

Synthesis of γ -Zirconium Phosphate by the Fluoro-Complex Method and the Intercalation Behavior of Some α -Diimines

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Abstract. The ammonium form of γ -zirconium phosphate has been synthesized by the direct precipitation method from fluorozirconate solution in the presence of ammonium dihydrogen phosphate. The hydrogen form $Zr(HPO_4)_2 \cdot 2H_2O$, was obtained by acid treatment of the ammonium form. α -Zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$, with a relatively large particle size resulted from fluorozirconate solution in the presence of concentrated orthophosphoric acid. The intercalation behavior of such α -diimines as 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) toward γ -zirconium phosphate was investigated, and it was found that about 0.2 mol of bpy and 0.5 mol of phen have been incorporated respectively per one mol of the host, with the expansion of interlayer distances. Further incorporation of Cu(II) ions into the interlayer space of these intercalates was possible. The bpy intercalate took up more Cu(II) ions than γ -zirconium phosphate, indicating that effective pillars are constructed between layers and the ion exchange of Cu(II) ions is facilitated thereby.

Key words. γ -zirconium phosphate, α -diimine, intercalation.

1. Introduction

Crystalline γ -zirconium bis(hydrogenphosphate)dihydrate, $Zr(HPO_4)_2 \cdot 2H_2O$ (referred to as γ -ZrP hereafter) has been known as an inorganic ion exchanger having a layer structure with a somewhat wider interlayer distance (12.2 Å) than that (7.6 Å) of the well-known ion exchanger α -zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$ (α -ZrP). γ -ZrP has been synthesized by either the reflux method [1] or the hydrothermal method [2, 3], but no attempt seems to have been made to prepare γ -ZrP by the direct precipitation method. Alberti *et al.* prepared γ -titanium phosphate from hydrofluoric acid solutions containing a high concentration (10 mol dm⁻³) of orthophosphoric acid [4]. It was thus considered that γ -ZrP might be prepared by an analogous method from the solutions having a similar composition to that adopted for preparing the γ -titanium phosphate. As described below, this initial attempt was unsuccessful and only α -ZrP with a relatively large particle size was obtained. Since the sodium salt or ammonium salt of γ -ZrP has been obtained by the reflux method as well as the hydrothermal method from the solutions contain-

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ing a high concentration of sodium or ammonium ions, our next trial was the direct precipitation of the salt form of γ -ZrP. The ammonium salt was chosen because Kobayashi had obtained a stoichiometric compound from ammonium ion media in his autoclave experiment, but a non-stoichiometric one from sodium or potassium ion media [3]. In the present work, ammonium salt crystallites were obtained and were easily converted to the hydrogen form.

In the next step, the intercalation behavior of organic guest molecules into the interlayer region of γ -ZrP was investigated. Ferragina *et al.* have studied the intercalation of 2,2'-bipyridine [5] and 1,10-phenanthroline [6] into α -ZrP and the *in situ* formation of some transition metal complex pillars. In their experiment, it was necessary to pre-swell the layers *via* preparation of the metastable ethanol intercalate, otherwise the direct intercalation of these α -diimines was not possible. Since γ -ZrP has a larger interlayer spacing than α -ZrP, direct intercalation of the imines is expected to take place.

On the other hand, the free area associated to each P-OH group on the faces of the layers is smaller for γ -ZrP (17.8 \AA^2) than that for α -ZrP (24.0 \AA^2) [7], which may result in greater difficulty in accommodating a large amount of bulky molecules for γ -ZrP. Experimental evidence will afford some information on packing of the guest molecules in the layer of the host.

Finally, when the α -diimine molecules are intercalated, the interlayer distance may expand and a kind of pillaring may be possible between layers. The possibility of taking up transition metal ions into the intercalate was studied by using Cu(II) ions.

2. Experimental

2.1. SYNTHESIS OF γ -ZrP

A weighed amount of zirconium oxychloride, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, was dissolved in dilute hydrofluoric acid. To this solution was added ammonium dihydrogen phosphate $\text{NH}_4\text{H}_2\text{PO}_4$ as an aqueous solution. The resulting solution was 0.2M ($1\text{M} = 1 \text{ mol} \cdot \text{dm}^{-3}$) in Zr(IV), 1.6M in NH_4^+ and 1.1M in HF. The mixture was maintained at 60° with a continuous supply of humidified air under suction, in a polyethylene vessel for 5 to 7 days. Crystallites thus obtained were centrifuged, then washed with deionized water until pH 5. These were identified as the ammonium form of γ -ZrP by means of X-ray powder diffractometry (Table I). A Rigaku Geigerflex RAD-2B diffractometer with Ni-filtered CuK_α radiation ($\lambda = 1.542 \text{ \AA}$) was employed. γ -ZrP was obtained by treating the ammonium form with 1M HCl and washing with deionized water until pH 5, and identified by X-ray powder patterns (Table I). Particle size distribution was measured with a Shimadzu SA-CP3 particle analyzer. Further characterization was made by ignition loss of the crystallites and density measurements, which ranged over $2.1 \sim 2.3 \text{ g} \cdot \text{cm}^{-3}$.

In a preliminary experiment, an attempt was made to prepare γ -ZrP from the solution with a high concentration of orthophosphoric acid under the same condition as used for the preparation of γ -titanium phosphate. This was unsuccessful and only α -ZrP with a relatively large particle size resulted.

Table I. X-ray powder diffraction patterns for (1) ammonium- and (2) hydrogen-form of prepared zirconium phosphate

(1) Ammonium Form							
This work			Kobayashi [3]				
$2\theta(^{\circ})$	$d(\text{\AA})$	I/I_0	$2\theta(^{\circ})$	$d(\text{\AA})$			
7.73	11.43	100	7.7	11.47			
15.37	5.76	23	15.4	5.75			
21.60	4.11	6					
24.27	3.66	5					
26.79	3.32	14	26.8	3.32			
27.99	3.18	5	27.8	3.21			
31.74	2.82	31	31.8	2.81			
			33.7	2.66			
(2) Hydrogen form							
γ -1 $d(\text{\AA})$	I/I_0	γ -2 $d(\text{\AA})$	I/I_0	γ -3 $d(\text{\AA})$	I/I_0	Yamanaka, Tanaka [2] $d(\text{\AA})$ I/I_0	
12.41	100	12.21	100	12.28	100	12.25	100
5.87	13	5.81	21	5.84	8	5.84	70
						5.15	3
4.65	4	4.62	7	4.63	3	4.63	19
4.52	4	4.48	4	4.50	2	4.50	12
4.37	7	4.34	12	4.35	6	4.35	23
3.76	16	3.74	22	3.74	12	3.75	39
3.52	19	3.50	26	3.50	16	3.50	37
3.32	3	3.31	7	3.31	3	3.32	37
3.27	1	3.26	2	3.26	1		
3.21	2	3.19	4	3.20	1	3.20	19
3.11	4	3.09	6	3.10	4	3.10	13
3.07	7	3.06	4	3.06	4	3.06	19
3.03	2	3.02	2	3.03	2		
2.76	7	2.75	11	2.75	7	2.75	17
2.69	0	2.68	2			2.68	11
2.64	1					2.64	9
2.62	1						
2.49	0					2.49	6
2.45	4	2.44	3	2.45	2	2.45	8
2.41	1			2.41	1	2.41	6
2.34	2	2.34	3	2.33	2	2.34	4
2.23	1						
2.18	2	2.17	4			2.18	12
2.11	1						
2.08	0					2.08	6
1.95	8	1.95	8	1.95	6	1.95	18
1.87	1					1.87	6
						1.75	7

2.2. INTERCALATION OF α -DIIMINES INTO γ -ZrP

α -Diimines such as bpy, phen and terpyridine (tpy) were used as possible guest molecules. In an Erlenmeyer flask, a 0.05M ethanol/water (1:1) solution of guest compound was contacted with γ -ZrP with a mole ratio of 2 to 1 at fixed temperatures (25 or 50°) for fixed periods (24 or 48 h). Then the solids were filtered, washed with ethanol/water (1:1) solution and air dried. Interlayer distances were estimated from X-ray powder patterns. The chemical composition of the intercalate was determined by using elemental analysis data, mainly based on carbon content, because the carbon to nitrogen mole ratio obtained experimentally was not always stoichiometric, as was sometimes observed in analysis of the intercalates.

Another experiment was performed by using an ethanol solution of 2,2'-biquinoline as a guest molecule under similar conditions to those adopted above, except for the solvent used.

2.3. UPTAKE OF Cu(II) INTO THE γ -ZrP- α -DIIMINE INTERCALATE

The γ -ZrP/bpy intercalate and the γ -ZrP/phen intercalate were used for the uptake experiment of Cu(II). γ -ZrP/bpy or γ -ZrP/phen intercalate was suspended in copper(II) acetate aqueous solution and the mixture was shaken at 25° for 20–24 h. The resulting pale blue colored solid was washed with deionized water, then air-dried. The change in interlayer distance was measured. The uptake amount of Cu(II) was determined by EDTA titration with PAN indicator for the aqueous phases before and after the reaction. For comparison, the uptake of Cu(II) ion into γ -ZrP was studied in the same way as adopted for the imine-intercalates. In this case also, a pale blue solid was obtained. Further, ion exchange reaction of the complex ion $[\text{Cu}(\text{bpy})_2]^{2+}$ with γ -ZrP was investigated at 25° by using an aqueous solution of newly prepared $[\text{Cu}(\text{bpy})_2](\text{ClO}_4)_2$. The pH values changed from 6.3 to 3.35 as a result of ion exchange. Infrared spectra have been measured on γ -ZrP, γ -ZrP/bpy, γ -ZrP/phen, γ -ZrP/bpy/Cu(II), and γ -ZrP/ $[\text{Cu}(\text{bpy})_2]^{2+}$ with a JASCO IR-810 spectrophotometer or a Perkin Elmer 1640 FT-IR spectrophotometer. Electronic reflectance spectra have been measured on γ -ZrP/bpy/Cu(II) and γ -ZrP/Cu(II) with a Hitachi 340 recording spectrophotometer.

3. Results and Discussion

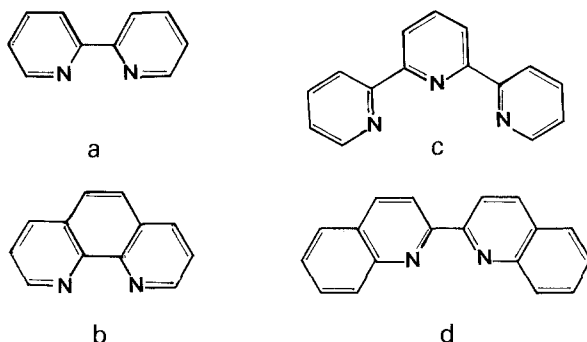
3.1. SYNTHESIS OF γ -ZrP

Direct precipitation of γ -ZrP from fluorozirconate solution in the presence of concentrated orthophosphoric acid (8 to 12M) was unsuccessful. Under these conditions, α -ZrP was deposited in pure form with a median particle diameter of about 20 μm . On the other hand, direct precipitation of the ammonium form of γ -ZrP was possible when ammonium dihydrogen phosphate was used instead of orthophosphoric acid. The ammonium form was $\text{NH}_4\text{ZrH}(\text{PO}_4)_2$ and its X-ray powder patterns are nearly identical to those reported by Kobayashi (Table I). This material easily exchanged NH_4^+ ions with H^+ ions by contacting with 1M HCl. The obtained crystallites have median particle diameters ranging over 0.9 to 1.2 μm and

were identified with γ -ZrP. The yield was usually less than 15%, leaving a problem to be improved.

3.2. INTERCALATION OF α -DIIMINES

α -Diimines such as bpy, phen, and tpy (Scheme 1) were directly intercalated between the layers of γ -ZrP from ethanol/water (1 : 1) solution. This is in contrast to the case for α -ZrP [5, 6], in which pre-swelling of layers was necessary by use of ethanol or *n*-butanol. The large interlayer distance of γ -ZrP clearly favors the intercalation. The amount of the intercalated guest molecules (bpy and phen) depends on such experimental conditions as temperature and duration, but is nearly comparable to the corresponding amount for α -ZrP, presumably because of the restricted free area around the P-OH group. On the contrary, 2,2'-biquinoline was not taken up from ethanol solution. A mixed solvent of ethanol and water could not be used because of the low solubility of the reagent. Thus, it remains unknown whether the phenomenon is due to steric or solvent effects. The interlayer distances of the intercalated γ -ZrP, γ -ZrP/bpy and γ -ZrP/phen increased as expected (Table II). It is noteworthy that, regardless of the amount of guests intercalated, a



Scheme I. α -Diimines investigated in this work: (a) 2,2'-bipyridine, (b) 1,10-phenanthroline, (c) terpyridine, and (d) 2,2'-biquinoline.

Table II. Interlayer distances and chemical composition of (1)bpy- and (2)phen-intercalates of γ -zirconium phosphate

Sample no.	Mixing mol ratio of γ -ZrP to guest	Reaction temp. ($^{\circ}$ C)	Contact time (h)	d (\AA)	Chemical composition
bpy-1	1 : 2	r.t.	24	15.71	$\text{Zr}(\text{HPO}_4)_2(\text{bpy})_{0.17} \cdot 0.5\text{H}_2\text{O}$
bpy-2	1 : 2	r.t.	48	15.22	$\text{Zr}(\text{HPO}_4)_2(\text{bpy})_{0.23} \cdot 1.8\text{H}_2\text{O}$
bpy-3	1 : 2	50	24	14.62	
bpy-4	1 : 2	25	24	15.49	$\text{Zr}(\text{HPO}_4)_2(\text{bpy})_{0.17} \cdot 0.6\text{H}_2\text{O}$
bpy-5	1 : 2	25	24	14.41	$\text{Zr}(\text{HPO}_4)_2(\text{bpy})_{0.17} \cdot 0.4\text{H}_2\text{O}$
phen-1	1 : 2	50	24	17.23	$\text{Zr}(\text{HPO}_4)_2(\text{phen})_{0.51} \cdot 7.3\text{H}_2\text{O}$
phen-2	1 : 2	25	24	17.06	
phen-3	1 : 2	50	24	17.01	

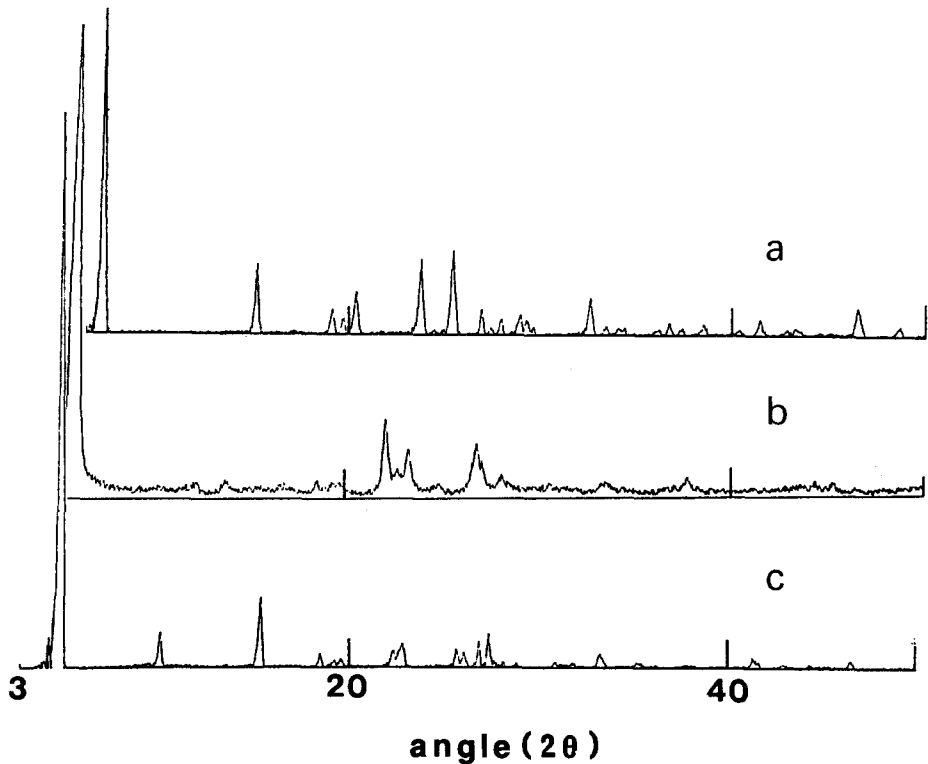


Fig. 1. X-ray powder diffraction patterns of (a) γ -ZrP(γ -2), (b) γ -ZrP/bpy (bpy-3), and (c) γ -ZrP/phen (phen-1).

reflection peak in the powder patterns corresponding to the original γ -ZrP interlayer spacing, disappeared, leaving only the peak of a newly formed phase (Figure 1).

In the case of ion exchange of metal cations on α -ZrP and its analogues, the ion-exchanged new phase coexisted with the original α -ZrP until half saturation of the exchange capacity, i.e., two reflection peaks corresponding to two solid phases being observed. The absence of this phenomenon in the intercalation of bulky organic molecules is understood for some reasons. First, if the guest molecules are packed more or less parallel to the layers of the host then some functional groups (P—OH) may be covered by the molecules and not available for further intercalation. This means that the host is 'saturated' and the original interlayer spacing is no longer held. Secondly, if the guest molecules are packed in a rather vertical fashion between layers, adjacent P—OH group will not be hindered, but a considerably larger interlayer distance will result. Since the intralayer structure is considered to be of a covalent character and rather rigid compared to interlayer interactions which involve van der Waals forces as well as hydrogen bonds, the layers are expected to hang together as units. Water of crystallization in γ -ZrP may also be loosely bound compared to that in α -ZrP. This should again cause disappearance of the original distances. Chemical composition as well as interlayer distances of some intercalates

are shown in Table II, indicating that the uptake amount of organic guest molecules does not always reflect the interlayer distances.

The increment of interlayer distances may yield some information on the packing mode of the guest molecules. Since the anhydride of γ -ZrP, known as β -ZrP, has an interlayer distance of 9.4 Å [1], the decrease as a result of dehydration is 2.8 Å which is equal to the van der Waals diameter of water [8]. The increment of interlayer distance in the case of γ -ZrP/phen intercalate is about 7.6 ~ 7.8 Å, based on β -ZrP. This value may indicate that the phen molecules (7.9 Å × 11.6 Å) are packed slightly slanted, most likely with N atoms protonated to P—OH groups. In the case of the γ -ZrP/bpy intercalate, the interlayer distance ranges over 14.4 to 15.7 Å depending upon the particular batch. The increment is thus 5.0 to 6.3 Å. This suggests that bpy molecules (6.1 Å × 11.7 Å) are packed almost vertical or slightly slanted against host planes. The amount of the guest molecules intercalated is relatively large for phen compared to bpy, in spite of the fact that the former is bulkier than the latter. The same trend has been observed in the case of α -ZrP as a host [6]. Ferragina *et al.* have mentioned that both phen and bpy molecules are oriented in a slanted fashion in α -ZrP but the projection of the phen molecule on the basal plane of layers would cover them much less than the case for the bpy molecule, allowing access to phen molecules. In the case of γ -ZrP, this argument might be partly true but the full explanation must await further structural evidence. Terpyridine was taken up by only 0.11 mol per mol of the host, which reflects its more chain-like structure compared to bpy. Even in this case, the original γ -ZrP phase did not remain.

3.3. UPTAKE OF Cu(II) INTO THE INTERCALATE

Both bpy and phen are well-known ligands for many transition metal ions. There may be complex formation when some metal ions are introduced into the ligand-intercalated host material. At the same time, the interlayer space expanded by these organic pillaring molecules has a possibility of accommodating more metal ions than does the original γ -ZrP, simply by ion exchange. As a matter of fact, Cu(II) ions were easily taken up into the intercalates, and the interlayer distances increased to some extent (Table III). In the γ -ZrP/bpy intercalate, up to 0.63 mol of Cu(II) was taken up per mol, whereas in the γ -ZrP/phen intercalate, only 0.19 mol of Cu(II) was incorporated per mol of γ -ZrP. The mol ratio of metal to guest molecule in the intercalate is roughly 3:1 for bpy and 0.4:1 for phen, respectively. It was suspected that this large difference in the ratio may indicate the presence of ion exchange rather than complex formation, at least for the major part of the metal ions. For comparison, the Cu(II) uptake experiment was performed on γ -ZrP itself and 0.49 mol of Cu(II) was absorbed per mol of γ -ZrP, without change in interlayer distance.

The possibility of complex formation was examined by comparing electronic reflectance spectra of γ -ZrP/bpy/Cu(II) and γ -ZrP/Cu(II). The almost identical broad absorption band over the range 500 ~ 1100 nm was observed for both materials. Thus, at least most of Cu(II) in the γ -ZrP/bpy/Cu(II) compound is considered to be ion exchanged as Cu²⁺ ions with residual protons in P—OH groups, although the possibility of some complex formation of Cu(II) with bpy

Table III. Copper(II) ion uptake of γ -ZrP/bpy- and γ -ZrP/phen intercalates and γ -ZrP

Sample No.	Mixing mol ratio of Cu ²⁺ to bpy	Cu(II)exchanged (mol/mol host)	Interlayer distance (Å)
ZrP/bpy/Cu(II)-1	1:1	0.15	15.72
ZrP/bpy/Cu(II)-2	2:1	0.30	16.48
ZrP/bpy/Cu(II)-3	large excess Cu ²⁺	0.63	16.01
ZrP/phen/Cu(II)-1	large excess Cu ²⁺	0.19	17.39
ZrP/Cu(II)-1	large excess Cu ²⁺	0.49	12.14

cannot be ruled out (see later). In a separate experiment, the complex ion [Cu(bpy)₂]²⁺ was ion exchanged on γ -ZrP. In this case, two solid phases with interlayer distance, 15.2 Å and 12.2 Å were observed, indicating that some of the original γ -ZrP remained.

With the available data so far obtained, the following explanation is most likely. In the γ -ZrP/bpy intercalate, the bpy content is rather small, and bpy molecules function as effective pillars which form the large porous network within the original layers. This enables Cu(II) ions to diffuse into the pores and exchange with phosphate protons, resulting in larger uptake of Cu(II) than that in γ -ZrP. On the other hand, phen molecules are taken up in a much greater amount than bpy, causing closer packing of guest molecules. This may result in less absorption of Cu(II) than that for the γ -ZrP/bpy intercalate or even for γ -ZrP in spite of the larger interlayer distance. Thus, for the purpose of metal ion loading, the optimum conditions must be present, depending upon packing fashion, molecular size of guests and interlayer distance, etc.

3.4. INFRARED SPECTRA

Infrared spectra have been measured on γ -ZrP, γ -ZrP/bpy, and γ -ZrP/bpy/Cu(II) and γ -ZrP/phen as well as bpy and phen (Figures 2 and 3). In γ -ZrP/diimine intercalates, the spectra were mostly composites of those of γ -ZrP and the respective diimine, except for the absorption bands around the region 1700 – 1400 cm⁻¹, where the bands assigned to the —C=N— or =C—N= stretching vibrations, appear in the spectra of the free bases. It can be deduced that, upon protonation these bands shift to higher frequency, as is the case for the porphyrins [9]. This was the case for the intercalates of bpy and phen, respectively. Thus, the free bpy has strong absorption at 1580, 1560 and 1240 cm⁻¹, whereas these bands almost disappeared in the intercalate. Instead, the bands around 1620 cm⁻¹ was found to be strengthened. As the host γ -ZrP has a band at 1620 cm⁻¹ due to the bending vibration of water, we consider that the strengthened absorptions are due to the superposition of absorption of water and the protonated diimine. Similarly, the free phen has strong absorptions at 1422 and 1507 cm⁻¹, while the intercalate has bands at 1472, 1544 and around 1600 cm⁻¹ (Figure 3).

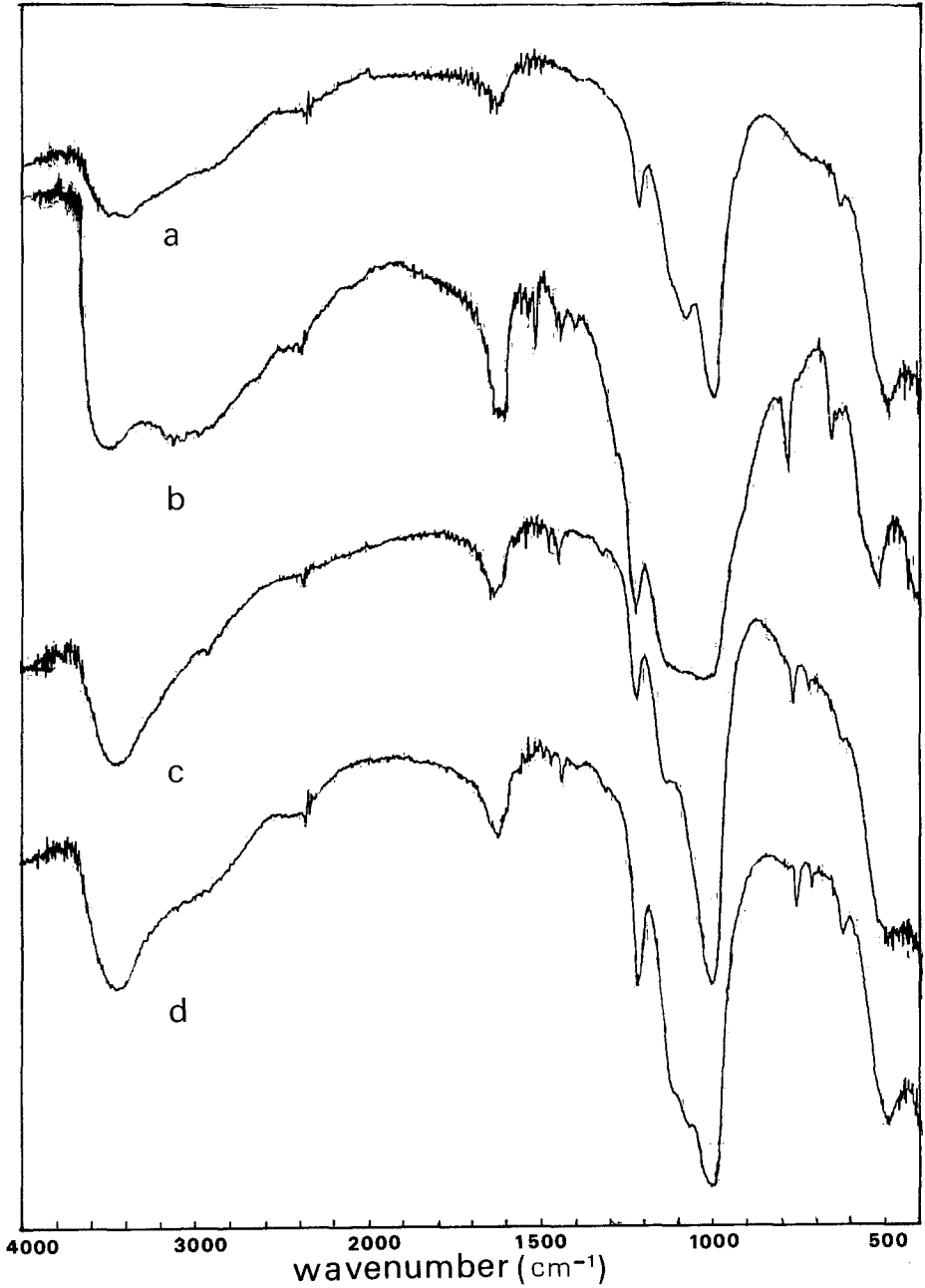


Fig. 2. Infra-red spectra of (a) γ -ZrP, (b) γ -ZrP/bpy, (c) γ -ZrP/bpy/ Cu^{2+} , and (d) γ -ZrP/ $[\text{Cu}(\text{bpy})_2]^{2+}$.

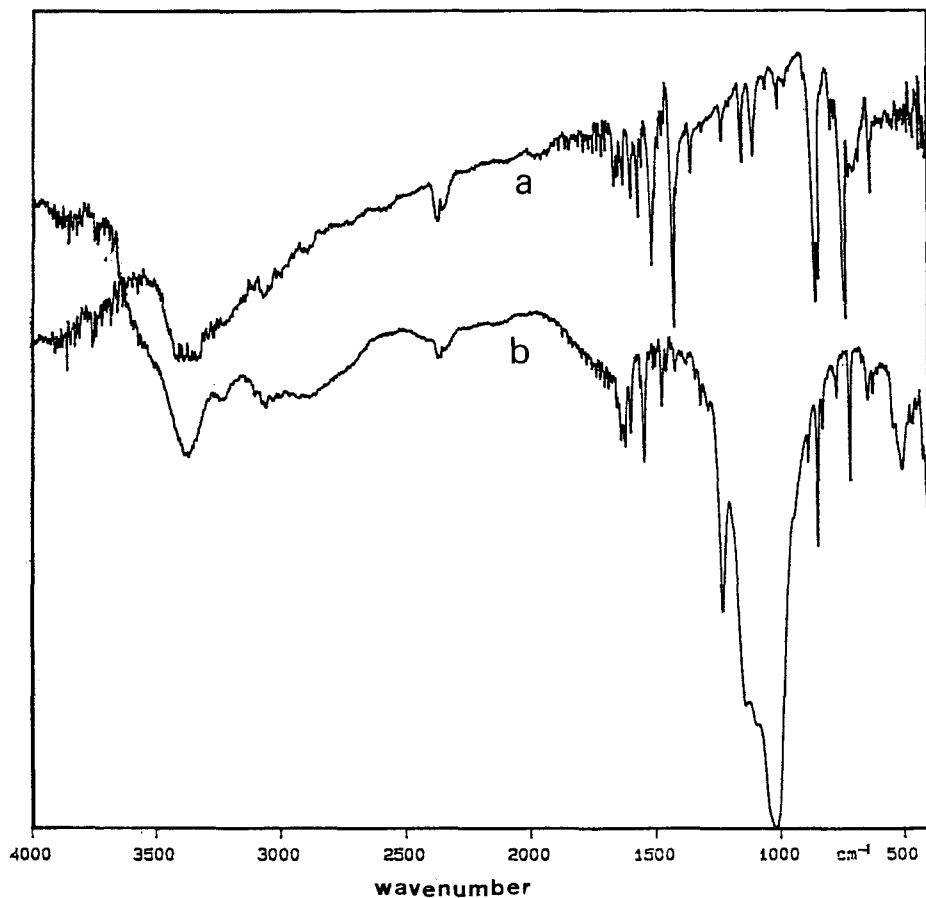


Fig. 3. Infrared spectra of (a) phen and (b) γ -ZrP/phen.

When the bases are protonated at N atoms, it might be difficult for the bases to be coordinated to a metal ion, unless the N atoms are oriented toward the metal as a result of deprotonation. In Figure 2(b) the bpy intercalate of γ -ZrP has a broad band around 3100 cm^{-1} . One possibility is that this is a band of N—H stretching vibration, but in γ -ZrP/bpy/Cu(II), the band disappears and the band at 1620 cm^{-1} seems to have been weakened. A decrease in protonated N atoms is likely to show a possible coordination of some ligands to metal ions. Precise examination of chemical species involved, however, must await further studies.

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