Pillar Chemistry. Part 5.† Intercalation of 2,2′-Bipyridine, 1,10-Phenanthroline, and 2,9-Dimethyl-1,10-Phenanthroline into γ-Zirconium Phosphate and Formation of Interlayer Copper(II) Complexes‡

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2,2′-Bipyridine (bipy), 1,10-phenanthroline (phen), and 2,9-dimethyl-1,10-phenanthroline (dmphen) can be intercalated into γ-$Zr(HPO_4)_2{\cdot}2H_2O$ as such (*i.e.* without first pre-swelling the matrix) to give materials having the final formulation γ-$Zr(HPO_4)_2L_x{\cdot}nH_2O$ (x = 0.48—0.50). With dmphen, if the γ-$Zr(HPO_4)_2{\cdot}2H_2O$ is first pre-swelled using ethanol, a further, pure layered phase of composition γ-$Zr(HPO_4)_2(dmphen)_{0.28}{\cdot}2H_2O$ is obtained; bipy and phen do not give this latter phase. Indirect evidence, *X*-ray diffraction and i.r. spectroscopy, indicates that the orientations of the amines in the interlayer are different from those in the α-$Zr(HPO_4)_2{\cdot}H_2O$ analogues, probably due to the presence of specific hydrogen bonding by the interlayer water molecules. All four materials exchange Cu^{II}. As expected, given its lower interlayer ligand density compared with the other materials, γ-$Zr(HPO_4)_2(dmphen)_{0.28}{\cdot}2H_2O$ takes up Cu^{II} most readily. Further, within the series γ-$Zr(HPO_4)_2L_x{\cdot}nH_2O$ the order of uptake, phen > dmphen > bipy, is not that expected from ligand steric requirements alone and the uptake is in all cases slower than that in the α-$Zr(HPO_4)_2{\cdot}H_2O$ analogues, both results indicating the importance of ligand–matrix interactions. The final pure layered materials obtained have $[\overline{Cu^{2+}}]:[\overline{L}]$ ratios of 1 : 1 [γ-$(dmphen)_{0.28}$] and 1 : 2[γ-$(dmphen)_{0.48}$ and γ-$(bipy)_{0.48}$]; γ-$(phen)_{0.50}$ gave $[\overline{Cu^{2+}}]:[\overline{L}]$ = 0.8 : 1. Spectroscopic evidence shows that Cu^{II} co-ordinates to the amine ligand only in the bipy and phen cases, whereas both dmphen-containing materials exchange Cu^{2+} into cavities widened by the dmphen but without co-ordination to the intercalated ligand.

Our development of intercalation co-ordination chemistry[1] has involved the well characterised, thermally stable α-$Zr(HPO_4)_2{\cdot}H_2O$ as starting matrix.[2–4] The major reason for this is that it can not only be readily swelled, like the smectite clays, also of current interest in pillaring studies,[5] but also has an ordered basal structure.[6] Consequently, although structural studies are restricted to indirect spectroscopic methods, it has at least been possible to rationalise the behaviour of the complex composites obtained on the basis of ligand (or complex): basal unit ratios.

It is of obvious interest to extend such investigations to analogues having a more expanded interlayer distance, such as γ-$Zr(HPO_4)_2{\cdot}2H_2O$ (d_{002} = 12.27 Å).[7] However, although intuitively more amenable to intercalation pillaring studies, the absence of a crystal-structure analysis is a limitation to rationalising the ordering present. Despite this limitation, we have found that γ-$Zr(HPO_4)_2{\cdot}2H_2O$ can intercalate large aromatic amines to give well defined ordered composites. This paper describes those of 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), and 2,9-dimethyl-1,10-phenanthroline (dmphen) all of which have properties different from those of the α analogue, which may be ascribed to differing orientations adopted by the amines. Further, unlike α-$Zr(HPO_4)_2{\cdot}H_2O$, on exchange with Cu^{II} not all provide evidence for the formation of complexes in which metal–ligand interactions are involved.

Experimental

Materials.—The compound γ-$Zr(HPO_4)_2{\cdot}2H_2O$ was prepared, characterised, and stored as described in the literature.[8] 2,2′-Bipyridine, 1,10-phenanthroline, and 2,9-dimethyl-1,10-phenanthroline were Fluka purissim. p.a. products. All other chemicals were of the highest purity available and were used as received.

Intercalation of the Amines into γ-$Zr(HPO_4)_2{\cdot}2H_2O$.—Two different intercalation materials with ligand: γ-$Zr(HPO_4)_2{\cdot}2H_2O$ ratios of *ca.* 1:4 and 1:2 were obtained with dmphen, of formulae γ-$Zr(HPO_4)_2(dmphen)_{0.28}{\cdot}2H_2O$ and γ-$Zr(HPO_4)_2(dmphen)_{0.48}{\cdot}2.2H_2O$. The former, having a basal spacing d_{002} = 17.7 Å, was obtained by contacting the pre-swelled ethanolic form of γ-$Zr(HPO_4)_2{\cdot}2H_2O$ (d_{002} = 16.4 Å) (1 g) with a 0.1 mol dm^{-3} absolute ethanol solution (100 cm^3) dmphen at 45 °C for 6 d. The latter, with d_{002} = 19.4 Å, was obtained by contacting pure γ-$Zr(HPO_4)_2{\cdot}2H_2O$ (1 g) with a 0.1 mol dm^{-3} solution of dmphen in ethanol–water (1 : 1) (100 cm^3) at 25 °C for 2 weeks. The same experiment performed at 45 °C to shorten the contact time always gave a two-phase material. By contrast, with the latter method, bipy and phen gave well ordered materials after contact for only 5 d: γ-$Zr(HPO_4)_2(bipy)_{0.48}{\cdot}0.3H_2O$ and γ-$Zr(HPO_4)_2(phen)_{0.50}{\cdot}3H_2O$, with interlayer distances of 14.7 and 18.6 Å, respectively.

All the new phases were monitored by *X*-ray diffractometry (x.r.d.) and the amine and water contents determined by t.g.a. The materials are listed in Table 1.

Uptake of Copper(II).—A series of samples of the amine-

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† For Part 4 see ref. 3.

‡ *Non-S.I. unit employed:* G = 10^{-4} T.

Table 1. Amine-intercalated γ-zirconium phosphates

Material[a]	d_{002}/Å			Found (%)[d]		
		b	c	C	H	N
γ-$Zr(HPO_4)_2(bipy)_{0.48}\cdot 0.3H_2O$	14.25	13.8	14.14	0.30 (0.35)	0.015 (0.020)	0.065 (0.075)
γ-$Zr(HPO_4)_2(phen)_{0.50}\cdot 3.0H_2O$	18.6	14.0	15.9	0.30 (0.35)	0.020 (0.020)	0.060 (0.065)
γ-$Zr(HPO_4)_2(dmphen)_{0.48}\cdot 2.2H_2O$	19.4	16.65	18.4	0.30 (0.40)	0.025 (0.030)	0.055 (0.065)
γ-$Zr(HPO_4)_2(dmphen)_{0.28}\cdot 2.0H_2O$	17.7	13.2	14.6	0.35 (0.45)	0.020 (0.030)	0.055 (0.075)

[a] ± 0.01 H_2O; formulation from t.g.a. of three independent preparations; [b] After calcination at 220 °C; [c] After calcination at 220 °C then standing in air at 25 °C for 24 h; [d] Calculated values are given in parentheses.

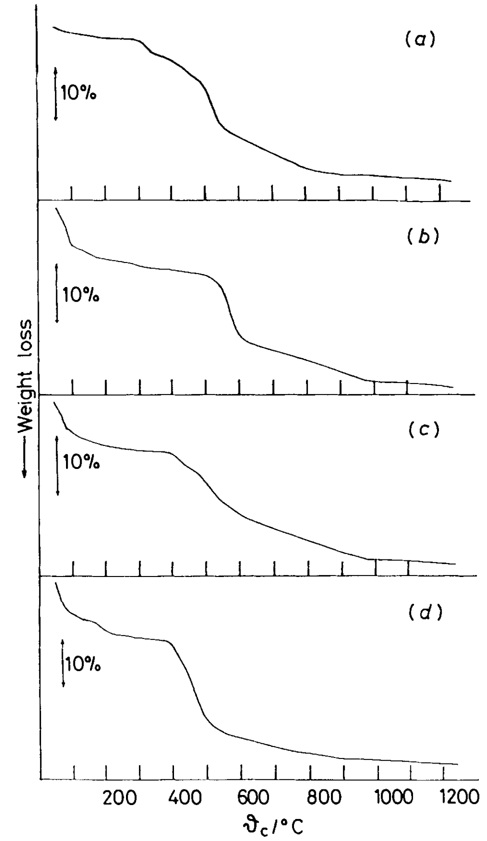

Figure 1. T.g.a.–d.s.c. of amine-intercalated materials: (a) γ-$Zr(HPO_4)_2(bipy)_{0.48}\cdot 0.30H_2O$; (b) γ-$Zr(HPO_4)_2(phen)_{0.50}\cdot 3H_2O$, (c) γ-$Zr(HPO_4)_2(dmphen)_{0.28}\cdot 2H_2O$, and (d) γ-$Zr(HPO_4)_2(dmphen)_{0.48}\cdot 3H_2O$

intercalated material (0.5 mmol) was contacted with a 5 mmol dm^{-3} copper(II) solution [as $Cu(O_2CMe)_2$] such that $[Cu^{2+}]$:$[\overline{\text{Amine}}]$ = 1 : 1 at 45 °C (a bar over a metal ion or amine signifies its presence in the solid state, *i.e.* $[\overline{\text{amine}}]$ = [intercalated amine]). At set time intervals the suspension was filtered, the supernatant analysed for Cu^{II} and the pH measured. The uptake of Cu^{II} *vs.* time is illustrated in Figure 4.

X-Ray diffractograms were taken for both wet and air-dried copper-exchanged solids in order to follow phase changes. They are shown as plots of angle 2θ (3—15) *vs.* $[Cu^{2+}]$: [L] in the d_{002} to d_{004} region to simplify discussion (Figures 5 and 6). However, the entire region up to $2\theta = 40°$ was also scanned in all cases, where reflections characteristic of differences in basal structure between the α and γ forms of zirconium phosphate occur.

Analyses and Physical Measurements.—The *X*-ray powder diffraction patterns (Tables 2 and 3) of the materials were taken on a Philips diffractometer using nickel-filtered Cu-K_α radiation, with 2θ angles believed accurate to 0.05°. A Mettler 2000C simultaneous t.g.a./d.s.c. thermoanalyser was used for determining the amine and water contents of the materials (heating rate 5 °C min^{-1}, ignition up to 1 200 °C to constant weight in an air flow). A Varian Techtron model 1 100 atomic absorption spectrophotometer was used for analysing metal-ion concentrations. E.s.r. and electronic spectra (as reflectance) were obtained as described previously[2] and i.r. spectra (Perkin-Elmer 893G instrument) were recorded as mulls rather than KBr discs to avoid any phase changes during sample preparation.

Results and Discussion

The most obvious point to make from inspection of Table 1 is that these bulky amines intercalate into the γ form of zirconium phosphate differently from into the α form. The compound γ-$Zr(HPO_4)_2\cdot 2H_2O$ provides two forms with dmphen, whereas α-$Zr(HPO_4)_2\cdot H_2O$ gives only one. Similarly, bipy will load into γ-$Zr(HPO_4)_2\cdot 2H_2O$ up to a ratio [bipy]:[γ-$Zr(HPO_4)_2$] = 1:2, whereas 1:4 is the maximum ratio attainable with the α form. In addition, γ-$Zr(HPO_4)_2(bipy)_{0.48}\cdot 0.3H_2O$ stands out because it contains very little interlayer water per γ-$Zr(HPO_4)_2$ unit.

These differences are due to the presence of differing interlayer environments in the two matrices as reflected in differences in the t.g.a. (Figure 1). That of the bipy-containing material is different from those of the other three intercalated materials; there is no clear loss of zeolitic water at 100—120 °C. Instead, the water is lost gradually up to 250 °C. Subsequent decomposition of γ-$Zr(HPO_4)_2(bipy)_{0.48}$ occurs in three well defined stages at 340, 480, and 580 °C. The dmphen-containing materials also decompose in three well defined steps, whereas after loss of the zeolitic water at ca. 120 °C the phen analogue decomposes in a single step, at *ca.* 350 °C.

The water losses are accompanied by interlayer contraction in all cases [with α-$Zr(HPO_4)_2(bipy)_{0.25}\cdot H_2O$ loss of water leads to layer *expansion*[1]]. Further, on standing only γ-$Zr(HPO_4)_2(bipy)_{0.48}$ reacquires ambient water to return to the original d_{002} = 14.7 Å [from d_{002} (anhydrous phase) = 13.8 Å *i.e.* a layer contraction of *ca.* 0.34 Å; according to ref. 9 the phosphate layers in the α form contract by *ca.* 0.90 Å per H_2O molecule lost]. The other materials go through metastable intermediate phases before returning to stable partially contracted ones, as shown in Table 1. Only γ-$Zr(HPO_4)_2(dmphen)_{0.48}$ shows the *ca.* 1 Å contraction found previously in the α phase,[2] whereas the contraction is higher for γ-$(phen)_{0.50}$ and γ-$(dmphen)_{0.28}$.

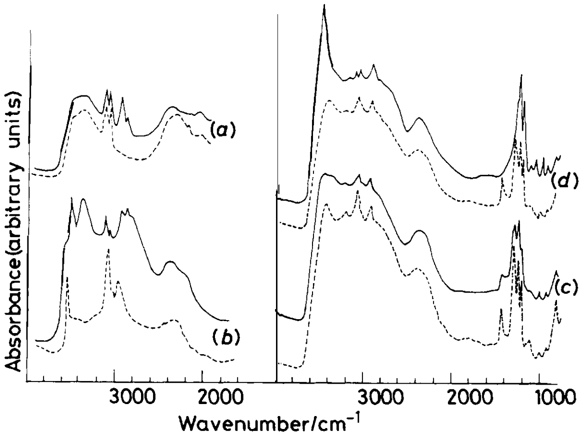

Figure 2. I.r. spectra of intercalated materials (see Figure 1). ——, as prepared; – – – –, after heating at 220 °C for 2 h

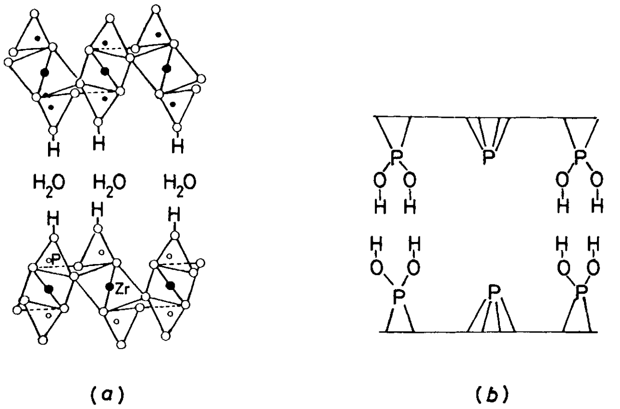

Figure 3. Schematic diagram of the interlayer believed to be present in γ-$Zr(HPO_4)_2{\cdot}2H_2O$: (*a*) according to the partial *X*-ray structure determination of Yamanaka and Tanaka;[7] (*b*) reconstructed on the basis of the high-resolution n.m.r. study of Clayden[10]

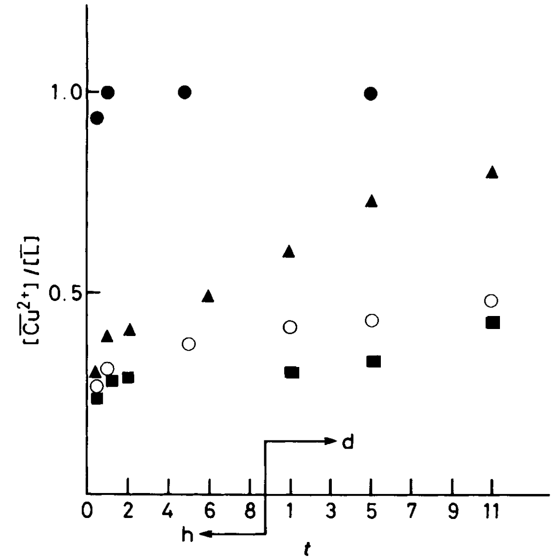

Figure 4. Uptake of Cu^{2+} by amine-intercalated materials: ■, γ-$Zr(HPO_4)_2(bipy)_{0.48}{\cdot}0.3H_2O$, ▲, γ-$Zr(HPO_4)_2(phen)_{0.50}{\cdot}3H_2O$, ●, γ-$Zr(HPO_4)_2(dmphen)_{0.28}{\cdot}2H_2O$, and ○, γ-$Zr(HPO_4)_2(dmphen)_{0.48}{\cdot}2.2H_2O$

Clearly, as water is lost the amine readjusts in orientation between the phosphate layers, *i.e.* there is specific hydrogen bonding between the P–OH groups and the amine in each case. Thus, the i.r. spectrum of γ-$Zr(HPO_4)_2(bipy)_{0.48}{\cdot}0.3H_2O$ shows no lattice water $\nu(OH)$ bands at *ca.* 3 500 cm^{-1} but does show a $\nu(OH)$ band at 2 925 cm^{-1}, which is no longer present after dehydration (Figure 2). These results suggest that the water molecule is involved in strong hydrogen bonding.

Unfortunately, it is not easy to suggest a possible orientation of the bipy between the layers, in the absence of a crystal-structure analysis of the starting γ-$Zr(HPO_4)_2{\cdot}2H_2O$. Two models of the interlayer region in γ-$Zr(HPO_4)_2{\cdot}2H_2O$ are available in the literature. In the first, based on partial x.r.d. results, Yamanaka and Tanaka[7] suggest that the basal phosphate groups are packed much closer than is the case for the α analogue (leading to a basal lateral dimension of 3.3 *vs.* 5.2 Å for the α form) and the free P–OH groups point directly towards one another in the interlayer as shown schematically in Figure 3 (presumably there is strong directional hydrogen bonding between these groups and the water molecules to allow such a high interlayer distance). More recently, Clayden,[10] on the basis of high resolution magic angle spinning (m.a.s.) n.m.r. studies, put forward a model in which only half of the phosphate groups present have exchangeable protons, *i.e.* 'naked' P are also present.[10] Although the orientations of the $P(OH)_2$ and P groups are not known, the interlayer region would be expected to be a mixture of hydrophobic and hydrophilic environments.

Which of these two models better rationalises the difference in stoicheiometry and interlayer distance between the amine intercalates of α-and γ-zirconium phosphate? Recalling that anhydrous γ-$Zr(HPO_4)_2$ has d_{002} = 9.4 Å, the expansion of 13.8 − 9.4 = 4.4 Å for the bipy-containing material suggests that the amine lies almost flat between the layers (bipy has a thickness[11] of *ca.* 3.3 Å). On the Yamanaka model, this implies that there is a high packing density within the layers, with the amine straddling more than one basal unit, leaving little space for water molecules. Similar comments apply to γ-$Zr(HPO_4)_2(dmphen)_{0.28}{\cdot}2H_2O$, which has an even smaller interlayer distance when the water is removed. All the changes point to the Yamanaka model, because Clayden's model would give rise to intercalation of the (hydrophobic) amine in the channels formed by the naked P atoms.

Copper(II) *Uptake and Pillar Formation.*—Inspection of Figure 4 shows that γ-$Zr(HPO_4)_2(dmphen)_{0.28}{\cdot}2H_2O$ takes up Cu^{2+} the fastest; this is in line with intuition because it has the lowest interlayer ligand density and hence easier accessibility to metal ions. A ratio $[Cu^{2+}]:[dmphen] = 1:1$ is arrived at after *ca.* 1 h. The other three materials, all of which have a higher ligand density, all take up Cu^{2+} much more slowly. However, the order is not that expected from simple ligand steric requirements, bipy > phen > dmphen; uptake is slowest for bipy (*i.e.* for the material with both high ligand density and lowest d_{002})· This provides further indirect evidence for the presence of differing orientations of the amines between the layers, and hence different accessibilities.

After 11 d, both γ-$Zr(HPO_4)_2(bipy)_{0.48}{\cdot}0.3H_2O$ and γ-$Zr(HPO_4)_2(dmphen)_{0.48}{\cdot}2.2H_2O$ had arrived at a $[Cu^{2+}]:[L]$ ratio of 0.5:1, whereas the phen analogue loaded more Cu^{2+} to give $[Cu^{2+}]:[L] = 0.8:1$. The final materials are listed in Table 3.

The γ-$Zr(HPO_4)_2(dmphen)_{0.48}$-intercalated material gives rise to intermediates when withdrawn along the uptake curve and these are so complex that factors other than ligand orientation operate. Thus, at $[\gamma\text{-}Zr(HPO_4)_2(dmphen)_{0.48}{\cdot}2.2H_2O]:[Cu^{2+}] = 0.25:1$, Figure 6, the same interlayer distance is obtained [although differing in overall x.r.d. pattern, *i.e.* (**3**) and (**4**) of Table 3 are not isostructural] as that of the final phase given by γ-$Zr(HPO_4)_2Cu_{0.28}(dmphen)_{0.28}{\cdot}2H_2O$ in which $[Cu^{2+}]:[L] = 1:1$. This is an indication that: (*i*) specific interlayer sites are present (which are different from those in the

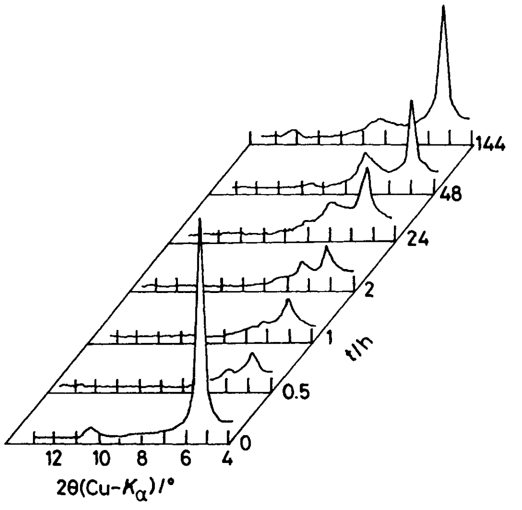

Figure 5. X.r.d. changes of the material with $\overline{[Cu^{2+}]:[(dmphen)_{0.28}]}$ = 1:1 after various times of contact in mother-liquor and subsequent drying

Table 2. *X*-Ray diffraction data for amine intercalates

d/Å	*I*	*d*/Å	*I*	*d*/Å	*I*	*d*/Å	*I*
γ-$Zr(HPO_4)_2(bipy)_{0.48}{\cdot}0.3H_2O$				γ-$Zr(HPO_4)_2(phen)_{0.50}{\cdot}3H_2O$			
14.71	100	3.77	20	18.60	100	3.30	20
6.53	3	3.53	3	9.4	20	3.25	20
6.32	3	3.23	20	5.82	20	3.15_5	3
5.21	3	3.13	3	4.97	20	3.11	3
4.51	3	3.58_5	3	4.07	3	3.02_5	3
3.96	20	2.36	3	3.94	3	2.89	3
				3.64_5	3	2.71	8
				3.42	3	2.66	3
γ-$Zr(HPO_4)_2(dmphen)_{0.28}{\cdot}2H_2O$				γ-$Zr(HPO_4)_2(dmphen)_{0.48}{\cdot}2.2H_2O$			
16.71	100			19.40	100	3.76	7
8.49	3			9.92	7	3.53	3
4.20	8			6.20	3	3.32	35
3.63	7			5.65	3	3.18	3
3.29	20			4.87	3	2.90	3
3.18	3			4.58	3	2.82	3
3.82	3			4.40	3	2.74	3
2.60	3			4.11	3	2.67	8
				4.03	8		

α analogue, where partial elution of dmphen occurs on metal-ion exchange[4]) and (*ii*) that considerable interlayer rearrangement occurs in the second stage of the uptake.

For uptake of Cu^{2+} by γ-$Zr(HPO_4)_2(dmphen)_{0.28}{\cdot}2H_2O$, the intermediates formed are even more complex and their time course of formation (Figure 5) is not that expected simply for co-ordination of the metal ion to the ligand. The x.r.d. patterns of Figure 5 refer to samples withdrawn at set time intervals, starting from 1 h after contact. In other words, the amount of Cu^{2+} is the *same* for each point. Despite this (and differently from bipy and phen, which do not show phase changes to the final forms of Table 3 during uptake of Cu^{2+}) some 6 d are required before the pure expanded phase, d_{002} = 17.7 Å, is given. Before this stage is reached (*i.e.* after 2 h) internal rearrangements through almost disordered phases are discernible, among which is a layered one with d_{002} = 14.50 Å. The latter then disappears and a phase with d_{002} = 12.26 Å appears [γ-$Zr(HPO_4)_2{\cdot}2H_2O$ itself?] before arriving at the final material in Table 3.

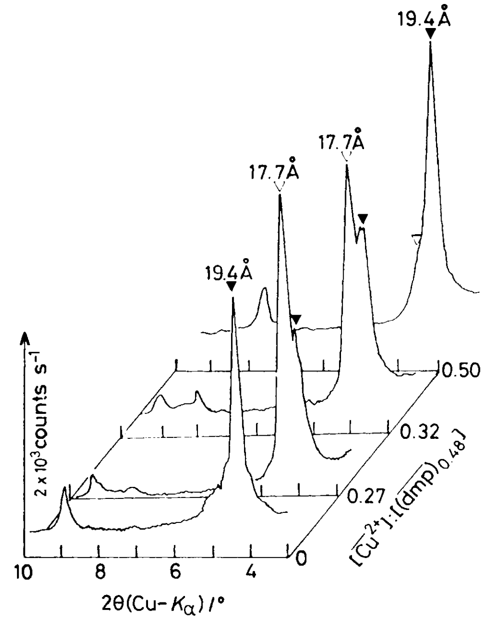

Figure 6. X.r.d. changes of the material with $\overline{[Cu^{2+}]:[(dmphen)_{0.48}]}$ during uptake

The Cu^{2+}-exchanged materials of Table 3 do not undergo expansion on uptake of Cu^{2+}, so that, as before,[1–4] we use electronic and e.s.r. spectra to probe whether the metal ion is merely exchanged into the all-O cavities or co-ordinated to the intercalated amine. The e.s.r. spectra of the materials of Table 3 and their low-$[Cu^{2+}]$ doped analogues (nominally 5% Cu^{2+}, prepared for higher resolution of the more diagnostic ∥ components but also to ensure that we are not concerned with organic fragments in solid solution) are shown in Figure 7.

The Cu^{2+}-phen material [*i.e.* (**2**) of Table 3] gives a *d–d* band

Table 3. Formulation of Cu^{2+}-exchanged materials and their e.s.r. data (*X*-band, 77 K)

	Material	d_{002}/Å	E.s.r.			
			g_1	g_2	g_3	$A_{\parallel}$/(G)
(1)	γ-$ZrH_{1.56}Cu_{0.22}(bipy)_{0.48}(PO_4)_2{\cdot}0.5H_2O$	14.2_4	2.238	2.076	—	—
	5% Cu^{2+}-exchanged		2.285	2.086	—	122
(2)	γ-$ZrH_{1.2}Cu_{0.4}(phen)_{0.50}(PO_4)_2{\cdot}2H_2O$	18.6	2.225	2.098	1.89	<50
	5% Cu^{2+}-exchanged		2.244	2.075	—	160
(3)	γ-$ZrH_{1.5}Cu_{0.25}(dmphen)_{0.48}(PO_4)_2{\cdot}2.7H_2O$	19.4	2.375	2.13	2.024	110
(4)	γ-$ZrH_{1.76}Cu_{0.12}(dmphen)_{0.28}(PO_4)_2{\cdot}1.5H_2O$	17.7	2.388	2.13	2.024	60
	5% Cu^{2+}-exchanged		2.364	2.13	—	—

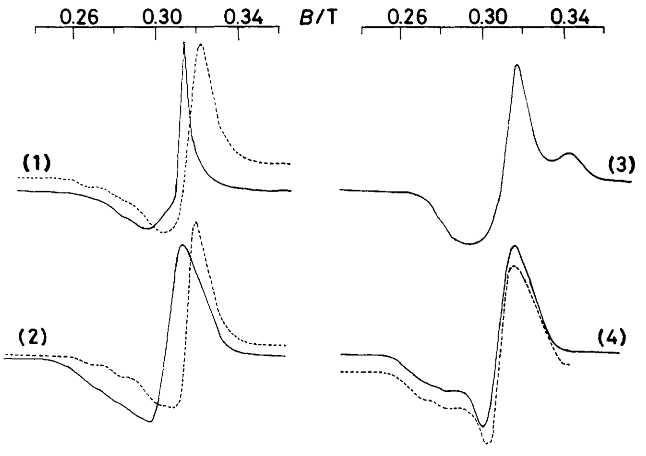

Figure 7. E.s.r. spectra (77 K, X-band) of Cu^{2+}-exchanged materials. Numbering as in Table 3. – – – –, Diluted (5% nominal Cu^{2+}) materials

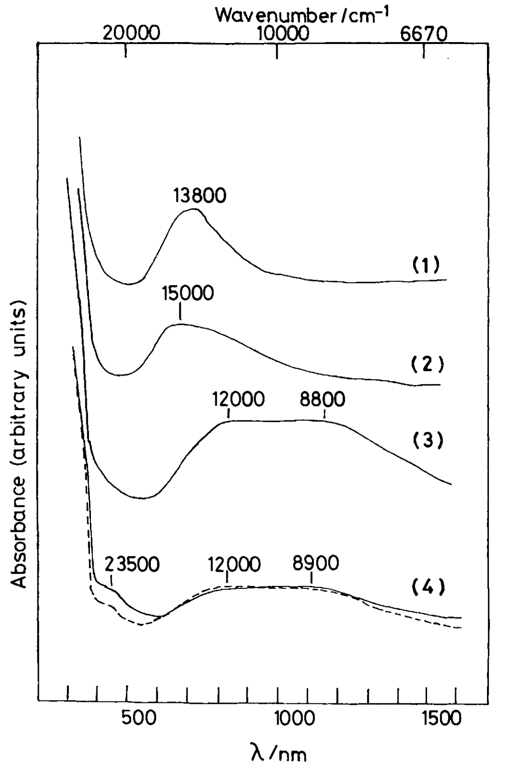

Figure 8. Electronic spectra (as reflectance) of Cu^{2+}-containing materials. Numbering as in Table 3. – – –. The intermediate of Figure 6 (see text)

(Figure 8) at 15 000 cm^{-1} {*i.e.* lying at an energy higher than for both α-$ZrH_{1.6}[Cu(phen)_2]_{0.20}(PO_4)_2$ and α-$ZrH[Cu(phen)]_{0.50}\cdot 3H_2O$[2]} with a $g_\perp$ value of 2.22_5. Both values are indicative of a tetragonal octahedral geometry and in agreement with the presence of a $[CuN_2O_2 + 2O(x)]$ formulation for the cation between the layers,[12] *i.e.* a complex pillar has been formed [$O(x)$ refers to matrix oxygen atoms]. The magnetically dilute e.s.r. spectrum of the material essentially confirms this conclusion: $A_\parallel = 160$ G.[11] Conversely, γ-$ZrH_{1.56}Cu_{0.22}(bipy)_{0.48}(PO_4)_2\cdot 0.5H_2O$ gives a $g_\parallel$ value which, although characteristic of co-ordination of the Cu^{2+} to the intercalated bipy rather than simply bonding to the cavity oxygen atoms, is higher than expected for a tetragonal geometry.[13] In addition, the *d–d* spectrum shows a major band at 13 800 cm^{-1}. Both values are very different than those found for the analogues with α-zirconium phosphate:[1] α-$ZrH_{1.5}[Cu(bipy)(H_2O)]_{0.25}(PO_4)_2\cdot 3H_2O$ was assigned a tetragonal octahedral $[CuN_2O + 2O(x)]$ geometry on the basis of *d–d* bands at 14 800 and 15 750 cm^{-1} with e.s.r. parameters $g_\parallel = 2.23_8$ and $A_\parallel = 165(5) \times 10^{-4}$ cm^{-1}.[2] They are, instead, in agreement with the presence of a significant pseudo-tetrahedral distortion to give $[CuN_4 + (1 \text{ or } 2)O(x)]$ or $[CuN_2O_2 + (1 \text{ or } 2)O(x)]$. The latter possibility, which implies that half of the bipy molecules are present in solid solution, may be excluded because dehydration causes no change in both spectra. Use of literature correlations[14] gives a dihedral angle between the bipy-containing planes of *ca.* 30°.

The dmphen analogues (**3**) and (**4**) of Table 3 have very different spectral characteristics. Both show absorption spectra with *d–d* bands at the same low energy: 12 000 and 8 800 cm^{-1}. Further, the high $g_\perp$ parameters are indicative of Cu–O bonding alone, *i.e.* after exchange the Cu^{2+} does not co-ordinate to the dmphen but to the cavity oxygen atoms. There is evidence, however, that this oxygen co-ordination is not simply inside separated cavities within the interlayer. Thus, the e.s.r. spectrum of the Cu^{2+}-doped form is almost identical to that of the undiluted form, *i.e.* (**4**) of Table 3 (see Figure 7). Further, material (**4**) has a *d–d* spectrum with no near-u.v. absorption, whereas (**3**) shows a clear low-intensity peak at 23 500 cm^{-1}. In addition, the former (with $d_{002} = 19.4$ Å) clearly goes through an intermediate related to (but not isostructural with) (**3**) during uptake of Cu^{2+}, as shown by the 'x.r.d. titration' in Figure 6. However, the purest intermediate phase appears at *ca.* $[Cu^{2+}]:[(dmphen)_{0.48}] = 1:4$, *i.e.* corresponding to material (**4**) in Table 3.

When a material was prepared with this ratio and its x.r.d. pattern monitored with time immediately after separation from the mother-liquor it first gave $d_{002} = 19.4$ Å and then went through a recrystallisation to give the $d_{002} = 17.7$ Å phase after 4 d.

These results can be rationalised if it is assumed that a binuclear species is present in (**3**) and (**4**), possibly related to copper(II) acetate[15] or the binuclear 1 : 1 copper(II)–pyridine N-oxide complexes[16] (as also suggested by the presence of half-field $M = \pm 1$ lines in the e.s.r. spectra). This species has H_2O molecules as bridges in the $(dmphen)_{0.48}$ case, but cavity oxygens in $(dmphen)_{0.28}$. Although speculative, this model would nicely account for the absence of an autoreduction in all three dmphen-containing materials (as instead found in the α analogue[4]). It also provides some evidence that the Clayden model for the interlayer may be incorrect. Thus, the dmphen covers about half of the available P(OH) sites in the interlayer of γ-$Zr(HPO_4)_2\cdot 2H_2O$. If the sites remaining were naked (and ordered) P, no oxygen atoms would be available to allow formation of binuclear species. This is yet further, indirect, evidence that the interlayer in γ-zirconium phosphate is as described by Yamanaka and Tanaka.[7] Although confirmation must await a full crystal (or powder X-ray Rietvelt) structure analysis of the parent γ-$Zr(HPO_4)_2\cdot 2H_2O$ matrix, co-ordination of the amines to other metal ions should throw further light on the nature of the suggested binuclear sites. This work is underway.

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References

1 C. Ferragina, M. A. Massucci, A. La Ginestra, P. Patrono, and A. A. G. Tomlinson, *J. Phys. Chem.*, 1985, **89**, 4762.
2 C. Ferragina, M. A. Massucci, A. La Ginestra, P. Patrono, and A. A. G. Tomlinson, *J. Chem. Soc., Dalton Trans.*, 1986, 265.

3 Part 4, C. Ferragina, M. A. Massucci, A. La Ginestra, P. Patrono, and A. A. G. Tomlinson, *J. Chem. Soc., Dalton Trans.*, 1988, 851.

4 C. Ferragina, M. A. Massucci, A. La Ginestra, P. Patrono, and A. A. G. Tomlinson, *Mater. Res. Bull.*, 1987, 261.

5 E. P. Giannelis, E. G. Rightor, and T. J. Pinnavaia, *J. Am. Chem. Soc.*, 1988, **110**, 3880 and refs. therein.

6 A. Clearfield, in 'Inorganic Ion-Exchange Materials,' ed. A. Clearfield, CRC Press, Boca Raton, Florida, 1982, Ch. 1; J. M. Troup and A. Clearfield, *Inorg. Chem.*, 1977, **16**, 3311.

7 S. Yamanaka and M. Tanaka, *J. Inorg. Nucl. Chem.*, 1979, **41**, 45.

8 A. Clearfield and J. A. Stynes, *J. Inorg. Nucl. Chem.*, 1964, **26**, 117.

9 G. Alberti and U. Costantino, in 'Intercalation Chemistry,' eds. M. S. Whittingham and A. J. Jacobson, Academic Press, New York, 1982, Ch. 5.

10 N. J. Clayden, *J. Chem. Soc., Dalton Trans.*, 1987, 1877.

11 A. I. Kitaigorodsky, 'Molecular Crystals and Molecules,' Academic Press, New York, 1973; G. O. Morpurgo, G. Dessy, and V. Fares, *J. Chem. Soc., Dalton Trans.*, 1984, 461 and refs. therein.

12 B. J. Hathaway, in 'Comprehensive Coordination Chemistry,' Pergamon, Oxford, 1987, vol. 5; I. N. Marev, V. K. Belyaeva, E. B. Smirnova, and I. F. Dolmanova, *Inorg. Chem.*, 1978, **17**, 1667.

13 H. Yokoi and A. W. Addison, *Inorg. Chem.*, 1977, **16**, 1341.

14 A. W. Addison, in 'Copper Coordination Chemistry, Biochemical and Inorganic Perspectives,' eds. K. D. Karlin and J. Zubieta, Adenine Press, New York, 1981.

15 G. F. Kokoszka, H. C. Allen, jun., and G. Gordon, *J. Chem. Phys.*, 1965, **42**, 3693.

16 K. T. McGregor, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, 1973, **12**, 731 and refs. therein.

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