Intercalation behavior of n-alkylamines into an A-site defective layered perovskite $H_2W_2O_7$

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Abstract

Intercalation behavior of n-alkylamines into a protonated form of an A-site defective layered perovskite $H_2W_2O_7$ has been investigated. Results from XRD indicate these materials are layered with the corresponding interlayer spacing governed by the n-alkylamine chain length, and a reversible intercalation and deintercalation property is observed among these intercalation compounds. The IR spectra of the intercalation compounds with n-alkylamines clearly show that n-alkyl chains possess an all-trans conformation, and $H_2W_2O_7$ accommodate n-alkylamines ($C_nH_{2n+1}NH_2$: $n = 3, 4, 7, 8, 12, 16$) to form intercalation compounds via an acid–base mechanism. A linear relationship between the interlayer distance and the number of carbon atoms in n-alkyl chains is observed to show a bilayer arrangement of the n-alkyl chains with a tilt angle of $\sim71.6°$. Elemental analysis studies reveal that the amounts of intercalated n-alkylamines are about 2.0 mol per $[W_2O_7]$. Despite the surface geometry of $H_2W_2O_7$ is almost identical to those of layered perovskites $H_2[A_{n-1}B_nO_{3n+1}]$, the amounts of intercalated n-alkylamines of them are different. A reasonable explanation is given through our research.

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Keywords: A-site defective layered perovskite; n-Alkylamines; Intercalation; $H_2W_2O_7$

1. Introduction

Various layered compounds have the capability to accommodate organic ions and molecules to form intercalation compounds, and the reaction mechanisms include ion exchange, ion–dipole interaction, hydrogen bonding, redox reactions, and acid–base reactions [1,2]. Intercalation chemistry is a subject of considerable interest because of its applications in many fields, such as those related to catalysis, superconductors, magnetic determinations and supports for catalytic methods [3–8]. The acid–base reactions are involved in intercalation chemistry for protonated forms of various layered compounds [9–14]. In recent years, there has been a growing interest in intercalation behaviors of n-alkylamines into the protonated forms of layered perovskites [15–25]. The study of Tsunoda et al. [24] indicates that these different protonated

forms of layered perovskites $H_x[A_{n-1}B_nO_{3n+1}]$ ($x \geqslant 1$) show the similar intercalation behaviors of n-alkylamines. For instance, the changes of interlayer spacing depend on the chain length of n-alkylamine intercalated; the n-alkylamines intercalated show a bilayer arrangement with a tilt angle of $\sim60°$ and also the amounts of the intercalated n-alkylamine are about 0.9–1.0 mol per $[A_{n-1}B_nO_{3n+1}]$.

$H_2W_2O_7$ is a protonated form of an A-site defective layered perovskite which can be derived from an Aurivillius phase $Bi_2W_2O_9$ through selective leaching of bismuth oxide sheets by acid treatment [26]. Kudo et al. [27] have prepared the intercalation compounds of $H_2W_2O_7/$ $C_8H_{17}NH_2$ (DA_8) and $H_2W_2O_7/C_{12}H_{25}NH_2$ (DA_{12}) in order to further identify the layered structure of $H_2W_2O_7$. However, they failed to prepare the other intercalated n-alkylamines compounds in the same way. We report here the systematic study of the intercalation behavior of n-alkylamines into $H_2W_2O_7$, and a general method to prepare other intercalated n-alkylamines compounds has been found. Furthermore, our research shows that the

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amounts of intercalated *n*-alkylamines into $H_2W_2O_7$ are different from those of protonated forms of $H_x[A_{n-1}B_nO_{3n+1}]$ ($x \geqslant 1$), studied by Tsunoda et al. [24], though they have similar surface geometry of perovskite-like slabs. Reasonable explanation is made through our research.

2. Experimental section

2.1. Intercalation of n-alkylamines

$H_2W_2O_7$ was prepared using a procedure similar to that described in Refs. [26,27]. The intercalation was carried out by individually suspending 0.5 g of $H_2W_2O_7$ in 20 mL $\sim$50 wt% solutions of each *n*-alkylamine ($C_nH_{2n+1}NH_2$, $n = 3, 4, 7, 8, 12, 16$) dissolved in heptane at room temperature under condition of rest for 7 days. The product was separated by centrifugation, washed with heptane, and air-dried. DA_n represents intercalation compounds of $H_2W_2O_7/C_nH_{2n+1}NH_2$, where *n* stands for the number of carbon atoms in *n*-alkylamines ($n = 3, 4, 7, 8, 12, 16$), and DA_3, DA_4, DA_7, DA_8, DA_{12}, DA_{16} denotes $H_2W_2O_7/C_3H_7NH_2$, $H_2W_2O_7/C_4H_9NH_2$, $H_2W_2O_7/C_7H_{15}NH_2$, $H_2W_2O_7/C_8H_{17}NH_2$, $H_2W_2O_7/C_{12}H_{25}NH_2$, $H_2W_2O_7/C_{16}H_{33}NH_2$, respectively.

2.2. Analysis

X-ray powder diffraction (XRD) patterns of the products were recorded on D/Max-2550 XRD with CuKα radiation ($\lambda = 1.5148$ Å). The interlayer distances of intercalation compounds were determined based on [001] reflections. Elemental analyses were conducted on a Vario EL β elemental analyzer. The infrared (IR) spectra were recorded on AVATRA370 IR Spectrometer with the KBr-disk technique. SEM photograph was taken on JEOL JSM-6700F at beam energy 10.0 kv.

3. Results and discussion

3.1. Intercalation reaction

The effect of length of alkyl chain on the preparation of *n*-alkylamine intercalated $H_2W_2O_7$ was investigated. For $n = 7, 8$, and 12, the *n*-alkylamine completely intercalated products can be prepared with $H_2W_2O_7$ as the host in heptane under condition of rest for 7 days. For $n = 3$ and 4, intercalation was not complete since the [001] reflection of $H_2W_2O_7$ at $d = 0.96(2)$ nm is always observed in XRD patterns (Figs. 1a and b). So the intercalation process of short chain *n*-alkylamine is very slow. However, for $n = 16$, intercalation did not happen because no change in the XRD pattern is observed (Fig. 1c). The reason might lie in that *n*-hexadecylamine is too large for the limited interlayer distance in $H_2W_2O_7$. The completely intercalated products of DA_3, DA_4, and DA_{16} could be obtained using DA_{12} instead of $H_2W_2O_7$ as the host for 7 days, and the procedure of intercalation is the same as that described

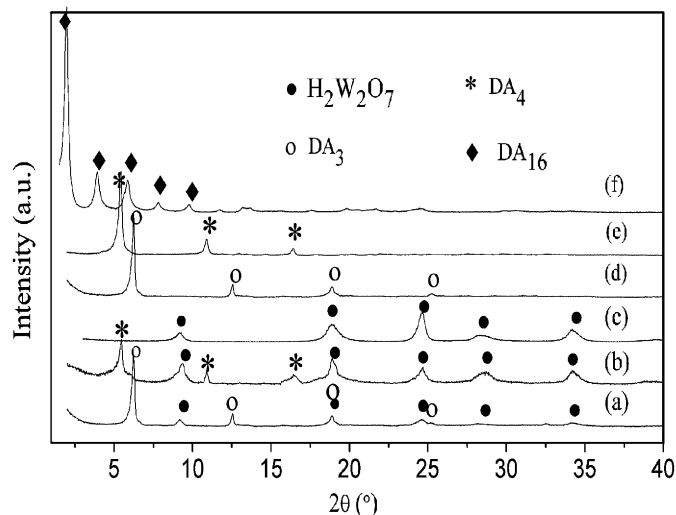Fig. 1. Powder XRD patterns of reaction products of *n*-alkylamine ($C_nH_{2n+1}NH_2$, $n = 3, 4, 16$) with $H_2W_2O_7$ (a), (b), and (c) and DA_{12} (d), (e), and (f) for 7 days.
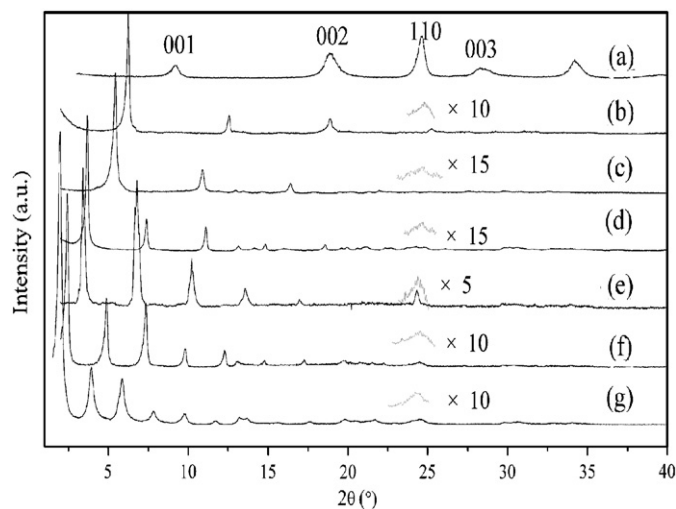

Fig. 2. XRD patterns of (a) $H_2W_2O_7$, (b) DA_3, (c) DA_4, (d) DA_7, (e) DA_8, (f) DA_{12}, and (g) DA_{16}.

above (Figs. 1d–f). This demonstrates that DA_{12} has enough interlayer distance for intercalation of *n*-hexadecylamine, and the intercalation products have the capability for re-intercalation with other smaller or larger molecules. Furthermore, DA_{12} also can be prepared using DA_4 or DA_{16} as the host. This indicates that the mesostructured lamellar phase has a reversible intercalation and deintercalation property.

3.2. Characterization of DAₙ

Fig. 2 shows the XRD patterns of $H_2W_2O_7$ and its intercalation products with *n*-alkylamines. After intercalation, the [001] reflections of $H_2W_2O_7$ shift to lower angles. The basal space of the intercalation products with *n*-alkylamines increases with an increase of the number of

carbon atoms in *n*-alkyl chain: 1.40(2) nm (DA$_3$), 1.62(1) nm (DA$_4$), 2.39(1) nm (DA$_7$), 2.61(2) nm (DA$_8$), 3.58(2) nm (DA$_{12}$), and 4.51(1) nm (DA$_{16}$), indicating formation of lamellar mesostructured compounds. In contrast, the reflections, which are assigned as [110] in the XRD pattern of H$_2$W$_2$O$_7$, are observed at the same position in the reaction products. Thus, *n*-alkylamines are successfully intercalated into H$_2$W$_2$O$_7$ without any structural change in the perovskite-like slabs. The morphologies of the intercalation compounds were also studied by SEM. Fig. 3 shows the SEM image of DA$_{16}$. The layered structure can be clearly seen from the SEM image which is in line with the XRD pattern mentioned above. The warped shape of the intercalated thick platelets might be caused by mechanical stress due to interlayer expansion.

Fig. 4 demonstrates the IR spectra of DA$_7$, DA$_{12}$, and DA$_{16}$. It is well-known that the positions of the CH$_2$ antisymmetric stretching band (2920 cm^{-1}), the CH$_2$ symmetric stretching band (2850 cm^{-1}), and bending (scissoring) vibration (1466 cm^{-1}) of CH$_2$ groups (abbreviated: γ_{as}(CH$_2$), γ_s(CH$_2$) and δ(CH$_2$), respectively.) are sensitive to chain conformation [28]. Both γ_{as}(CH$_2$) band and γ_s(CH$_2$) band shift to lower wavenumbers or δ(CH$_2$) band shift to higher wavenumber as order (kinkand gauche-blocks) is introduced into the *n*-alkyl chains [29,30]. In the IR spectrum of DA$_{12}$, the γ_{as}(CH$_2$) band and the γ_s(CH$_2$) band are observed at 2918.1 and 2849.2 cm^{-1}, respectively, and these band positions correspond to an all-trans conformation [24,31]. The IR spectra of DA$_7$ and DA$_{16}$ also exhibit these bands at the similar wavenumbers, indicating that the *n*-alkyl chains possess all-trans conformation in DA$_7$ and DA$_{16}$. This assertion is further supported by bending (scissoring) vibration which shifts to 1468.5, 1468.8 and 1469.0 cm^{-1} for DA$_7$, DA$_{12}$ and DA$_{16}$, respectively. In addition, Fig. 4 shows the broad peaks centered at $\sim$2100 cm^{-1} in these IR spectra of DA$_7$, DA$_{12}$, and DA$_{16}$. The same broad peaks are also observed
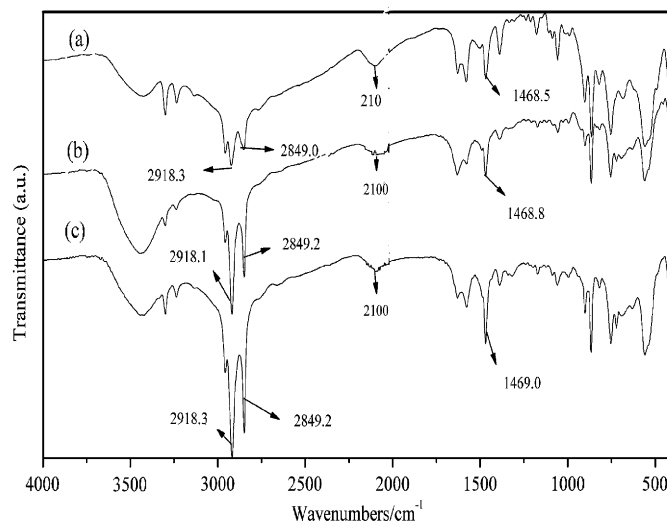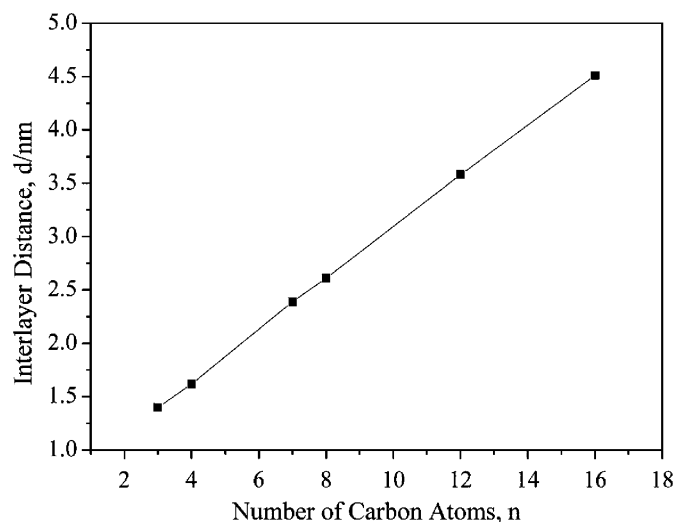

Fig. 4. IR spectra of (a) DA$_7$, (b) DA$_{12}$, and (c) DA$_{16}$.

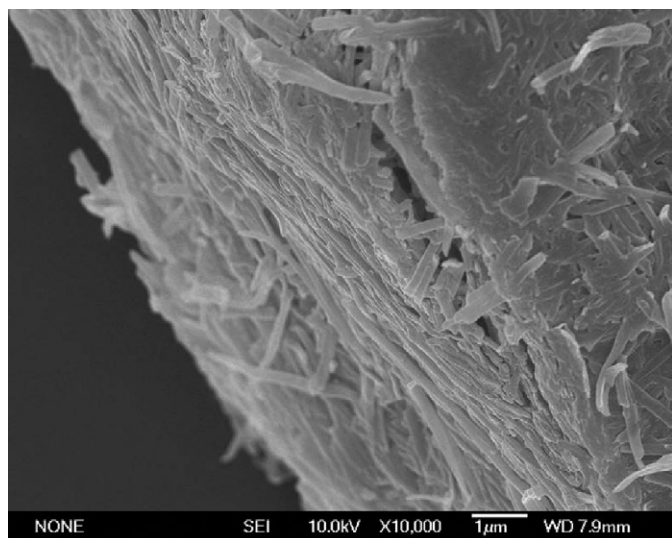Fig. 5. Plot of interlayer distance, *d* versus the number of carbon atoms in the alkyl chain, *n*, for DA$_n$.

in DA$_3$, DA$_4$ and DA$_8$. This feature is due to a combination of the asymmetrical −NH$_3^+$ bending vibration and the torsional oscillation of the −NH$_3^+$ group as it interacts with the apical oxygen of the W–O framework [32]. It is the evidence for the presence of ammonium (NH$_3^+$) terminal groups in DA$_n$. From the above analysis, we propose an acid–base mechanism for the intercalation process of *n*-alkylamines. This is why the intercalation process of short chain *n*-alkylamine is very slow, which may be due to a decrease in basicity for the short chain *n*-alkylamine.

The relationship between the interlayer distance, *d* and the number of carbon atoms in the *n*-alkyl chain, *n*, is demonstrated in Fig. 5. A linear relationship is clearly observed, as expressed with $d = 0.241n + 0.67$. Since IR analysis of DA$_7$, DA$_{12}$, and DA$_{16}$ indicates that the *n*-alkyl chains in these intercalation compounds essentially exhibit the all-trans conformation, the linear relationship observed

Fig. 3. SEM image of DA$_{16}$.

in Fig. 5 strongly suggests similar conformations for the *n*-alkyl chains in DA$_3$, DA$_4$, and DA$_8$. The interlayer distance increases linearly with a slope of 0.241 nm/CH$_2$. This slope is larger than 0.127 nm/CH$_2$ for an all-trans fully extended alkyl chain [33], hence the alkyl chains must be arranged as bilayers in the interlayer region, tilted with an angle of sin^{-1}(0.241/2 × 0.127), i.e., ~71.6°, with respect to the surface of the *A*-site defective perovskite-like slabs (*ab* plane). Fig. 6 schematically shows the structure of the stable intercalated materials saturated with alkylamine bilayers. Intercalation behavior of *n*-alkylamines into H$_2$W$_2$O$_7$ mentioned above is similar to those of protonated forms of layered perovskites H$_x$[$A_{n-1}B_nO_{3n+1}$] ($x \geqslant 1$) [24]. Only the tilt angle (~71.6°) is bigger than those of protonated forms of layered perovskites which is at ~60°, possibly resulting from ammonium's (R–NH$_3^+$) anti-repelling effect to *A*-site cations.

3.3. The amounts of intercalated n-alkylamines

The amounts of intercalated *n*-alkylamines in DA$_n$ were determined by elemental analysis. The results of elemental analysis for DA$_n$ are listed in Table 1 together with *n*-alkylamine contents of DA$_n$ calculated from carbon contents on the basis of elemental analysis results. The amounts estimated from nitrogen contents deviate from the values listed in Table 1 slightly, and the margin of error in the amounts of *n*-alkylamines is within 4%. These calculated results indicate that the average content of amine intercalated in H$_2$W$_2$O$_7$ is around 2.0 mol of amine/formula unit of the host solid.

The results from Tsunoda et al. research [24] indicate that the amounts of *n*-alkylamines in fully intercalated compounds are essentially 0.9–1.0 mol per [$A_{n-1}B_nO_{3n+1}$] in Dion–Jacobson phases H[$A_{n-1}B_nO_{3n+1}$] or Ruddlesden–Popper phases H$_2$[$A_{n-1}B_nO_{3n+1}$]. All the protons of

Fig. 6. Ideal structural model of DA$_n$ along [001] showing the arrangement of the *n*-alkylamine molecules.

Table 1
Elemental analysis and *n*-alkylamine contents of DA$_n$

DA$_n$	C (mass%)	N (mass%)	H (mass%)	*n*-alkylamine contents (mol per [W$_2$O$_7$])
DA$_3$	12.56	4.87	3.78	2.08
DA$_4$	14.74	4.10	3.85	1.92
DA$_7$	24.14	3.98	5.12	2.07
DA$_8$	26.46	3.84	5.41	2.06
DA$_{12}$	33.99	3.28	6.79	2.02
DA$_{16}$	40.14	3.01	8.14	2.06

Dion–Jacobson phases H[$A_{n-1}B_nO_{3n+1}$] are involved in the acid–base reactions, while only half of the interlayer protons of Ruddlesden–Popper phases H$_2$[$A_{n-1}B_nO_{3n+1}$] react with *n*-alkylamines because of steric hindrance. However, very interestingly, the study of Uma [34] indicates anion-deficient layered perovskite Dion–Jacobson phases H[Ca$_2$Nb$_{3-x}$M$_x$O$_{10-x}$] (*M* = Al, Fe; *x* < 1) also show the intercalation behaviors of *n*-alkylamines. But the quantity of amine intercalated in H[Ca$_2$Nb$_{3-x}$M$_x$O$_{10-x}$] (*M* = Al, Fe; *x* < 1) decreases with *x* and that the average content of amine intercalated in H[Ca$_2$Nb$_2$MO$_9$] (*M* = Al, Fe; *x* < 1) is around 0.6 mol of amine/formula unit of the host solid which differ from that of Dion–Jacobson phases H[$A_{n-1}B_nO_{3n+1}$]. The intercalation of less than 1 mol of amine/formula unit of the host most likely ascribe that, unlike in H[Ca$_2$Nb$_3$O$_{10}$] [25], all the interlayer protons of H[Ca$_2$Nb$_2$MO$_9$] (*M* = Al, Fe) do not have the same acidity. In our present study, the results can be further compared with the intercalation behavior of *n*-alkylamines into layered perovskite Ruddlesden–Popper phases H$_2$[$A_{n-1}B_nO_{3n+1}$]. The average content of amine intercalated in an *A*-site defective Ruddlesden–Popper phase H$_2$W$_2$O$_7$ is around 2.0 mol of amine/formula unit of the host solid. This means that all the interlayer protons of H$_2$W$_2$O$_7$ are involved in the acid–base reactions without steric hindrance. This observation can be reasonably interpreted by the surface geometry of H$_2$W$_2$O$_7$ and the size of *n*-alkylamines. Fig. 7 demonstrates a proposed structural model along the *ab* plane for the DA$_n$ intercalation compounds. Compared with Ruddlesden–Popper phases H$_2$[$A_{n-1}B_nO_{3n+1}$], in which the interlayer protons occupy the cavities on the [100] surface of the perovskite-like slabs [24] because of its interaction with *A*-site cations, the interlayer protons in our model can be averagely distributed at random in an *A*-site defective Ruddlesden–Popper phase H$_2$W$_2$O$_7$. The amount of protons in H$_2$W$_2$O$_7$ is equal to the number of cavities or the number of WO$_6$ octahedra. According to the literature [35], the value of interatomic distances (W–O) is 0.221 nm in WO$_6$ octahedron, this means that the area of each WO$_6$ octahedron is about 0.098 nm^2. Considering the fact that each WO$_6$ octahedron area and cavity area shares one interlayer proton, the average area for each interlayer proton is about 0.196 nm^2 since each WO$_6$ octahedron and each cavity has the same area, and this area is sufficient to accommodate
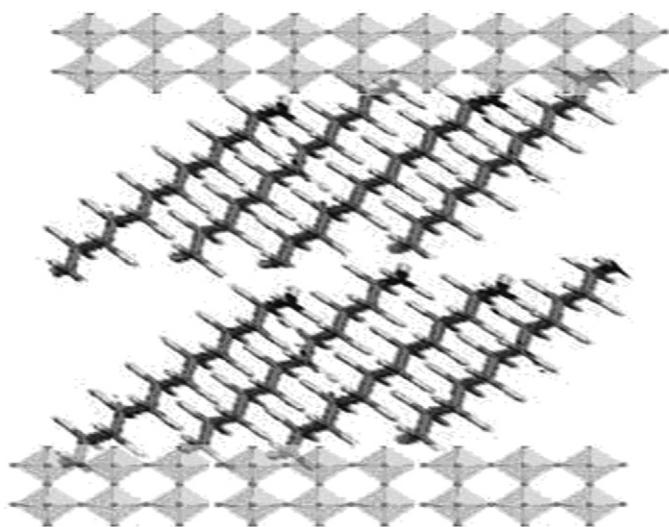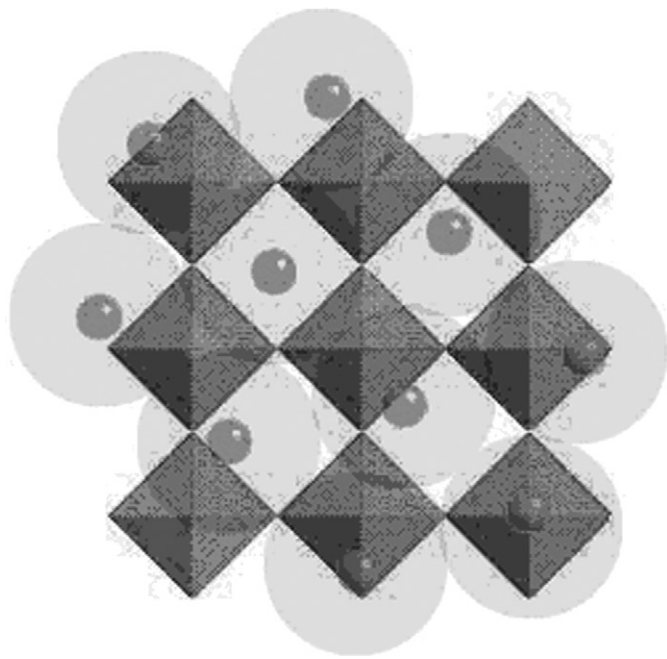
Fig. 7. Idealized structural model along the *ab* plane. Small circles represent H$^+$, large circles indicate cross section of *n*-alkylamine.

n-alkylamines, because the cross section area of *n*-alkylamines with all-trans *n*-alkyl chain is about 0.186 nm^2 [36].

4. Conclusion

We have demonstrated that H$_2$W$_2$O$_7$ can accommodate *n*-alkylamines to form intercalation compounds via the acid–base mechanism. The six *n*-alkylamines examined exhibit only one type of orientation in the interlayer space of H$_2$W$_2$O$_7$: a bilayer arrangement of the *n*-alkyl chains with a tilt angle of $\sim 71.6°$. The intercalated *n*-alkylamines composites show a reversible intercalation and deintercalation behavior. The amounts of intercalated *n*-alkylamines are 2.0 mol per [W$_2$O$_7$], and all the interlayer protons of H$_2$W$_2$O$_7$ are involved in the acid–base reactions without steric hindrance, although the surface geometry of H$_2$W$_2$O$_7$ is almost identical to those of layered perovskites H$_2$[$A_{n-1}B_nO_{3n+1}$]. The present study provides fundamental information about the intercalation behavior of *n*-alkylamines into an *A*-site defective layered perovskite H$_2$W$_2$O$_7$, which could provide reference to those of layered perovskites H$_x$[$A_{n-1}B_nO_{3n+1}$] ($x \geqslant 1$) or anion-deficient layered perovskites H[Ca$_2$Nb$_{3-x}M_x$O$_{10-x}$] (M = Al, Fe; $x < 1$).

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