Chemical States and Lattice Dynamics of \(\alpha\)-Diimine \(\text{Fe}^{2+}\) Complexes Intercalated into \(\gamma\)-Zirconium Phosphate

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The \(\alpha\)-diimine \(\text{Fe}^{2+}\) complexes, \([\text{Fe(phen)}]_2^{2+}\), \([\text{Fe(bpy)}]_2^{2+}\), and \([\text{Fe(terpy)}]_2^{2+}\), (phen: 1,10-phenanthroline, bpy: 2,2’-bipyridyl, terpy: \(\alpha\alpha\alpha\’\alpha\’\alpha\’\)-tripyridine) were intercalated into zirconium dihydrogenphosphat(phosphate dihydrate (\(\gamma\)-zirconium phosphate, \(\gamma\)-ZrP), \(\text{Zr}(\text{PO}_4)\cdot(\text{H}_2\text{O})\cdot2\text{H}_2\text{O}\). The rate of the intercalation, the molar ratio of Fe to Zr, was found to be 3.82—7.76%. Mössbauer spectra indicated that one part of \([\text{Fe(phen)}]_2^{2+}\) and \([\text{Fe(bpy)}]_2^{2+}\) changed from a low-spin \(\text{Fe}^{2+}\) to high-spin \(\text{Fe}^{2+}\) state on intercalation, but \([\text{Fe(terpy)}]_2^{2+}\) did not change in chemical state. The lattice dynamics of the complexes and the intercalation compounds were investigated in terms of the temperature dependence of the area intensity on the Mössbauer spectra. A linear relationship was established for all the complex salts and the intercalation compounds investigated between the \(\ln(A(T)/A(82))\) and absolute temperature, \(T\), where \(A(T)\) and \(A(82)\) show the intensities of a doublet at \(T\) and 82 K of the Mössbauer spectra, respectively. From the slope of the linear relation, the \(\Theta^*\) values, which were derived based on the Debye approximation of lattice vibration, were evaluated for the complex salts and the intercalation compounds. The \(\text{Fe}^{2+}\) complexes showed \(\Theta^*\) values of 1.27 to 2.32\(\times\)10\(^6\), whereas the intercalation compounds showed very similar values to each other, ranging from 2.19 to 2.39\(\times\)10\(^6\), irrespective of different \(\alpha\)-diimine ligands. The results were explained in terms of the characteristic layered structure of zirconium phosphate, and by the tight bond between the \(\alpha\)-diimine \(\text{Fe}^{2+}\) complexes and the host \(\gamma\)-ZrP.

Key words: intercalation; Mössbauer Study; \(\alpha\)-diimine \(\text{Fe}^{2+}\)-complex; lattice dynamics; \(\gamma\)-zirconium phosphate

Recent studies on the intercalation of ions or small molecules into various layered compounds have shown new chemical properties on ion exchange, redox reactions, and a novel drug carrier system.1—4 Because of its excellent stability toward temperature, oxidizing agents and radiation, investigation of the intercalation of crystalline zirconium phosphate (ZrP) has been attractive. The intercalation of metal ions into layered structure of a crystalline ZrP has been studied as well as the intercalation of polar organic molecules such as alcohols, glycols, and amine.5—7 Among these studies, the ion-exchange properties of zirconium phosphate towards divalent metal ions have been investigated extensively by Allulli et al.3 in relation to the chemical composition and structure.

Studies of the crystal structures of ZrP have revealed that three crystalline phases are present depending on the preparation, i.e., \(\alpha\)-ZrP is known as mono hydrate, \(\text{Zr}(\text{HPO}_4)\cdot\text{H}_2\text{O}\), \(\beta\)-ZrP as anhydrous \(\text{Zr}(\text{HPO}_4)\), and \(\gamma\)-ZrP as \(\text{Zr}(\text{HPO}_4)\cdot(\text{H}_2\text{O})\cdot2\text{H}_2\text{O}\), respectively.8—10 The ion-exchange and uptake behaviors of alkaline metal ions have been investigated using \(\gamma\)-ZrNH\(_2\)H\(_2\)PO\(_4\).10—11 Allulli et al. studied the ion-exchange mechanism of divalent metal ions on one half converted zirconium phosphate, \(\text{ZrMn}(\text{PO}_4)\cdot2\text{H}_2\text{O}\) (\(\text{M} = \text{Na}\) and \(\text{Li}\)), and found that the ion exchange occurs in two steps, from 0 to 80% and from 80 to 100% conversion of the exchange.12 Ferragina et al. studied in detail the intercalation of 2,2’-bipyridyl into \(\alpha\)-ZrP as well as the subsequent uptake of 3d transition metal ions such as Mn\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\) into the intercalate.13—14

Alonzo et al. studied the uptake of iron in \(\alpha\)-ZrP to prepare \(\gamma\)-ZrP as well as the subsequent uptake of \(\gamma\)-ZrP. It has been shown that the interlayer separation is 7.6 Å for the \(\alpha\)-form, 9.28 Å for \(\beta\) , and 12.2 Å for the \(\gamma\)-form.9 In the present work, the \(\gamma\)-form with the largest interlayer separation was used. Although temperature dependence of resonance intensity for ionically bonded compounds and molecular compounds has been investigated, little is known regarding intercalation compounds.19—22 The temperature dependence of the Mössbauer intensity of \(\alpha\)-diimine \(\text{Fe}^{2+}\) complex intercalated into ZrP was studied in order to clarify the chemical bond between the guest and host, and also the effects of the ligand mass.

Experimental

1,10-Phenanthroline, 2,2’-bipyridyl and \(\alpha\alpha\alpha\’\alpha\’\alpha\’\)-tripyridine were obtained from Kanto Chemical Co., Inc., \(\text{ZrOCl}_2\); 8\(\text{H}_2\text{O}\), \(\text{NaH}_2\text{PO}_4\).

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Preparation of the Host Material γ-ZrP (γ-Zr(PO4)(H3PO4)·2H2O) was prepared by following the method described in the literature. Reagent grade ZrOCl2·8H2O (8 g) was dissolved in 25 ml of water, and the solution was added gently to 50 ml of 3 N HCl solution containing NaH2PO4·2H2O of 62.5 g under constant stirring and refluxing until the solution was changed to slurry. The gelatinous reaction mixture was transferred into a Pyrex glass tube and subjected to hydrothermal treatment in an autoclave at 185 °C for one week. After filtration, the crystalline γ-ZrP was washed with 1 N HCl on filter paper. It was washed with water fully to remove Cl– ions and then dried in a silica gel desiccator. The prepared γ-ZrP was identified by X-ray diffraction. Further characterization of γ-ZrP was performed by thermogravimetric analysis (TG) of Seiko Denshi Co., Ltd. The programmed rate of heating was 1 °C/min.

Preparation of Fe2+ Complexes [Fe(phen)3]Cl2 ·H2O, [Fe(bpy)3]Cl2, [Fe(bpy)3]Cl2 ·7H2O, [Fe(bpy)3]Cl2 ·4H2O were prepared by a method analogous to that for [Fe(phen),Cl]2·H2O.

Intercalation of Fe2+ Complexes into γ-ZrP Intercalation of Fe2+ complexes into γ-ZrP was performed in a 100 ml Pyrex glass vial at 50 °C for 48 h based on a suspension method under constant stirring. The molar ratio of the Fe2+ complex to γ-ZrP was 1 : 2 for all the complexes investigated. A saturated water solution of Fe2+ complex was used for intercalation. After intercalation, the intercalation compound was separated by filtration, then washed with water. The prepared intercalation compounds were stored in silica gel desiccator until measurement.

Measurement X-Ray diffraction patterns of the intercalation compounds were measured with Ni-filtered CuKα radiation (40 kV, 20 mA) using a Geigerflex RAD-C diffractometer of Rigaku-Denki Co., Ltd. Mössbauer spectra were measured using a Wissel Mössbauer spectrometer in an absolute acceleration mode against a moving 370 MBq 57Co (Rh) source. The velocity scale was calibrated using 57Fe-enriched iron foil at room temperature. A Heli-Tran LF-3-110 Cryochip from Air Product Co., Ltd. was used to measure Mössbauer spectra at various temperatures ranging from 315 to 82 K. Mössbauer spectra were fitted with a least square fitting program of Lorentzian functions.

Neutron Activation Analysis Neutron activation analysis was applied in order to determine the atomic ratio of Fe to Zr in the intercalation compounds. Accurately weighted intercalation compounds (ca. 100 mg) were sealed in a polyethylene sheet and irradiated for 24 h with a thermal neutron flux of 1011 n· cm–2 ·s–1 under a 100 kW operation at F-24 of the TRIGA II Nuclear Reactor at the Atomic Energy Institute of Rikkyo University. Reference materials used were 100 mg of prepared γ-ZrP and 15 mg of (NH4)2Fe(SO4)2 ·6H2O which were irradiated simultaneously with the intercalation compounds. The γ-rays of 56Fe and 42Zr of the intercalation compounds and the reference materials were measured with a high-purity Ge detector after cooling radioactivities for a week, and the atomic ratios of Fe to Zr in the prepared intercalation compounds were evaluated.

Results and Discussion

X-Ray Diffraction Patterns The X-ray diffraction patterns (XRD) of the intercalation compounds are shown in Fig. 1. The interlayer distance along the c-axis of γ-ZrP is 12.19 Å, whereas those intercalated with [Fe(phen)3]2+, [Fe(bpy)3]2+, and [Fe(terpy)2]2+ were enlarged up to 19.66, 18.86, and 18.70 Å, respectively. The distance observed on [Fe(phen)]2+ intercalation is consistent with 19.9 Å, as reported by Tomita et al. The diffraction peak of 12.19 Å was completely disappeared in all the intercalation compounds. The increment of interlayer distance may be related to the packing mode of guest molecules. In the present case, the interlayer distances observed for three intercalated compounds are obviously greater than 15.2 Å reported for the bis-type γ-ZrP/Cu(bpy)32+ 29) Regarding the intercalation of Cu2+ ions, Tomita et al. concluded from the electronic spectra that Cu2+ ions incorporated into γ-ZrP/bpy host were exchanged with residual protons in P-OH groups. In fact, it was observed in the present experiments that the pH values of the saturated solution of [Fe(phen)]2+ containing γ-ZrP changed from 7.0 to 2.0 when the Fe complex ions were intercalated into the host. This indicates that the intercalation of tris-type Fe chelates proceeds via ion exchange.

Ratio of the Host to Guest in Intercalation Compounds The neutron activation analysis, and the results are listed in the second column of Table 1. The molar ratio of Fe to Zr was found to be 3.82 to 7.76% within the α-dimine complexes, [Fe(bpy)]2+, [Fe(bpy)]2+, and [Fe(terpy)]2+ were intercalated. The effects of the anions on the uptake of [Fe(bpy)]X, (X = Cl, Br and ClO4) into γ-ZrP were examined in water at 50 °C for 48 h, since the solubility is largely different among the perchlorate, chloride and bromide. In the intercalation experiments, the saturated solution of each Fe2+ complex salt was used at 50 °C. The results, however, showed that the intercalation (uptake) did not depend on the counter anions of the complex. These results are similar to those reported so far for the bis-type copper complex29) and other divalent transition elements, although the
geometrical sizes of the cations are different.

**Chemical States of Iron in Intercalation Compounds**

Mössbauer spectra at room temperature of $[\text{Fe(phen)}_3]^{-}$\((\text{ClO}_4)_2 \cdot \text{H}_2\text{O}\), $[\text{Fe(bpy)}_3]^{\text{Cl}_2} \cdot 7\text{H}_2\text{O}\), and $[\text{Fe(terpy)}_2]^{\text{Br}_2} \cdot 4\text{H}_2\text{O}$ are shown in Fig. 2, and those of $[\text{Fe(phen)}_3]^{2+}$, $[\text{Fe(bpy)}_3]^{2+}$ and $[\text{Fe(terpy)}_2]^{2+}$ intercalated into $\gamma$-ZrP are in Fig. 3. Based on the Mössbauer spectra, one part of $[\text{Fe(phen)}_3]^{2+}$ and $[\text{Fe(bpy)}_3]^{2+}$ changed to high-spin Fe$^{2+}$ on intercalation, while $[\text{Fe(terpy)}_2]^{2+}$ did not change. The spectral areas of 62.9% for $[\text{Fe(phen)}_3]^{2+}$ and 71.7% for $[\text{Fe(bpy)}_3]^{2+}$ remained as original low-spin Fe$^{2+}$ under the present intercalation conditions. Mössbauer parameters of the intercalation compounds showed that the low-spin Fe$^{2+}$ states had no remarkable influence on intercalation. In the case of terpy complex, the $\alpha,\alpha',\alpha''$-tripyridine acts as a tridentate ligand, and the bond between the Fe-ion and the ligand is more stable because of the chelate effects. It is, therefore, concluded that the terpy complex was more stable than other phen and bpy complexes on intercalation under the present condition.

**Temperature Dependence of Mössbauer Spectra for α-Diimine Fe$^{2+}$ Complex Salts and Intercalation Compounds**

The logarithmic resonance area ratio, $\ln[A(T)/A(82)]$, of the spectra for $[\text{Fe(phen)}_3]([\text{ClO}_4)_2 \cdot \text{H}_2\text{O}\), $[\text{Fe(bpy)}_3]Cl_2 \cdot 7\text{H}_2\text{O}\), $[\text{Fe(terpy)}_2]Br_2 \cdot 4\text{H}_2\text{O}$ are plotted against absolute temperature in Fig. 4, where $A(82)$ is the resonance area of the quadrupole doublet of the low spin Fe$^{2+}$ at 82 K, and $A(T)$ the resonance area at $T$ K. For each Fe$^{2+}$ complex salt and intercalation compound, a good linear relationship was established for the investigated temperature range from 82 to 314 K. $[\text{Fe(terpy)}_2]Br_2 \cdot 4\text{H}_2\text{O}$ showed the most mild slope in these complex salts investigated, whereas $[\text{Fe(phen)}_3]^{-}$\((\text{ClO}_4)_2 \cdot \text{H}_2\text{O}\) the steepest. The intensity of a Mössbauer spectrum depends on the intermolecular bond strength such as van der Waals interaction, hydrogen bond, or ionic bond. Therefore, it also depends on the anions of the complex. For the effective thickness of the absorber to be thin enough, the relative value of the recoil-free fraction, $f^r$, is given by an expression as

$$f^r=\exp(-3E_T/Tc^2k\Theta)$$

where $E_T$ is the Mössbauer transition energy, $M$ the effective mass of the resonance absorber, $k$ the Boltzmann constant, $c$ the velocity of light, $\Theta$ the characteristic Debye tempera-
and imine complexes. The complexes act as pillars between the guest Fe\(^{2+}\) pounds. This indicates that the ionic character of the bond between the Fe\(^{2+}\) and ZrP/L[ZrP[Fe(phen)]\(^{2+}\) strongly. The logarithmic area ratio, ln\(A/A(82)\), of (a) Low-Spin Fe\(^{2+}\) and (b) the High-Spin Fe\(^{2+}\) Doublets Observed in \(\gamma\)-ZrP/[Fe(phen)]\(^{2+}\) Plotted against Absolute Temperature. \(A(82)\) and \(A(T)\) indicate the resonance areas of the quadruple doublet of Fe\(^{2+}\) at 82 and \(T\) K, respectively.

Since the relative value of \(f_a\) can be replaced by a given resonance area, \(A\), of a spectrum, Eq. (1) can be written as

\[
d\ln A/dT = -3E_{2/3}/Mc^2\Theta^3\tag{2}
\]

In the Debye model for lattice vibration, the characteristic Debye temperature, \(\Theta\), is related to \(h\nu_0/k\), where \(\nu_0\) is the characteristic frequency of lattice. If the intermolecular force constant is denoted as \(a\), then \(\nu_0\) is proportional to \((a/M)^{1/2}\). From the slope of the lines in Fig. 4, the \(\Theta^3M\) values for the complex salts were evaluated and are listed in Table 1, together with those for the intercalation compounds. The values for the complex salts show characteristic intermolecular interactions, resulting in different intermolecular bond strength.

The \(\Theta^3M\) values for the low-spin Fe\(^{2+}\) of the intercalation compounds showed larger values than those for the neat complex salts, and lie in a closer range than those for the neat complex salts. By the analogy for organotin compounds,\(^{21,22}\) the \(\Theta^3M\) values in the present case will show the bond strength between the intercalated tris-type Fe\(^{2+}\) complex and \(\gamma\)-ZrP. The chemical bond is, of course, essentially ionic in character; \(i.e.,\) in Zr(PO\(_3\))\(_2\)(HPO\(_4\))\(_2\)H\(_2\)O(\(\gamma\)-ZrP), H\(^+\) ions are replaced by [Fe(phen)]\(^{2+}\). Similar \(\Theta^3M\) values were obtained among three intercalation compounds. This indicates that the ionic character of the bond between the guest Fe\(^{2+}\) and ZrP/Fe\(^{2+}\) is nearly the same, irrespective of different ligands. Therefore, the recoilless fraction which affects the intensity of the spectrum may be governed mainly by the two-dimensional strong chemical bond between \(\gamma\)-ZrP and Fe\(^{2+}\)\(\alpha\)-dimine complexes. The complexes act as pillars between the \(\gamma\)-ZrP layers.

The logarithmic area ratio, ln\(A(T)/A(82)\), of high-spin and low-spin Fe\(^{2+}\) ions on the Mössbauer spectra of \(\gamma\)-ZrP/[Fe(phen)]\(^{2+}\) is plotted against absolute temperature in Fig. 5. It is shown that the slope of the high-spin Fe\(^{2+}\) is more mild than that of the low-spin Fe\(^{2+}\). The \(\Theta^3M\) values for the high-spin Fe\(^{2+}\) of \(\gamma\)-ZrP/[Fe(phen)]\(^{2+}\) and \(\gamma\)-ZrP/Fe(bpy)\(^{2+}\) were found to be 4.56 and 4.23\(\times\)10\(^{-6}\), respectively. This fact can be attributed to the greater ionic radius of the high-spin Fe\(^{2+}\). The Mössbauer parameters of high-spin Fe\(^{2+}\) species observed in the intercalation compounds suggest a bis-type \(\alpha\)-dimine complex formed during intercalation, although the species is difficult to identify chemically at present.

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