule, but the space left between those amine chains is smaller than that observed for the dihydrate (Fig. 3e). For low *n* values the all-*trans* configuration is rather stable at high temperature. The value of the *b* parameter corresponding to $n = 3$ is in agreement with this point of view: the spacing of the layers fits exactly with the length of the diamine chain (Fig. 4d). For $n = 2$, the interlayer spacing of the monohydrate, as well as that of the anhydrous phase, is greater than that expected from consideration (i); this might be due also to the tendency of the diamine chain to assume a transverse orientation, leading to a displacement of the NH_3^+ ends from their ideal position.

From these results, it seems that the intercalation of diamine into the lamellar protonic oxide $HNb_3O_8 \cdot H_2O$ is governed at room temperature mainly by the tendency of the diamine chains to assume a transverse orientation compatible with an all-*trans* configuration.

Thus the hydration phenomenon appears, as for the monoamine intercalation (*12*), as a secondary phenomenon that allows the organic layer to be kept more dense. The high-temperature behavior of these intercalated oxides, which is characterized by the formation of numerous kinks, is also in agreement with that tendency to form a more dense organic layer. This behavior of $HNb_3O_8 \cdot H_2O$ oxide different than that of other titanoniobates is the consequence of the greater spacing of the sites available to the "NH_3^+" ends along *a*.

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