The Effect of Fe(II) Ions on the 1,10-Phenanthroline and Neocuproine Intercalates of γ-Zirconium Phosphate

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Abstract. 1,10-Phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (neocuproine), and 4,7-dimethyl-1,10-phenanthroline have been intercalated between layers of γ-zirconium phosphate (γ-ZrP). The observed interlayer distances are not a simple function of the size of guest molecules. Despite the fact that γ-ZrP takes up very few Fe^{2+} ions, the phen and neocuproine intercalates do take up some Fe^{2+} ions without further changes in the interlayer distances. The chemical environments around Fe^{2+} ions between layers of the intercalates were investigated by ^{57}Fe Mössbauer spectroscopy. A fairly large fraction of the Fe^{2+} ions was found to be in a high-spin state. The low-spin $[Fe(phen)_3]^{2+}$ ions are also ion exchanged on γ-ZrP, with the expansion of the interlayer up to 19.9 Å.

Key words. γ-Zirconium phosphate, 1,10-phenanthroline, neocuproine, intercalation, pillaring.

1. Introduction

In a previous paper [1], we reported the intercalation behavior of some α-diimines such as 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) towards zirconium dihydrogenphosphate phosphate dihydrate (γ-zirconium phosphate, γ-ZrP), $Zr(PO_4)(H_2PO_4)\cdot 2\,H_2O$. Further incorporation of Cu^{2+} ions into the expanded interlayer space of these intercalates was possible, and in the case of the bpy intercalate the effective pillaring by the guest molecules allows more uptake of Cu^{2+} ions than in the case of γ-ZrP. The loaded Cu^{2+} ions are considered to have been ion-exchanged with phosphate protons in the interlayer, which had been expanded by pillaring with bpy.

Recently the crystal structures of γ-type $M(IV)(PO_4)(H_2PO_4)\cdot 2\,H_2O$ (M = Ti, Zr) compounds have been presented [2, 3].

The present study was undertaken to obtain further information on the intercalation compounds of γ-ZrP with phen, its derivatives and other α-diimines. The Fe^{2+} ions have been used for the uptake experiment, because they are hardly absorbed on γ-ZrP itself and phen is the most popular ligand for Fe^{2+} ions; either a pillaring effect of phen or a coordination possibility may thus be expected.

2. Experimental

2.1. SYNTHESIS OF γ-ZrP

The synthesis of γ-ZrP was carried out in essentially the same way as reported previously [1]. Keeping the concentration of Zr(IV) ions (0.2 M) and HF solution (1.1 M) constant, the concentration of $NH_4H_2PO_4$ was varied between 1.6 and 2.4 M (1 M = 1 mol dm^{-3}) in order to check the reaction yield of the NH_4^+ form of γ-ZrP. The NH_4^+ form obtained was converted to γ-ZrP by treating the crystallites with 1 M HCl. The product was centrifuged, and washed with deionized water until the pH of the supernatant solution reached 5.0.

2.2. INTERCALATION OF ORGANIC BASES

The intercalation of phen into γ-ZrP was carried out at 50°C by using a 0.05 M solution (ethanol/water (1 : 1) mixed solvent) of phen and γ-ZrP, with the molar ratio of Zr to phen being 1 to 2. The reaction period ranged from 30 min to 4 days. The resulting solids were subjected to X-ray powder diffractometry and elemental analysis. Organic bases other than phen were treated in a similar way to the phen, with a fixed reaction period of 48 h.

The incorporation of Fe^{2+} ions into the intercalate was attempted by suspending the intercalate in a 0.01 M aqueous solution of $FeSO_4$ at 50°C for 48 h. In some cases, NH_2OH was added to the solution to avoid the oxidation of Fe(II) to Fe(III). The solid was then filtered, washed, air-dried and subjected to X-ray analysis and Mössbauer spectroscopy. The filtrate was used for pH measurement in order to check for a possible ion exchange reaction and also for analysis for Fe(II) in order to determine the metal ion uptake on the solid. Determination of Fe(II) was carried out spectrophotometrically after complexing Fe(II) with phen, by measuring the absorbance at 510 nm.

In a separate experiment, trisphenanthroline iron(II) perchlorate was prepared. By using an EtOH/H_2O (1 : 1) solution of the complex, cations were taken up in γ-ZrP by an ion-exchange process. The Mössbauer spectra were measured and compared with those obtained in the intercalation process mentioned above. Scanning electron microscopy (SEM) was also performed on γ-ZrP, the γ-ZrP/phen intercalate, and the γ-ZrP/phen/Fe^{2+} intercalate. For X-ray powder diffractometry, a Rigaku Geigerflex RAD-2B diffractometer using Ni-filtered Cu-K_α radiation was employed. Mössbauer spectra were recorded at 20 K, 80 K, and room temperature with an Austin Science S-600 Mössbauer spectrometer. The particle size distribution was measured with a Shimadzu SA-CP3 particle analyzer.

3. Results and Discussion

3.1. SYNTHESIS OF γ-ZrP

Variation of the NH_4^+ ion concentration between 1.6 and 2.4 M did not affect the final yield of γ-ZrP, which lay between $12 \sim 16\%$. Certainly the experimental condition deserves further improvement, though the method is valuable in that it does not need an autoclave. The median diameters of the product were about

1.0 ~ 14 μm and the interlayer distance of the crystallites was 12.1 ~ 12.2 Å. The SEM photograph shows that the crystals were rectangular platelets rather than the ribbon-shaped ones obtained by an autoclave method [4] (Figure 1).

3.2. INTERCALATION OF PHEN INTO γ-ZrP

Table I shows some results of the intercalation experiments. Major uptake of the guests seems to take place rather quickly (within several hours), whereas the equilibrium is reached very slowly. Maximum uptake of phen was 0.36 mol per mol of γ-ZrP. The median diameter of the host crystallites was slightly larger than that in the previous study [1], where 0.5 mol phen per mol of γ-ZrP had been incorporated within 24 h. The SEM photograph indicates that during intercalation the crystallites maintained their original appearance fairly well. The water content of the intercalates varied, depending upon the drying conditions. The errors may be amplified since the calculation of the water content depended entirely upon elemental analysis data for hydrogen, which include hydrogens of guest molecules and hydrogen phosphate groups of the host, as well as adsorbed water molecules. The interlayer distances converged to about 17.4 Å after more than 2 days' contact.

At any stage of intercalation, the X-ray reflection lines ascribed to the original γ-ZrP (e.g., $d = 12.2$ Å for the (001) plane) have disappeared. This indicates that the guest molecules interact with every crystallite of γ-ZrP, and the layers of the host hang together as units. At an early stage of the intercalation reaction, the guest molecules are considered to be dispersed between layers, then after a long contact time, some rearrangement of the guests may proceed until a more ordered distribution of the phen molecules between the layers is attained.

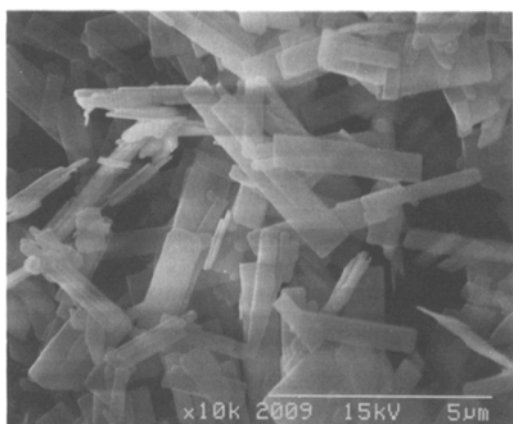## 3.3. INTERCALATION OF PHEN DERIVATIVES INTO γ-ZrP

The results of the intercalation experiments of the derivatives of 1,10-phenanthroline are given in Table II. Intercalation was achieved when EtOH–H$_2$O (1:1) solutions of phen, neocuproine, terpyridine and 4,7-dimethyl-1,10-phenanthroline were contacted with γ-ZrP. Neither bathophenanthroline (ethanol or n-butanol solution) nor bathophenanthroline disulfonic acid (disodium salt, EtOH–H$_2$O (1:1) solution) was intercalated. In the latter case, the powder patterns of the product agreed with those of the sodium form of γ-ZrP [5].

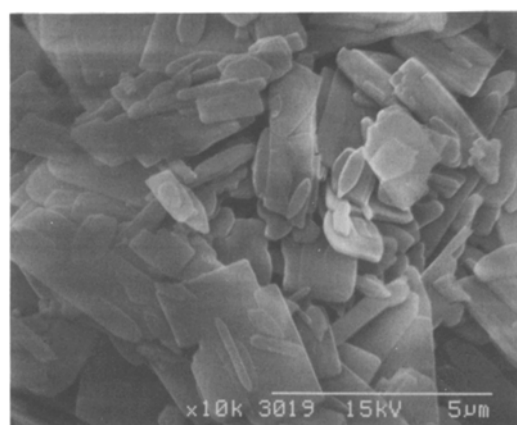Table I. Time dependence of intercalation of phen into γ-ZrP

Reaction duration	Interlayer distance (Å)	Composition
4 h	17.62	$ZrH_2(PO_4)_2(phen)_{0.31} \cdot 1.40\, H_2O$
12 h	17.50	$ZrH_2(PO_4)_2(phen)_{0.30} \cdot 1.57\, H_2O$
1 d	17.15	$ZrH_2(PO_4)_2(phen)_{0.36} \cdot 0.72\, H_2O$
2 d	17.40	$ZrH_2(PO_4)_2(phen)_{0.34} \cdot 1.15\, H_2O$
3 d	17.37	$ZrH_2(PO_4)_2(phen)_{0.34} \cdot 0.86\, H_2O$
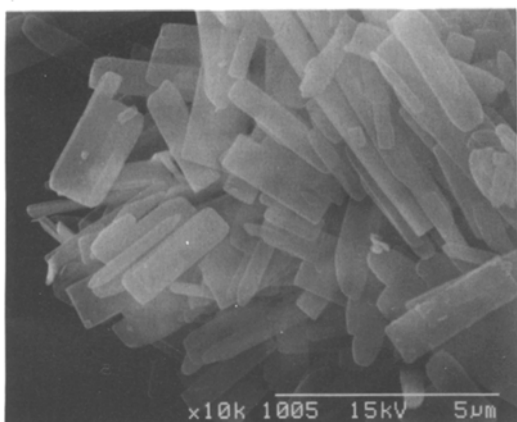
Fig. 1.   SEM photographs. (a) γ-ZrP, (b) phen-intercalated γ-ZrP, (c) [Fe(phen)$_3$]$^{2+}$ ion-exchanged γ-ZrP.

Table II. Intercalation of phen derivatives into γ-ZrP*

phen derivatives	Interlayer distance (Å)	Composition
neocuproine	17.03	$ZrH_2(PO_4)_2(ncp)_{0.21}\cdot0.63\,H_2O$
neocuproine hydrochloride	16.95	$ZrH_2(PO_4)_2(ncp)_{0.17}\cdot1.0\,H_2O$
terpyridine	14.89	$ZrH_2(PO_4)_2(terpy)_{0.15}\cdot0.96\,H_2O$
4,7-dimethyl-1,10-phenanthroline	18.76	$ZrH_2(PO_4)_2(dmphen)_{0.43}\cdot1.4\,H_2O$
tris-phen-Fe(II)-perchlorate	19.93	$ZrH_{1.728}(PO_4)_2([Fe(phen)_3])_{0.136}\cdot x\,H_2O**$

* Results for reaction duration of 2 days.
** Hydrated water was not determined.

The tris(1,10-phenanthroline)iron(II) ion, $[Fe(phen)_3]^{2+}$, on the other hand, was easily exchanged on γ-ZrP from EtOH–H_2O (1:1) solution, and gave a product having an interlayer distance of 19.9 Å.

As indicated in Table II, the relationship between the interlayer distance and the size of the guest molecule is not linear. The dimensions of some guest molecules are given in Scheme 1. If we assume that the observed interlayer distance of the
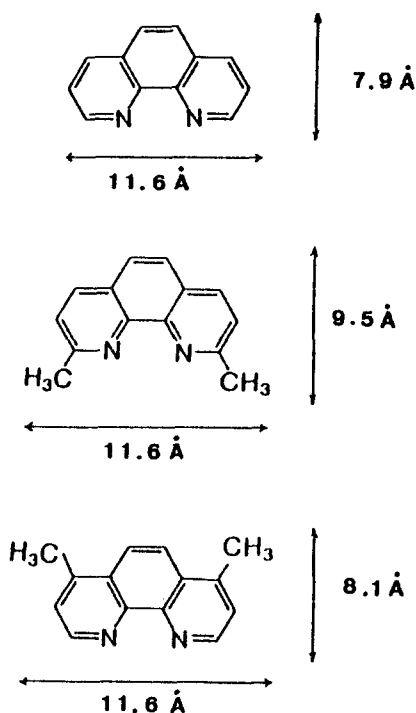
Scheme 1. Dimensions of phen and some derivatives.

intercalate minus that of β-ZrP (the anhydride of γ-ZrP), 9.4 Å [6], represents the space which a guest molecule occupies, then values of 8.0, 7.6, and 9.4 Å result for phen, neocuproine and 4,7-dimethyl-1,10-phenanthroline, respectively. In the case of phen, the observed increment (8.0 Å) agrees with the dimension of the phen molecule (7.9 Å), whereas in neocuproine, the increment is rather small, indicating that the guest molecule exists in a slanted fashion at an angle of about 55° ($\sin^{-1}(7.6/9.5) = 53°$), as is the case for alkylmonoamine intercalates [7].

The uptake of neocuproine is only 0.21 mol/mol γ-ZrP, reflecting the steric hindrance due to methyl groups at the 2- and 9-positions. 4,7-Dimethyl-1,10-phenanthroline can also be taken up and gave the largest interlayer distance among the three species. Thus, the interlayer distance is not a simple function of the size of the guest molecules and probably depends on the packing fashion resulting from steric factors as well as the uptake amount.

In the ion exchange with $[Fe(phen)_3]^{2+}$ ions, the interlayer space expanded to 19.9 Å. Subtracting 9.4 Å from this distance gives 10.5 Å, which is the space that $[Fe(phen)_3]^{2+}$ might occupy. It has been reported that, for this complex ion, the maximum distance from the center of the complex to the edge of the ligand is about 7 Å [8]. However, the ion is not spherical, and the geometrically smallest dimension is approximately 11.5 Å, corresponding to the length of the phen moiety. This value is still larger than the estimated distance by 1 Å. The complex ion may exist in a slightly distorted state, and even a partly decomposed state (see Mössbauer spectra, below).

An attempt to intercalate phen molecules into the NH_4^+ form of γ-ZrP from EtOH–H_2O (1:1) solution was unsuccessful. The NH_4^+ form has a smaller interlayer distance (11.2 Å) than γ-ZrP and the protonation of bases is also not possible.

Another important factor which influences the intercalation behavior of γ-ZrP is the solvent for guest bases. Terpyridine or phen can be intercalated when EtOH–H_2O (1:1) solvent is used, but not when pure EtOH is employed as a solvent.

3.4. UPTAKE OF Fe(II) IONS BY γ-ZrP AND ITS INTERCALATES

As shown in Table III, Fe^{2+} ions have a low affinity for γ-ZrP and no change in X-ray powder patterns was observed. In the base-intercalated γ-ZrP, the uptake could not be improved very much. The phen intercalate contacted with Fe^{2+}

Table III. Uptake of Fe^{2+} ions into γ-ZrP and its intercalates

Guest	Interlayer distance (Å)	Contact mole ratio*	Composition
none	12.22	1:2	$Zr(PO_4)_{1.076}(H_2PO_4)_{0.924}Fe_{0.076}$
none	12.22	1:1	$Zr(PO_4)_{1.038}(H_2PO_4)_{0.962}Fe_{0.038}$
phen(48h)	17.45	1:2	$Zr(PO_4)(H_2PO_4)(phen)_{0.340}Fe_{0.036}$
phen(2h)	17.92	1:1	$Zr(PO_4)(H_2PO_4)(phen)_{0.310}Fe_{0.165}$
neocuproine(48h)	16.95	1:2	$Zr(PO_4)(H_2PO_4)(ncp)_{0.230}Fe_{0.068}$
neocuproine(2h)	16.38	1:1	$Zr(PO_4)(H_2PO_4)(ncp)_{0.200}Fe_{0.144}$
$[Fe(phen)_3]^{2+}$	19.93	1:2	$Zr(PO_4)_{1.136}(H_2PO_4)_{0.864}[Fe(phen)_3]_{0.136}$
$[Fe(phen)_3]^{2+}$	19.93	1:2	$Zr(PO_4)_{1.162}(H_2PO_4)_{0.838}[Fe(phen)_3]_{0.162}$

* Contact mole ratio means Zr:Fe for γ-ZrP, and guest:Fe for the intercalates.

solution showed the orange-red color of $[Fe(phen)_3]^{2+}$, but no change in interlayer distance resulted. This indicates that some surface reaction occurred (see Mössbauer spectra, below).

It is of interest that the intercalation product from a brief contact (2h) with the base showed a relatively higher uptake of Fe^{2+} than that from contact over a longer time. In the case of a brief contact, there must have been some pillaring effect of phen or neocuproine. The reason is not immediately clear, but a smaller amount of uptake may result in a larger pore size which enables the host to accommodate more Fe^{2+} ions. Further, a poorly ordered state of the solid after the uptake of the base might result and this may favor the adsorption of Fe^{2+} ions.

3.5. MÖSSBAUER SPECTRA

In order to ascertain the chemical environment of Fe^{2+}, which has been incorporated into the ligand-loaded γ-ZrP, ^{57}Fe Mössbauer spectra were measured. The spectrum of $[Fe(phen)_3](ClO_4)_2$ (Figure 2a) gives isomer shift (δ) and quadrupole
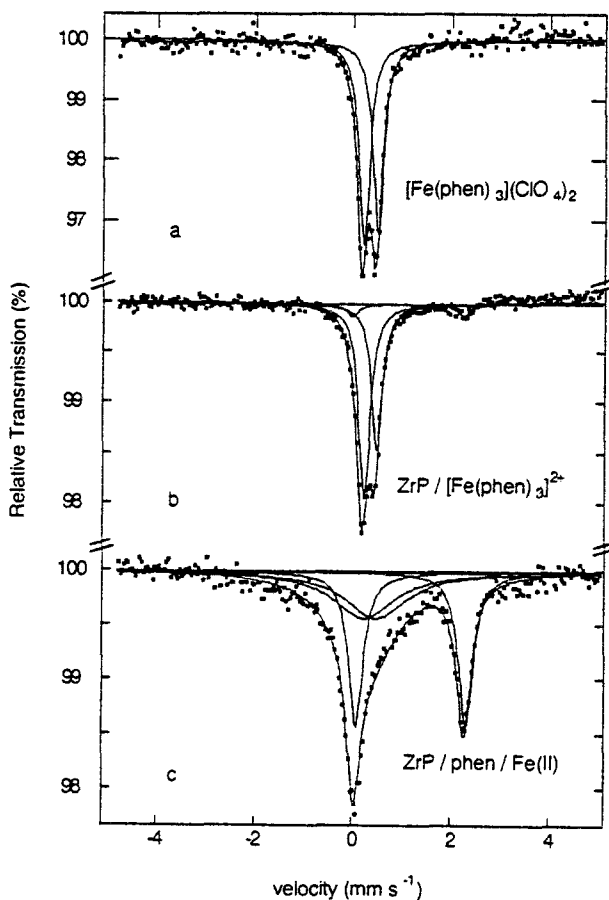

Fig. 2. Mössbauer spectra at room temperature. (a) $[Fe(phen)_3](ClO_4)_2$, (b) $[Fe(phen)_3]^{2+}$ ion-exchanged γ-ZrP, (c) Fe^{2+}-loaded phen-intercalated γ-ZrP.

splitting (ΔE_Q) values typical for low-spin Fe(II) (Table IV, site A). When the complex has been adsorbed in γ-ZrP, its Mössbauer spectrum (Figure 2b) was essentially analogous to that of the original trisphenanthroline complex, except that the additional minor high-spin Fe(II) component appeared (Table IV, site B for the sample γ-ZrP/[Fe(phen)$_3$]$^{2+}$). This high-spin species is difficult to identify chemically, but it is probable that a partly destroyed complex resulted during the uptake process.

On the other hand, the spectrum of the γ-ZrP/phen/Fe^{2+} intercalate (phen (2h) : ZrH$_2$(PO$_4$)$_2$(phen)$_{0.31}$) shows that the high-spin fraction (site B) is much larger than that in γ-ZrP/[Fe(phen)$_3$]$^{2+}$, and the absorption peaks due to [Fe(phen)$_3$]$^{2+}$ (site A) are also observed with a much broader width (2Γ) and a lower intensity (I) (Figure 2c). A contribution from a small amount of Fe(III) cannot also be ruled out. Thus, after an elapsed time of about 2 months, the relaxation spectrum characteristic of high-spin Fe^{3+} ion was more clearly observed. In γ-ZrP/phen/Fe^{2+}, formation of [Fe(phen)$_3$]$^{2+}$ ions is quite incomplete in the interlayer region. The small change in the interlayer distance supports this. Yet the crystallites have the orange-red color of the trisphenanthroline complex. This suggests that the adsorbed phen molecules have been released into the Fe^{2+}-containing aqueous solution, coordinated to the Fe^{2+}, and readsorbed on the surfaces as the iron–phenanthroline complex.

Neocuproine is a reagent which does not form a complex compound with iron because of steric hindrance due to the methyl groups at the 2- and 9-positions. This means that the octahedral complex does not form, whereas, in aqueous solution, the ligand coordinates to copper, since its coordination number is 4 rather than 6. When Fe^{2+} ions were contacted with the neocuproine intercalate (ncp(2h) : ZrH$_2$ (PO$_4$)$_2$(ncp)$_{0.20}$), at least three kinds of iron species are thought to be present (Figure 3). Temperature does not have as great an effect as in the phen system. The
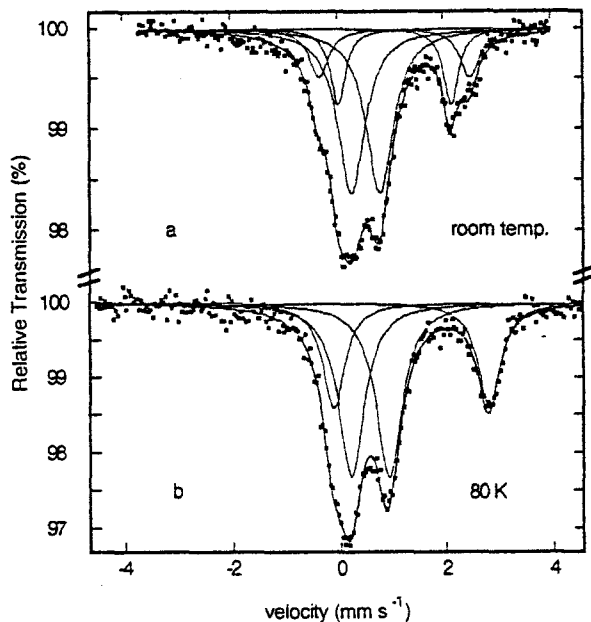

Fig. 3. Mössbauer spectra of Fe^{2+}-loaded neocuproine-intercalated γ-ZrP. (a) Room temperature, (b) 80K.

Table IV. Mössbauer data

Sample	Temp.	$\delta\dagger$ (mm·s⁻¹)	ΔE_Q (mm·s⁻¹)	$2\Gamma_1$** (mm·s⁻¹)	$2\Gamma_2$ (mm·s⁻¹)	I_1*** (%)	I_2 (%)	Site
γ-ZrP [Fe(phen)₃]²⁺	RT	0.33	0.25	0.28	0.27	2.0	1.5	A
		1.09	2.29	0.30	0.30	0.1	0.1	B
	80K	0.40	0.28	0.32	0.31	6.0	5.2	A
		1.18	3.06	0.53	0.53	0.2	0.2	B
	20K	0.26	0.26	0.27	0.27	5.0	4.4	A
		1.34	2.78	0.48	0.48	0.4	0.4	B
γ-ZrP/phen/Fe²⁺	RT	0.33	0.25	1.51	1.51	0.4	0.4	A
		1.17	2.24	0.36	0.36	1.4	1.4	B
	80K	0.38	0.25	0.96	0.96	1.3	1.3	A
		1.23	2.76	0.95	0.95	0.9	0.9	B
γ-ZrP/ncp*/Fe²⁺	RT	1.07	2.14	0.34	0.34	0.8	0.8	B₁
		1.07	2.84	0.44	0.44	0.5	0.5	B₂
		0.52	0.54	0.62	0.62	1.6	1.6	C
	80K	1.33	2.93	0.50	0.50	1.4	1.4	B
		0.55	0.71	0.59	0.59	2.3	2.3	C
[Fe(phen)₃] (ClO₄)₂·H₂O	RT	0.33	0.28	0.26	0.27	3.4	3.2	A
	80K	0.40	0.30	0.28	0.28	15.2	14.9	A
	20K	0.27	0.28	0.27	0.33	15.5	16.4	A
FeSO₄·7H₂O	RT	1.27	3.21	0.31	0.30	13.6	13.7	D
	80K	1.39	3.52	0.29	0.28	19.8	19.8	D

* ncp: neocuproine
** 2Γ: FWHM
*** I: intensity
† The δ values at RT and 80K are referred to iron at RT, and those at 20K to iron at 20K.

absorption peaks corresponding to site A were not observed, but some high-spin Fe(II) (sites B_1 and B_2) was found to be present. The site B_1 may be the same kind of species as the high-spin species found in γ-ZrP/[Fe(phen)$_3$]$^{2+}$. The candidates for B_1 and B_2 are partly hydrated Fe^{2+}, the mono-neocuproine complex or the bis-neocuproine complex. Mono- or bis-ligand complexes are unknown in aqueous solution but the possibility of their existence cannot be excluded in a tight cavity of a solid matrix, because the tris-ligand complex is difficult to form from a sterical point of view. At 80 K, B_1 and B_2 are not distinguishable and give a single broad high-spin Fe(II) quadrupole doublet. The intense absorption (site C) is difficult to assign, i.e. high-spin Fe^{3+} is possible but since some uptake experiments have been carried out under a reducing atmosphere in the presence of NH_2OH, the oxidation of Fe^{2+} to Fe^{3+} is unlikely, at least to any large extent. Moreover, the Mössbauer spectra closely resembled those obtained for the sample produced without reducing agent. This suggests that oxidation of Fe^{2+} is not a dominant process, at least before the sample was subjected to the spectral measurement.

According to recent work by Ferragina *et al.* [8], the uptake behavior of Cu^{2+} into the γ-ZrP/neocuproine intercalate is different from that into the bpy or phen intercalate, and Cu^{2+} ions are exchanged into cavities without coordination to the intercalated ligand. As mentioned before, our results for Cu^{2+} uptake by the bpy intercalate has been considered to be mainly ion exchange [1]. In the present study, an unexpected absorption (site C) has complicated the interpretation, but some novel species, rather than simply exchanged Fe^{2+} ions, may also exist in the interlayer space.

Further experimental evidence will be needed to ascertain this.

Acknowledgement

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