

正烷基单胺对层状甘氨酸-*N,N*-双甲基膦酸锆的插层

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Intercalation of *n*-Alkylmonoamine into Layered Zirconium Glycine-*N,N*-Dimethylphosphonate

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Abstract: The layered zirconium glycine-*N,N*-dimethylphosphonate (ZGDMP) was prepared and the intercalation behavior of *n*-alkylmonoamines was investigated. The X-ray diffraction powder patterns demonstrated that the *n*-alkylmonoamines were taken up in one step and there were no other intermediate phases. The interlayer distance correlated with the number of carbon atoms of the *n*-alkylmonoamine chains. The *n*-alkylmonoamines were intercalated into ZGDMP in such a way that the protons of the interlayer -CO₂H groups were replaced by the terminal -NH₃⁺ of the protonated *n*-alkylmonoamines. The intercalated *n*-alkylmonoamines were released from the lamellar ZGDMP at temperature of 150 to 250 °C.

Key words: zirconium glycine-*N,N*-dimethylphosphonate; intercalation; *n*-alkylmonoamine

0 Introduction

Intercalation chemistry of the layered zirconium phosphonates has been an intensive area of investigation in recent years^[1~5]. Although some zirconium phosphonates are able to incorporate guest molecules by means of intercalation reactions under mild conditions, for the type of α -zirconium phosphonates of general formula $\text{Zr}(\text{O}_3\text{PR})_2$ (Fig.1), the organic groups are arranged in a overcrowding double layer with 0.24 nm² of free area for each R group. Therefore guest

molecules can not be easily intercalated into $\text{Zr}(\text{O}_3\text{PR})_2$. Many efforts have been devoted to decrease the density of organic groups in order to create a controlled microenvironment for guests. Costantino et al.^[6~8] reported that homologous series of layered zirconium *n*-alkylamino-*N,N*-dimethylphosphonates, of general formula $\text{Zr}(\text{O}_3\text{PCH}_2)_2\text{NC}_n\text{H}_{2n+1}$, in which diphosphonate groups are bonded to metal atom on the same side of the layers due to the geometrical features of the diphosphonate moieties (Fig.2). The layered compounds with half of the organic groups have more available space

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in interlayer region than zirconium phosphonates. However, they found that few zirconium dimethylphosphonates showed attractive intercalation properties because alkyl group R had no $-\text{CO}_2\text{H}$, $-\text{SO}_3\text{H}$ functional groups.

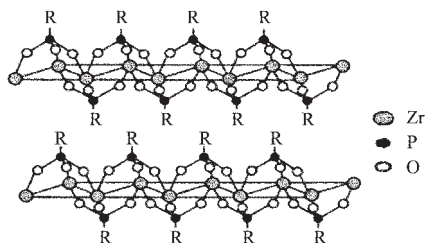


Fig.1 Construction sketch map of idea $\text{Zr}(\text{O}_3\text{PR})_2$

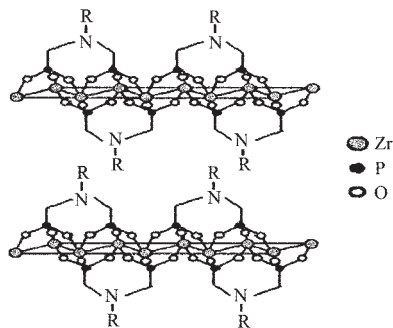


Fig.2 Construction sketch map of idea $\text{Zr}(\text{O}_3\text{PCH}_2)_2\text{NR}$

In the present study, a new layered zirconium dimethylphosphonate containing $-\text{CO}_2\text{H}$ functional group, of formula $\text{Zr}[(\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{COOH}] \cdot \text{H}_2\text{O}$ (ZGDMP), was synthesized, and intercalation behavior of some *n*-alkylmonoamines into ZGDMP was investigated. ZGDMP and intercalation compounds were determined by X-ray diffraction pattern, ^{13}C MAS NMR, infrared spectrum, elemental analysis and thermogravimetric analysis. It was shown that the intercalation of *n*-alkylmonoamines into ZGDMP presented distinct differences from zirconium phosphate and zirconium phosphonates.

1 Experimental

1.1 Starting materials

$(\text{H}_2\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{COOH}$ (DMPG) was prepared according to the literature^[9]. All other materials were analytical grades and used without further purification.

1.2 Physical measurements and chemical analysis

The change in the interlayer distance of the solid phase was examined by X-ray power diffractometry

(Rigaku D/max-3B) using Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda=0.15418\text{ nm}$) at 40 kV and 30 mA in the $2\theta=3^\circ\sim 40^\circ$ range. Thermogravimetric analysis (TG) was carried out on a NETZSCH STA 449C instrument under flowing argon using α -alumina as a reference compound from room temperature to 1000°C at $15^\circ\text{C} \cdot \text{min}^{-1}$ ramp rate. FTIR spectra were recorded using KBr pellet by Nicolet SX60 spectrometer. The nuclear magnetic resonance spectra were obtained on a Bruker AV300 at room temperature at 75.5 MHz for carbon. The carbon, nitrogen and hydrogen contents were determined with a PE-2400CHN instrument.

1.3 Preparation of the layered ZGDMP^[10]

ZGDMP was prepared according to the following procedure. A solution of DMPG (4.60 g, 0.02 mol) in 100 mL water was added into $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (0.02 mol, 6.45 g) and 40% hydrofluoric acid (0.20 mol) in 100 mL water with vigorous stirring and kept at 70°C for 120 h. The formed white solid was filtered, washed with deionized water to $\text{pH}=5\sim 6$ and dried in vacuo, 5.15 g of ZGDMP was obtained in 70.1% yield.

1.4 Intercalation of *n*-alkylmonoamines

The intercalation process was carried out by suspending about 0.5 g of the layered ZGDMP in a $0.1\text{ mol} \cdot \text{dm}^{-3}$ aqueous solution of *n*-alkylmonoamine at room temperature for five days. The resulting white solid was separated by centrifuging, washing with deionized water and drying at 60°C in vacuo for 10 h.

2 Results and discussion

Carbon, hydrogen and nitrogen elemental analyses for ZGDMP were determined as 14.20%, 2.64%, 4.10%, respectively. These values are very close to the calculated amounts of 14.25%, 2.67%, 4.15% for the proposed empirical formula of $\text{Zr}[(\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{COOH}] \cdot \text{H}_2\text{O}$.

X-ray power diffraction pattern shows in Fig.3 that the ZGDMP is a regularly layered compound. There are several sharp and intense peaks, with the first reflection at the 001 plane at 2θ of 6.940° , which corresponds to an interlayer distance of 1.273 nm. The interlayer separation originates from the attachment of the dimethylphosphonate groups with one organic

residue $-(\text{CH}_2)_2\text{NCH}_2\text{COOH}$.

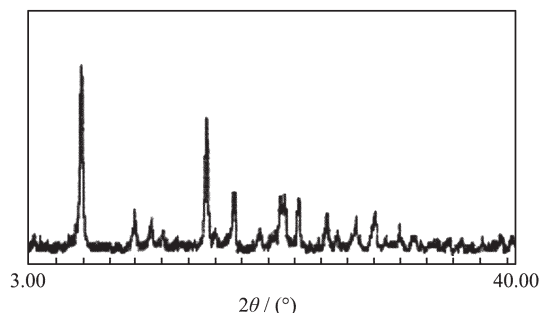


Fig.3 X-ray diffraction pattern for ZGDMP in the $2\theta=3^\circ\sim 40^\circ$

The X-ray diffraction powder patterns for the intercalation of *n*-alkylmonoamine into ZGDMP presented distinct differences with the increasing of the concentration of the *n*-alkylmonoamine. This behavior is illustrated with *n*-butylamine intercalation complex of ZGDMP and shown in Fig.4. Fig.4 shows that, with the increasing of the molar ratio of *n*-butylamine to ZGDMP, the intensity of the peak attributed to intercalated phase at 2θ of 4.080° (interlayer distance of 2.143 nm) gradually increases, whereas, the intensity of the peak attributed to host ZGDMP at 2θ of 6.940° (interlayer distance of 1.273 nm) gradually decreases. When the molar ratio of *n*-butylamine to ZGDMP was equal to 0.8:1, the peak attributed to host ZGDMP could not be detected, which indicated that the host

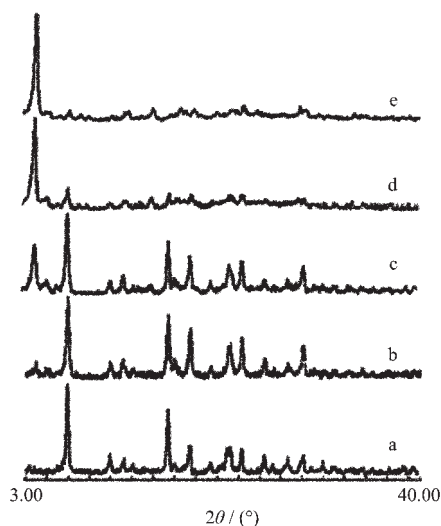


Fig.4 A comparison of the X-ray diffraction patterns for ZGDMP (a) and intercalation with *n*-butylamine at a ratio of amine: Zr being 0.2 (b), 0.4 (c), 0.6 (d), 0.8 (e)

compound had been fully converted into an intercalated phase. In addition, no peaks for intermediate phases with other interlayer distances were found before saturation, which indicated the intercalation reaction was proceeded in one step. This was obviously different from the phenomena that intercalation of *n*-butylamine into zirconium phosphate and zirconium phosphonates appeared several intermediate phases before saturation^[5,11]. Similar behavior was also found when methyl-, hexyl-, heptyl-, decyl- amine was intercalated into the ZGDMP.

As the *n*-alkylmonoamines are intercalated, a variation of interlayer distance with the number of carbon atoms of the alkyl chains is occurred. The interlayer distances of the different *n*-alkylmonoamines intercalation complex of ZGDMP are shown in Table 1.

Table 1 Interlayer distance of *n*-alkylmonoamines intercalation complexes of ZGDMP

Number of carbon atoms	1	4	6	7	10
Interlayer distance / nm	1.538	2.143	2.552	2.760	3.372

When the interlayer distances are plotted as a function of the number of carbon atoms (n_c) in the alkyl chain, a straight line is obtained (Fig.5), whose slope is calculated to be 0.204. This implies that the interlayer distance is increased by 0.204 nm for each additional carbon atom up to a carbon atom number of 10. From these results a linear correlation is calculated to be:

$$d \text{ (nm)} = 0.204n_c + 1.327$$

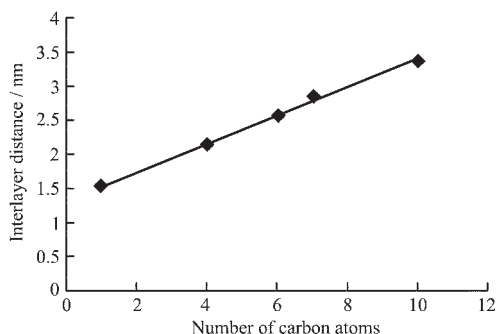


Fig.5 Interlayer distance of *n*-alkylmonoamine intercalation of ZGDMP as a function of the number of carbon atoms in the alkyl chain

Based on this relationship, the corresponding interlayer distance for an unknown *n*-alkylmonoamines intercalation complex of ZGDMP could be calculated.

Assuming that the alkyl chain of the *n*-alkylmonoamines has only *trans*, *trans* conformation and the guest molecules are intercalated perpendicular to the layered ZGDMP, the length of the alkyl chain should increase by 0.127 nm for each additional carbon atom^[12]. Therefore *n*-alkylmonoamines should form a bilayer when the increase of the interlayer distance is greater than 0.127 nm and a monolayer when the value is smaller than 0.127 nm. The experimental value of 0.204 nm indicates that *n*-alkylmonoamines form an inclined bilayer, and the chains of the *n*-alkylmonoamines deviate from the inorganic layers at an angle $\alpha = \arcsin(0.204/0.254) = 53.4^\circ$ in the interlayer region.

The ZGDMP is thermal stable 1 000 °C as shown in Fig.6(a). The mass loss of 4.72% in the interval 25 to 200 °C is in agreement with the expected 4.70% for loss of one water molecule. The second weight loss is due to the loss of CO₂ at temperature of 200 to 350 °C. The organic moiety of ZGDMP begins to decompose and oxidize at about 350 °C. At the end of the TG analysis, at 1 000 °C, the total mass loss is 28.7%, which is in good agreement with the calculated value (28.1%), when ZGDMP is converted to the form of zirconium pyrophosphate.

The thermogravimetric curve for the *n*-butylamine intercalation complex of ZGDMP is similar to that of

ZGDMP, as shown in Fig.6(b), except for difference in the mass loss for the first three stages from room temperature to 350 °C. From the thermogravimetric curve it is shown that the first weight loss below 100 °C is due to the loss of water. The second weight loss attributes to deintercalation of *n*-butylamine guest at 150 to 250 °C and the third weight loss ascribes to the loss of CO₂ at 250 to 350 °C. Similar mass loss behavior is also found when other *n*-alkylmonoamines are released from the *n*-alkylmonoamine intercalation complex of ZGDMP. Based on thermogravimetric curves and elemental analysis, the chemical formulas of the *n*-alkylmonoamines intercalation complexes of ZGDMP are proposed and listed in Table 2. One can see from Table 2, with the increase of aliphatic chain length of *n*-alkylmonoamines, the number of *n*-alkylmonoamines inserted and water absorbed is decreased.

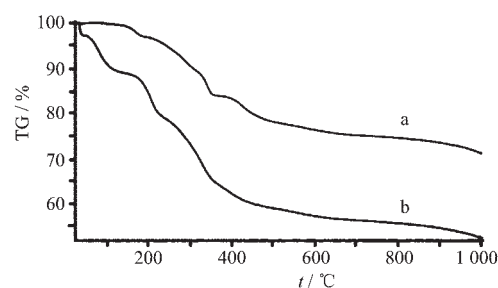


Fig.6 Thermogravimetric curves of ZGDMP (a) and the *n*-butylamine intercalation complex of ZGDMP (b)

Table 2 Percentages of carbon(C), hydrogen (H) and nitrogen(N) from elemental analyses, water (*P_w*) and *n*-alkylmonoamine (*P_a*) percentages from thermogravimetric analysis, proposed molecular formula for *n*-alkylmonoamine intercalation complex of ZGDMP

Amine	C	H	N	<i>P_w</i>	<i>P_a</i>	Molecular formula
Methylamine	13.51	4.22	3.18	13.83	6.85	$\text{Zr}[(\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{COOH}] \cdot (\text{CH}_3\text{NH}_2)_{0.96} \cdot 3.35\text{H}_2\text{O}$
Butylamine	17.42	4.29	3.10	11.41	10.06	$\text{Zr}[(\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{COOH}] \cdot (\text{C}_4\text{H}_9\text{NH}_2)_{0.62} \cdot 2.80\text{H}_2\text{O}$
Heptylamine	18.95	3.70	3.41	5.84	9.18	$\text{Zr}[(\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{COOH}] \cdot (\text{C}_7\text{H}_{15}\text{NH}_2)_{0.33} \cdot 1.34\text{H}_2\text{O}$
Decylamine	13.14	2.37	3.52	3.08	9.07	$\text{Zr}[(\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{COOH}] \cdot (\text{C}_{10}\text{H}_{21}\text{NH}_2)_{0.23} \cdot 0.86\text{H}_2\text{O}$

The absorbed water of ZGDMP exhibits stretching band centered at 3 440 cm⁻¹ in the infrared spectrum. The peak at 1 725 cm⁻¹ is attributed to the C=O stretching of CO₂H group. The bands appear at 1 240 and 1 142 cm⁻¹ represent P-OH vibrations and those at 1 047 and 999 cm⁻¹ are due to -PO₃ groups. After *n*-alkylmonoamine of intercalation into ZGDMP, the bands attributed to -CO₂⁻ vibrations appear at 1 682

and 1 399 cm⁻¹, and the band attributed to -NH₃⁺ vibration appear at 2 930 cm⁻¹. This indicates that *n*-alkylmonoamine is intercalated into ZGDMP in such a way that the protons of the interlayer -CO₂H groups are replaced by the terminal NH₃⁺ of the protonated *n*-alkylmonoamines.

A clear confirmation about the pendant organic groups (-CH₂)₂NCH₂COOH on the inorganic structural

layer is provided by ^{13}C MAS NMR spectrum, as shown in Fig.7(a), in which the carbon atoms of $(-\text{CH}_2)_2\text{NCH}_2\text{COOH}$ are numbered. The peak at 169 ppm corresponds to carbon atom of carboxyl group and the peak at 58 ppm is attributed to carbon atoms of methylene. After n -butylamine intercalation, the carbon atoms of n -butylammonium ion are numbered. C^1 , C^2 , C^3 and C^4 peaks appear at 13, 18, 29, and 39 ppm, respectively, in good agreement with the calculated value according to Lindeman-Admas experimental formula^[13]. The peak at 175 ppm is attributed to carbon atom of $-\text{CO}_2^-$. These suggest that n -butylamine is protonated by carboxyl group in the intercalation process, which has been also confirmed by the infrared spectrum.

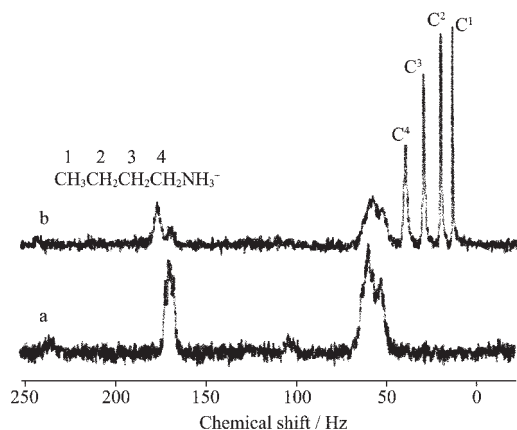


Fig.7 ^{13}C MAS NMR spectra of ZGDMP (a), the n -butylamine intercalation complex of ZGDMP (b)

3 Conclusions

A new layered zirconium diphosphonate, zirconium glycine- N,N -dimethylphosphonate, $\text{Zr}[(\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{COOH}] \cdot \text{H}_2\text{O}$ (ZGDMP) has been prepared. Its structure and composition have been determined by X-ray diffraction, ^{13}C MAS NMR, elemental analysis and thermogravimetric analysis. The intercalation of n -alkylmonoamines into ZGDMP presents distinct differences from zirconium phosphate and zirconium phosphonates with the increase of the concentration of the

n -alkylmonoamines. The intercalation reaction proceeded in one step, and only the intensity of the peak attributed to intercalated phase gradually increased as the n -alkylmonoamines were progressively inserted before saturation. The equation about the relationship between interlayer distance and the number of carbon atoms of the n -alkylmonoamine chains is proposed, which could be used to deduce the interlayer distance for an unknown n -alkylmonoamine intercalation complex of ZGDMP.

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