Pillaring of Layers in α-Zirconium Phosphate by 1,10-Phenanthroline and Bis(1,10-phenanthroline)copper(II): Formation of Complex Pillars *in situ*

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The complex $[Cu(phen)_2]^{2+}$ (phen = 1,10-phenanthroline) can be diffused between the layers of α-zirconium phosphate only if the layers are first pre-swelled by preparing the diethanol intercalate, α-$Zr(HPO_4)_2(EtOH)_2$. At maximum uptake a material of formula α-$ZrH_{1.6}[Cu(phen)_2]_{0.20}(PO_4)_2\cdot3H_2O$ is obtained and no further complex can be intercalated. *X*-Ray and spectroscopic evidence show that the $[Cu(phen)_2]^{2+}$ remains intact after intercalation, and probably has a tetragonal-octahedral geometry. A 'complex pillared' layer structure is still present after the zeolitic water has been removed. However, the geometry adopted by the $[Cu(phen)_2]^{2+}$ is now square-based pyramidal, and it is bonded asymmetrically between the phosphate layers. Further ions (Cu^{2+}, Pd^{2+}, or Ag^+) can be exchanged into the pillared cavities, to form solid solutions. 1,10-Phenanthroline itself diffuses into α-$Zr(HPO_4)_2(EtOH)_2$ to form the 'intercalated ligand' phase α-$Zr(HPO_4)_2(phen)_{0.50}\cdot2H_2O$ at maximum uptake. This is a pure, well ordered Stage I phase with an interlayer distance of 13.58 Å, and it is suggested that the phen is ordered throughout the layers in a 'slanted' fashion. This phase exchanges Co^{2+}, Ni^{2+}, and Cu^{2+} (in the order $Cu^{2+} \gg Co^{2+} > Ni^{2+}$) much more slowly than does the 2,2'-bipyridyl analogue, due to the steric hindrance caused by the bulkier ligand backbone and higher pillar density. Only in the case of Cu^{2+} does subsequent co-ordination to the phen proceed to complete formation of α-$ZrH[Cu(phen)]_{0.50}(PO_4)_2\cdot3H_2O$. In the cobalt and nickel analogues there is competition between phen-co-ordinated and cavity-co-ordinated metal ion. Spectroscopic evidence (u.v.–visible, e.s.r.) is presented which shows that these complex pillars formed *in situ* have very distorted geometries, caused by the steric constraints imposed by the interlayer region.

We recently reported that 2,2'-bipyridyl (bipy) can be diffused between the layers of α-zirconium phosphate provided the latter is first pre-swelled.[1,2] A pure intercalated phase was obtained formulated as α-$Zr(HPO_4)_2(bipy)_{0.25}\cdot2H_2O$, further bipy being then taken up in solid solution to yield α-$Zr(HPO_4)_2(bipy)_{0.35}\cdot2H_2O$; no further bipy could be intercalated. We suggested that this low loading was due to the fact that the bipy adopted a 'sidewise slanted,' transoid, orientation between the zirconium phosphate layers, hence covering up more than two basal units of the structure.[2] Classical ion-exchange uptake measurements and *X*-ray monitoring of the co-ordination of bivalent metal ions to this intercalated bipy were also carried out. It was found that the uptake and co-ordination were separable processes, the latter occurring very much more slowly than in the solution.

This development of an intercalation co-ordination chemistry, combined with a search for efficient pillaring materials for catalytic purposes, has now been extended to the 1,10-phenanthroline (phen) analogue. The aim is to investigate how the rigid backbone structure of phen influences the nature of the pillars formed between the layers.

Experimental

Materials.—Phosphoric acid and $ZrOCl_2\cdot8H_2O$ were Erba RP ACS products; the latter was recrystallised several times from water before use. 1,10-Phenanthroline was of purissimum purity (Fluka). All other products were of the highest purity available and were used as received. The phosphate α-$Zr(HPO_4)_2\cdot H_2O$ and other starting materials were prepared and utilised as reported previously;[2] α-$Zr(HPO_4)_2(EtOH)_2$[3] was prepared fresh before each reaction. The salt $[Cu(phen)_2][ClO_4]_2$ was prepared as reported in the literature[4] and gave satisfactory C, H, and N analyses.

Chemical Analyses and Physical Measurements.—As before, *X*-ray powder diffraction was used to follow phase changes, especially by monitoring the d_{002} reflection and its harmonics. A Philips diffractometer was used (nickel-filtered, Cu-K_α radiation); 2θ angles are believed to be accurate to 0.05°. The uptake of a species from solution was followed by monitoring concentration changes in supernatants *via* both spectrophotometry {at 710 nm for $[Cu(phen)_2]^{2+}$ and at 323 nm for phen} with a Perkin-Elmer 550S instrument and ethylene diaminetetra-acetate (edta) titration (for metal-ion containing solutions). A Mettler 2000C simultaneous t.g./d.s.c. thermal analyser was used to analyse water and amine contents of materials.

X-Ray photoelectron (x.p.e.) spectra were recorded for samples powdered on Scotch tape using a Vacuum Generators VG3 Mark II instrument and internal calibration with the C(1*s*) line. E.s.r. and electronic spectra (reflectance) were obtained as described previously.[2]

Intercalation of $[Cu(phen)_2]^{2+}$.—In initial experiments, batch contacting of α-$Zr(NaPO_4)(HPO_4)\cdot5H_2O$ (1 g) with a 1.5 mmol dm^{-3} solution of $[Cu(phen)_2][ClO_4]_2$ in ethanol–water (1:1), adjusted to pH 3.0 to encourage formation of the highly hydrated hydrogen form α-$Zr(HPO_4)_2\cdot(5 \pm 1)H_2O$,[5] gave only very low loading levels (< 0.03 mole ratio). Presumably, this is due to the large size of the intended guest, despite the fact that

Table 1. Analytical data

Material	d_{002}/Å	phen[a]	Total H_2O[a,b]	M[a]
α-$ZrH_{1.6}[Cu(phen)_2]_{0.20}(PO_4)_2{\cdot}3H_2O$	14.24	17.65 (17.1)	11.6 (12.8)	3.0 (3.0)
α-$ZrH_{1.52}Pd_{0.1}[Cu(phen)_2]_{0.20}(PO_4)_2{\cdot}3H_2O$[c]	14.24	—	—	—
α-$ZrH_{0.23}Cu_{0.67}[Cu(phen)_2]_{0.20}(PO_4)_2{\cdot}4H_2O$[c]	14.24	14.15 (15.0)	15.7 (15.0)	11.5 (11.55)
α-$ZrH_{1.13}Ag_{0.47}[Cu(phen)_2]_{0.20}(PO_4)_2{\cdot}2.5H_2O$[c]	14.24	16.0 (15.55)	9.0 (9.7)	10.9 Ag, 2.70 Cu (11.0 Ag, 2.75 Cu)
α-$Zr(HPO_4)_2(phen)_{0.50}{\cdot}2H_2O$	13.58	22.8 (22.0)	8.4 (8.8)	—
α-$Zr(HPO_4)_2(phen)_{0.50}$	12.62			
α-$ZrH[Cu(phen)]_{0.50}(PO_4)_2{\cdot}3H_2O$	15.77	18.5 (19.6)	12.0 (11.8)	6.65 (6.9)

[a] In %, calculated values are given in parentheses. [b] From t.g., lost at ⩽140 °C; results not entirely reproducible because of ready loss of small amounts of water gained on standing in air. Maximum uptake of cavity ion after repeated batch contact at 60 °C.

the matrix itself has a reasonably large (d_{002} = 10.4 Å)[5] interlayer distance. As before,[2] all subsequent operations were carried out with the metastable dialcohol intercalate (d_{002} = 14.20 Å)[3] as starting material.

A 1.5 mmol dm^{-3} solution (500 cm^3) of $[Cu(phen)_2][ClO_4]_2$ in ethanol–water (1 : 1) was contacted with α-$Zr(HPO_4)(EtOH)_2$ (2.54 mmol) at 25 °C. The suspension was agitated, the supernatant withdrawn periodically (10-cm^3 aliquots) for analysis without dilution {monitoring the band of $[Cu(phen)_2]^{2+}$ at 710 nm}, and the aliquot replaced in the batch. When no further uptake was apparent, the solid was filtered off and dried in air. Phase changes occurring during uptake were monitored separately by contacting a series of batches for various times, filtering off the partially exchanged material, and immediately measuring the *X*-ray pattern. A peak at 2θ = 6.2° (d_{002} = 14.24 Å) accompanied the intercalation process.

Intercalation of 1,10-*Phenanthroline into* α-$Zr(HPO_4)_2(EtOH)_2$.—Freshly prepared α-$Zr(HPO_4)_2(EtOH)_2$ was contacted with a 0.01 mol dm^{-3} solution of phen in ethanol–water (1:1) at 25 °C, exactly as for the bipy analogue.[2] A pure phase, pink in colour, of composition α-$Zr(HPO_4)_2(phen)_{0.50}{\cdot}2H_2O$ (Table 1) and interlayer spacing of 13.58 Å [Figure 3(*b*)] was obtained after leaving the components to stand for 24 h. The use of 0.1 mol dm^{-3} solutions of phen at 25 and 60 °C for longer contact times led to materials containing 0.53 and 0.55 mol of phen per mol of exchanger, respectively. In addition, attempts to obtain a pure layered phase with lower phen loading were unsuccessful: two phases, α-$Zr(HPO_4)_2{\cdot}H_2O$ and that having d_{002} = 13.58 Å, were always obtained.

The pink colour of the material varied in intensity depending on the thermal treatment, which suggested it was due to an impurity. Iron(II) di-imine complexes are known to give an intense absorption band at 20 000 cm^{-1}, with characteristic shoulders at 21 500 and 23 000 cm^{-1}.[6] Although the electronic reflectance spectrum gives similar bands, we could find no trace of iron in the x.p.e. spectrum, nor *via* atomic absorption analysis. The material also showed a very weak anisotropic e.s.r. signal with $g_{\parallel}$ 2.42; g = 2.00. All attempts to remove the colouration, by repeated recrystallisation of the $ZrOCl_2{\cdot}8H_2O$ and phen, washing of glassware with edta, and changing the alcohol used throughout the preparation, were unsuccessful. Although we cannot exclude the presence of iron impurities [the very high ε values of iron(II) di-imine complexes, *ca.* 10^4 dm^3 mol^{-1} cm^{-1},[6] may mean that traces escape detection by the other analytical methods], a second possibility is that the colouration is due to enhancement of low-energy low-intensity transitions in phen itself *via* solid-state effects.

Metal-ion Uptake by α-$Zr(HPO_4)_2(phen)_{0.50}{\cdot}2H_2O$.—A batch method was used, as described for the bipy analogue.[2] In preliminary experiments it was found that metal ions were taken up extremely slowly at 25 °C (weeks to arrive at maximum uptakes). All procedures were therefore carried out on suspensions thermostatted at 60 °C.

In separate experiments, a series of suspensions of 5 mmol dm^{-3} $M(O_2CMe)_2$ + α-$Zr(HPO_4)_2(phen)_{0.50}{\cdot}2H_2O$ (such that $[M^{2+}]$: [intercalated phen] = 1 : 1) was left to stand for various times. Each was filtered, the exchanged material immediately monitored by *X*-ray diffraction, and the supernatant solution analysed by edta titration. The uptake curves are shown in Figure 2.

Metal-ion Exchange into Pillared Cavities.—The intercalate α-$ZrH_{1.6}[Cu(phen)_2]_{0.20}(PO_4)_2{\cdot}3H_2O$ {or α-$ZrH[Cu(OH_2)(phen)]_{0.50}(PO_4)_2{\cdot}2.6H_2O$} was contacted with 5 mmol dm^{-3} aqueous solutions of $Cu(O_2CMe)_2$, $AgNO_3$, or $PdCl_2$. The solids were filtered off when no exchange of metal ion (analysis of supernatants) was complete. Analyses of all the materials are listed in Table 1.

Results and Discussion

Intercalated $[Cu(phen)_2]^{2+}$: *Uptake and Stability.*—The uptake of $[Cu(phen)_2]^{2+}$ by α-$Zr(HPO_4)_2(EtOH)_2$ as a function of time is shown in Figure 1. It occurs *via* ion exchange, since the pH of the supernatant decreases, from 6.1 to *ca.* 2.4, upon completion; 60% of the maximum loading is achieved after 30 min, 85% in 24 h, and 100% after 5 d. The final product has the composition α-$ZrH_{1.6}[Cu(phen)_2]_{0.20}(PO_4)_2{\cdot}3H_2O$, and gives an *X*-ray pattern expected for a well ordered material having an interlayer distance of 14.24 Å [Figure 3(*a*)]. The *X*-ray patterns of solids containing less than 0.14 mol of complex per mol of exchanger show the presence of this new phase, together with α-$Zr(HPO_4)_2{\cdot}6H_2O$, the latter decreasing as the uptake proceeds and being completely absent at 14% loading. Examination of the d_{004} reflections in the *X*-ray patterns demonstrates that the new phase is actually a mixture of two phases with very slightly different interlayer distances. The patterns also suggest that subsequent complex intercalation occurs *via* solid solution.

It was initially thought that further intercalation of complex was hindered by the strong decrease in pH. However, repeated renewal of the contact solution gave exactly the same final material.

Discussion of the thermal behaviour and spectra (electronic reflectance and e.s.r.) is confined to the material obtained after

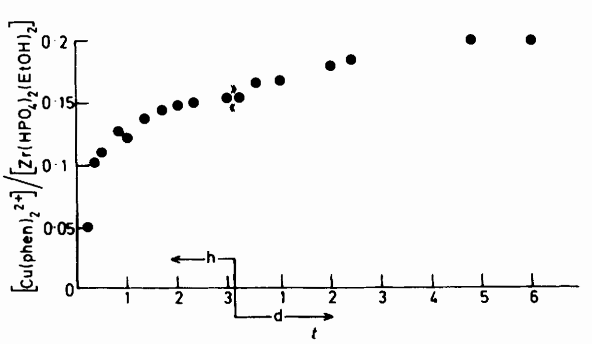


Figure 1. Curve showing uptake of $[Cu(phen)_2]^{2+}$ by α-$Zr(HPO_4)_2(EtOH)_2$ at 25 °C

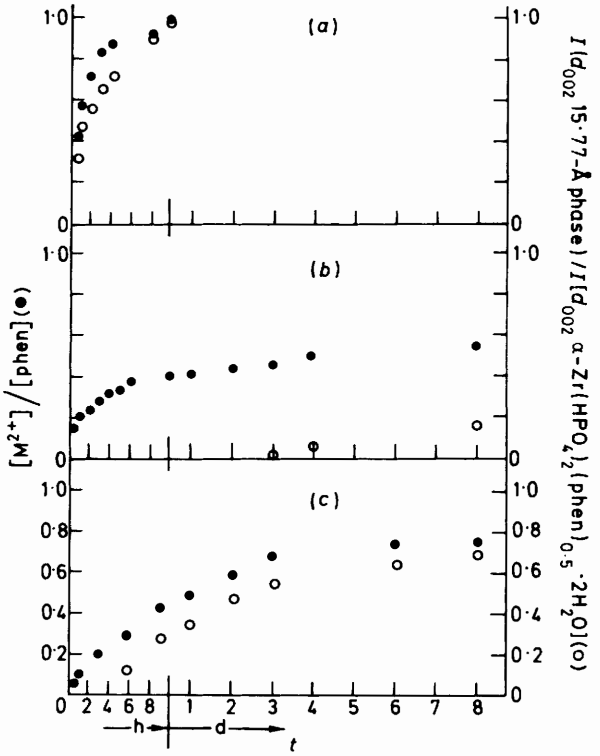


Figure 2. Uptake (●) and time course of the phase change to complex pillar (○) (as measured by estimates of the relative intensities of the d_{002} reflections *via* their areas: height × full width at half-maximum) for Cu^{2+} (*a*), Ni^{2+} (*b*), and Co^{2+} (*c*)

contact for 5 d. The material α-$ZrH_{1.66}[Cu(phen)_2]_{0.17}(PO_4)_2\cdot 3H_2O$ (d_{002} = 14.24 Å) obtained after contact for 24 h behaves in exactly the same way.

The t.g. results [Figure 4(*a*)] demonstrate that the interlayer water is zeolitic, being lost up to 200 °C and rapidly regained from the surroundings. The dehydration–rehydration cycle can be repeated four or five times with little significant loss of crystallinity of the material. The *X*-ray pattern of the dehydrated material shows d_{002} = 13.58 Å, an indication that little 'roof collapse' of the layers occurs. Indeed, despite major amorphisation as the temperature is raised, the layer structure is retained even at 400 °C, the interlayer distance being 13.3 Å. Above this temperature, weight losses occur in various stages, involving elimination of phen, condensation of the phosphate to pyrophosphate, and combustion of the remaining interlayer carbon.

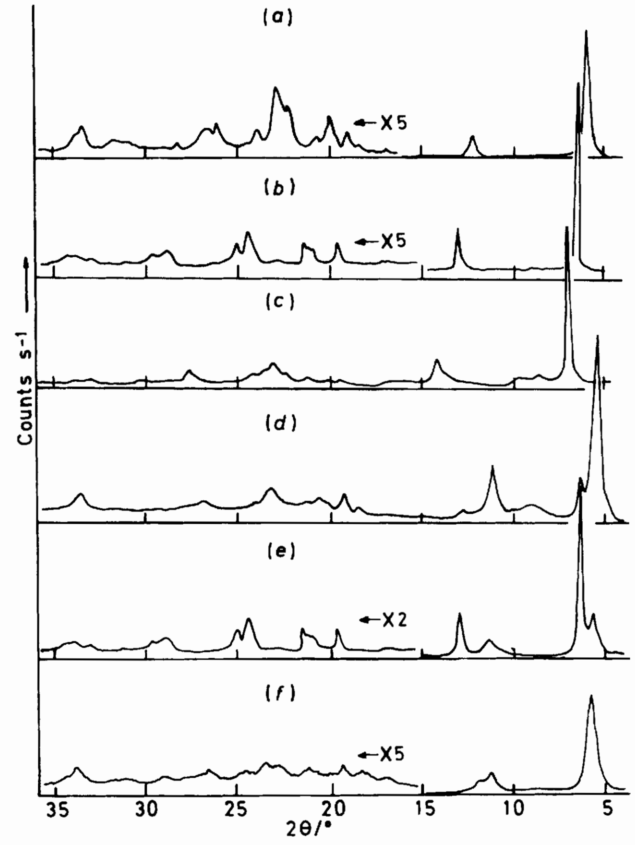


Figure 3. *X*-Ray powder patterns of materials at maximum loading: (*a*) α-$ZrH_{1.6}[Cu(phen)_2]_{0.20}(PO_4)_2\cdot 3H_2O$, (*b*) α-$Zr(HPO_4)_2(phen)_{0.50}\cdot 2H_2O$, (*c*) α-$Zr(HPO_4)_2(phen)_{0.50}$, (*d*) α-$ZrH[Cu(phen)]_{0.50}(PO_4)_2\cdot 3H_2O$, (*e*) α-$ZrH[Co(phen)]_{0.50}(PO_4)_2\cdot 3H_2O$, and (*f*) α-$ZrH[Ni(phen)]_{0.50}(PO_4)_2\cdot 3H_2O$

Local Pillar Structure in α-$ZrH_{1.6}[Cu(phen)_2]_{0.20}(PO_4)_2\cdot 3H_2O$.—Complexes containing $[Cu(bipy)_2]^{2+}$ and $[Cu(phen)_2]^{2+}$ are known to give similar electronic properties,[4,7] so that the extensive structure–spectra correlations established for $[Cu(bipy)_2]^{2+}$ complexes in the literature can be used for assessing gross changes in sterochemistry about the $[Cu(phen)_2]^{2+}$ pillar on intercalation.

The electronic reflectance spectrum of α-$ZrH_{1.6}[Cu(phen)_2]_{0.20}(PO_4)_2\cdot 3H_2O$ is characterised by a single, broad, *d–d* band at 13 900 cm⁻¹ [Figure 5(*a*)]. This may be compared with a value of 15 150 cm⁻¹ found for $[Cu(bipy)_2(O_2ClO_2)]ClO_4$, which has a distorted tetragonal-octahedral CuN_4 + 2O geometry with long Cu···O bonding interactions.[8] The lowering in energy may be a consequence of shorter Cu···O axial interactions and/or the fact that lattice phosphate groups are involved, but the energy is still within the range expected for tetragonal-octahedral geometry.[7] The e.s.r. spectrum (Table 2) substantiates this gross assignment, being 'normal' in type, *i.e.* with $g_{\parallel} > g_{\perp}$, so that the presence of geometries giving rise to d_{z^2} ground states (*e.g.* trigonal bipyramidal, *cis*-octahedral) can be excluded. The $g_{\parallel}$ value compares well with that for $[Cu(bipy)_2(O_2ClO_2)]ClO_4$,[8] and is considerably different than those ($g_{\parallel}$ 2.3–2.45)[9] characteristic of all-oxygen tetragonal-octahedral environments. The absence

Table 2. E.s.r. parameters of Cu^{2+}-loaded materials

Material	Treatment	$g_{\parallel}$	g	$10^4 A_{\parallel}/cm^{-1}$
α-$ZrH_{1.6}[Cu(phen)_2]_{0.20}(PO_4)_2 \cdot 3H_2O$	As prepared	2.278	2.073	137(3)
	After dehydration at 140 °C for 2 h	2.242	2.076	150(2)
	Rehydrated	2.275	2.084	138(3)
	After calcination at 550 °C	2.377	2.077	112(4)
	After calcination at 1 100 °C	2.255	2.077	140(2)
2% Cu^{2+}/α-$Zr(HPO_4)_2(phen)_{0.50} \cdot 2H_2O$	As prepared	2.245	2.073	140(3)
	After dehydration at 140 °C for 2 h	2.265	2.075	140(5)
α-$ZrH[Cu(phen)]_{0.50}(PO_4)_2 \cdot 3H_2O$	As prepared		see text	
	After dehydration at 140 °C for 2 h, then annealed at room temperature	2.285	2.071	72(3)
	After dehydration at 140 °C for 2 h, then annealed at 77 K	2.238	2.085	< 50

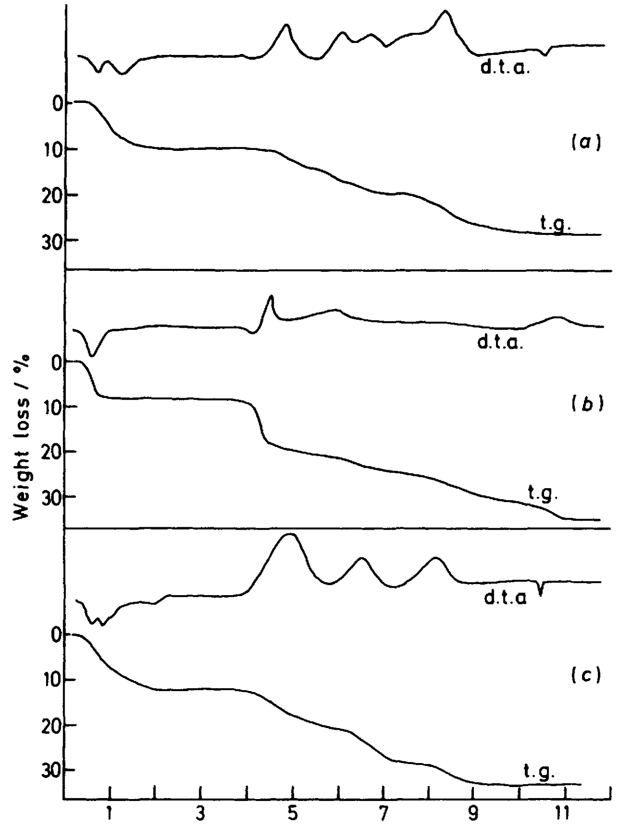


Figure 4. T.g. and d.t.a. curves for (*a*) α-$ZrH_{1.6}[Cu(phen)_2]_{0.20}(PO_4)_2 \cdot 3H_2O$, (*b*) α-$Zr(HPO_4)_2(phen)_{0.50} \cdot 2H_2O$, and (*c*) α-$ZrH[Cu(phen)]_{0.50}(PO_4)_2 \cdot 3H_2O$

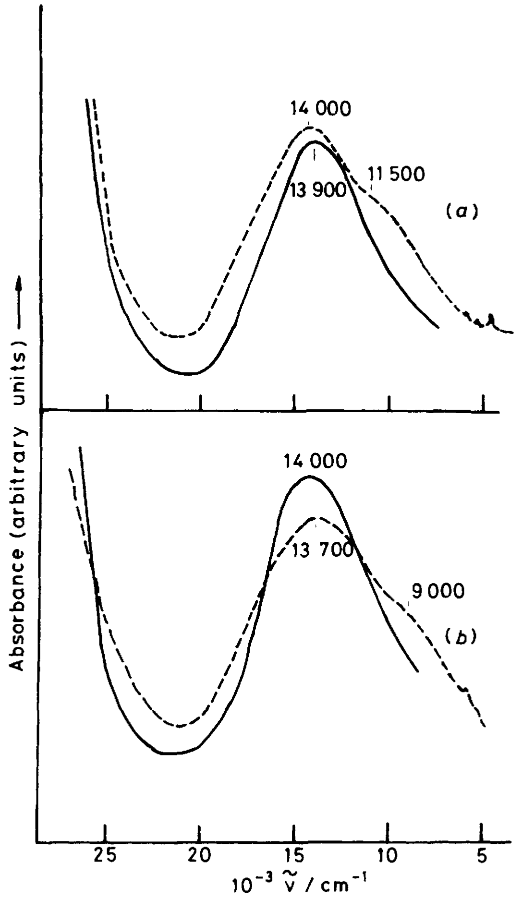


Figure 5. Electronic reflectance spectra of Cu^{2+}-containing materials: (*a*) α-$ZrH_{1.6}[Cu(phen)_2]_{0.20}(PO_4)_2 \cdot 3H_2O$ and (*b*) α-$ZrH[Cu(phen)]_{0.50}(PO_4)_2 \cdot 3H_2O$; ——, as prepared; – – –, after heating at 140 °C for 2 h

of two signals (one from a pillar-complexed Cu^{2+} and the other from an all-oxygen cavity-complexed Cu^{2+}) confirms that there has been no demetallation of the complex during intercalation {*cf.* $[Cu(bipy)_2]^{2+}$ which dissociates[2] to give $[Cu(bipy)]^{2+}$ + bipy during diffusion into α-$Zr(HPO_4)_2(EtOH)_2$[2]}. However, there is evidence that the matrix induces distortion in the pillar. The very clear hyperfine splitting on $g_{\parallel}$ gives an $A_{\parallel} = 140 \times 10^{-4}$ cm^{-1}, considerably lower than in tetragonal-octahedral model complexes[8] and indicative of some distortion of the phen molecules out of the tetragonal plane.

On dehydration the e.s.r. spectra remain essentially the same, apart from a lower resolution of the hyperfine components, an indication that the pillars are stable and relatively rigid. The *d–d* spectrum changes considerably, however, the main peak remains at 14 000 cm^{-1}, but with a clear shoulder at *ca.* 11 500 cm^{-1}. Both the band shapes and energies are in very good agreement with the presence of a square-based pyramidal CuN_4O moiety.[7] Given that the interlayer distance changes little on dehydration at 110 °C, this result implies that the co-ordination of $[Cu(phen)_2]^{2+}$ to the matrix is conditioned by the bulk and orientation of the phen molecules, which hinder

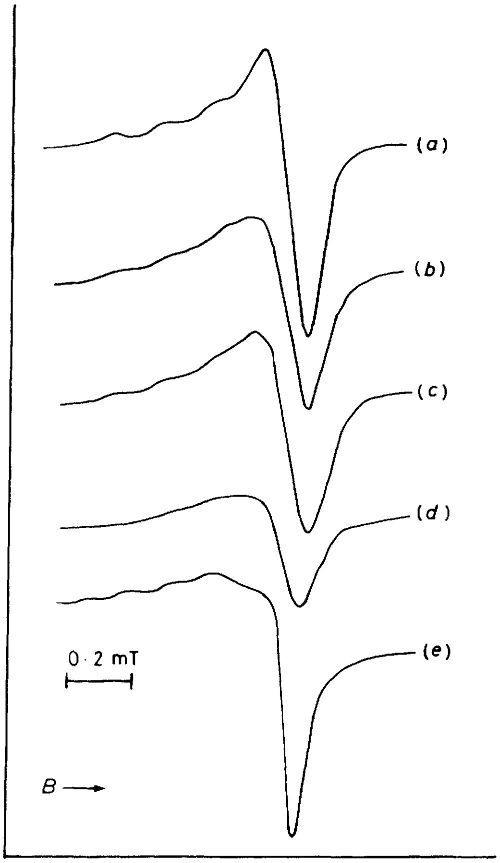


Figure 6. E.s.r. spectra (*X*-band) of α-ZrH$_{1.6}$[Cu(phen)$_2$]$_{0.20}$(PO$_4$)$_2$·3H$_2$O: (*a*) as prepared, (*b*) after heating *in vacuo* at 140 °C for 2 h, (*c*) on rehydration after three cycles of dehydration *in vacuo* at 140 °C for 2 h, (*d*) after heating at 550 °C *in vacuo* for 2 h, and (*e*) after heating at 1 100 °C for 3 h

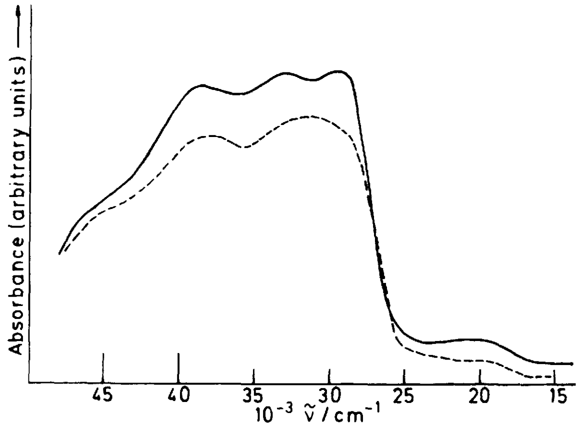
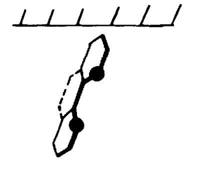


Figure 7. Electronic reflectance spectra of α-Zr(HPO$_4$)$_2$(phen)$_{0.50}$·2H$_2$O: ——, as prepared; – – –, after heating *in vacuo* at 140 °C for 2 h

anchorage of the pillar to both the 'roof' and 'floor' of the matrix *via* a second Cu ··· O–P$<$ interaction.

Particularly interesting is the fact that hyperfine structure, now characteristic of an all-oxygen environment, is visible even after calcination of the material at 1 100 °C [Figure 6(*e*)]. At such a high metal-ion loading, this result implies that the Cu^{2+} ions are well dispersed throughout the layers, not only after the removal of the phen, but also after completion of the phosphate ⟶ pyrophosphate condensation.

α-Zr(HPO$_4$)$_2$(phen)$_{0.50}$·2H$_2$O.—A major point of interest is the fact that, although bulkier and more rigid than bipy, the loading of phen into α-Zr(HPO$_4$)$_2$(EtOH)$_2$ is greater than that of bipy.[2] Although many lateral packing modes between the layers can be envisaged, the *X*-ray powder pattern is characteristic of a well ordered phase (very sharp d_{002} peak). This strongly suggests that a single type of packing, with well defined intercalant layer angle, is present. If we assume, as before,[2] that there is no inhomogeneous intra-layer 'ruffling' of the Zr atoms after insertion of the phen, the free height available is *ca.* 7.38 Å [*i.e.* 13.58 minus the layer thickness (6.3 Å)[10]]. This figure is much higher than would be expected for an orientation in which the phen lies completely flat between the layers. Particularly attractive is an orientation in which the phen molecule is oriented in a slanted fashion with respect to the layers. An angle of *ca.* 65° between the phen plane and the phosphate layer would then give rise to an interlayer distance of *ca.* 13.7 Å and the projection of the phen molecule on the basal plane of the phosphate layers would cover them much less than is the case for the bipy analogue[2] hence allowing access to more phen molecules.



Removal of the water gives partial, reversible, layer shrinkage (to 12.62 Å). Now, free phen, Hphen$^+$, and H$_2$phen^{2+} give characteristic bands in the u.v. region which allow them to be distinguished from one another. The bands at 265 and 229 nm for free phen shift to 272 and 220 nm on monoprotonation, and a weak shoulder at 290 nm disappears. For the diprotonated form, the long-wavelength band shifts to 279 nm whilst the short-wavelength band shifts to 224 nm, a new band appearing at 205 nm accompanied by weak shoulders at 307 and 318 nm.[11] In the spectrum of α-Zr(HPO$_4$)$_2$(phen)$_{0.50}$·2H$_2$O there is a very clear band at 263 nm and an ill defined shoulder at *ca.* 220 nm (Figure 7), in accord with a free-base formulation. On dehydration there is little change in the most structure-diagnostic band at 263 nm (Figure 7, dotted line). Both u.v. spectra and the minimal layer shrinkage on dehydration thus point to the absence of strong Lewis acid–base interactions between the phen and the layers. This is in agreement with a slanted orientation, but still leaves open the role of water, which may be present in a specific hydrogen-bonding form between the phen and the layers.

After dehydration the material remains stable up to 300 °C (free phen melts at 117 °C),[12] as shown by the exothermic peak in the d.t.a., indicative of the initiation of combustion.

In-situ Co-ordination of Co^{2+}, Ni^{2+}, *and* Cu^{2+} *to Intercalated phen in* α-Zr(HPO$_4$)$_2$(phen)$_{0.50}$·2H$_2$O.—Although the interlayer distance is much larger in α-Zr(HPO$_4$)$_2$(phen)$_{0.50}$·2H$_2$O than in the bipy analogue,[2] the greater bulk of the phen and its higher pillar density has a drastic effect on the rate of diffusion of metal ions between the layers. Even after contacting at 60 °C, diffusion rates were still much lower than for the bipy analogue at 25 °C.

Uptake of Cu^{2+} goes to completion after 20 h [see Figure 2(*a*)]. After 8 d, 75% Co^{2+} and 55% Ni^{2+} are exchanged, and

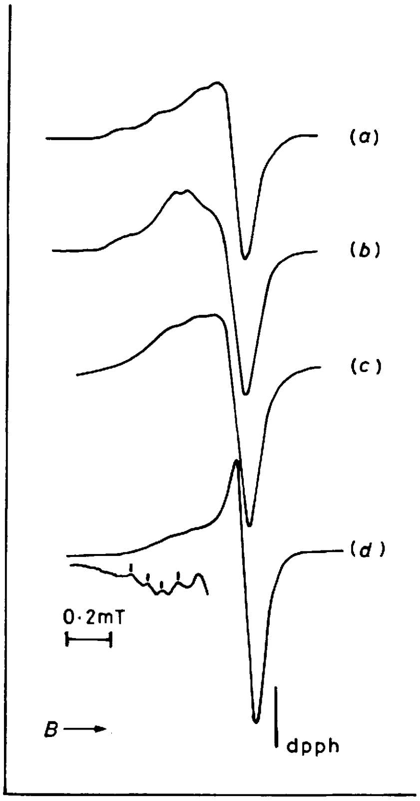


Figure 8. E.s.r. spectra of Cu^{2+}-containing materials pillared *in situ*: (*a*) 2% Cu^{2+}-exchanged α-$Zr(HPO_4)_2(phen)_{0.50}\cdot 2H_2O$, (*b*) α-$ZrH[Cu(phen)]_{0.50}(PO_4)_2\cdot 3H_2O$, (*c*) as for (*b*), after heating *in vacuo* at 140 °C and annealing at 77 K, and (*d*) as for (*b*), after heating *in vacuo* at 140 °C and annealing at room temperature; inset shows low-field portion under double-modulation conditions. dpph = Diphenylpicrylhydrazyl

the processes go to completion in 20 d and 1 month, respectively, the pH of the contact solutions having decreased to *ca.* 3.70.

For all three metal ions, the *in-situ* co-ordination leads to layer phases having practically the same interlayer distance: d_{002} = 15.77 Å [Figure 3(*d*)—(*f*)]. For Cu^{2+}, co-ordination is slightly retarded in comparison with uptake, although the two processes are coincident as uptake becomes progressively slower (from *ca.* 90% exchange to completion). Conversely, the Co^{2+}- and Ni^{2+}-exchanged materials do not entirely undergo the phase change even after complete uptake; *ca.* 10% of the starting phen phase is still present in the case of Co^{2+} [Figure 3(*e*)] whilst Ni^{2+} forms no more than 30% of the expanded layer phase [Figure 3(*f*)].

Three possibilities arise: (*i*) the cavity competes with the pillar (*i.e.* phen) for incoming metal ion; (*ii*) the pillar preferentially co-ordinates the metal ion, but not so as to give an expanded layer phase; and (*iii*) the metal ion co-ordinates to the pillar, changing its orientation between the layers and leading to an expanded interlayer distance.

As regards Cu^{2+}, which process intervenes depends on the extent of loading. At very low loading a single e.s.r. signal (A) is observed with $g_{\parallel}$ and $A_{\parallel}$ as expected for a tetragonal-octahedral CuN_2O_2 + 2O moiety (Figure 8). As there is no change in interlayer distance at such low loading (*ca.* 2%), process (*ii*) occurs. As loading increases, with increase in the interlayer distance, a second, indistinct, signal (B) appears, which becomes dominant after *ca.* 70% Cu^{2+} loading. These results suggest that process (*iii*) now intervenes, although signal A is still present even at 100% loading. The implication is that

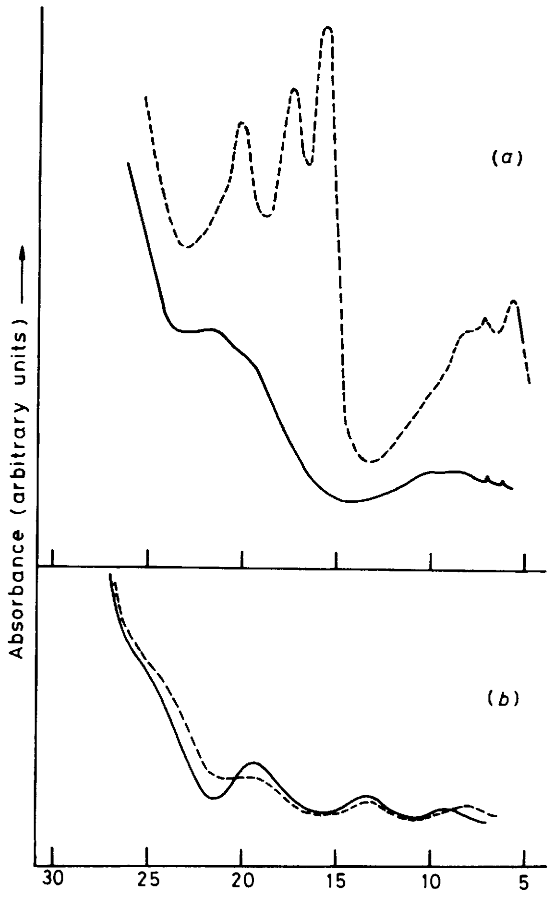


Figure 9. Electronic reflectance spectra of α-$Zr(HPO_4)_2(phen)_{0.50}\cdot 2H_2O$ (*a*) 80% Co^{2+}-exchanged and (*b*) 45% Ni^{2+}-exchanged: ——, as prepared; – – –, after heating *in vacuo* at 120 °C for 2 h

the stereochemistry of Cu^{2+} is sufficiently flexible so as to be able to adapt to a geometry imposed by the phen, the other tetragonal donor atoms being two matrix oxygen atoms and two water molecules. (That the water molecules are not removed at higher temperatures, as is the case with the bipy analogue,[2] may be due to the greater interlayer distance than in the latter, which would permit easier diffusion.)

Further evidence for the above suggestion is available from the e.s.r. spectrum of the anhydrous final material. At room temperature this gives a single signal, having a very low $A_{\parallel}$ = (72 ± 3) × 10^{-4} cm^{-1}, confirmed by a double-modulation experiment. When the material was annealed at 77 K immediately after dehydration a single signal with an even lower $A_{\parallel}$ (< 50 × 10^{-4} cm^{-1}) was observed. In neither case was there evidence for the presence of signal A. Further, both materials remained layered (d_{002} = 12.85 Å) although that annealed at 77 K was more ordered than that annealed at room temperature and also showed less tendency to re-absorb ambient water.

It is well known that a very low $A_{\parallel}$ parameter in the e.s.r. spectra of Cu^{2+}-containing materials is diagnostic of a pseudo-tetrahedral environment.[13] The best known cases are the Type I ('blue') copper proteins, for which $A_{\parallel}$ is usually < 100 × 10^{-4} cm^{-1}, and many attempts have been made to mimic this characteristic *via* modelling of copper(II) complexes.[14] Extensive correlations of $g_{\parallel}$ *vs.* $A_{\parallel}$ and of $g_{\parallel}$ *vs.* the dihedral angle between the tetrahedral planes have been derived.[15] Use of the $g_{\parallel}$ *vs.* dihedral angle correlations of Addison[15] provides an estimate of 70 ± 3° for the sample annealed at room temperature and 58 ± 3° for that annealed at low temperature. (Assuming that a CuN_2O_2 chromophore is present from the closeness of the plots for CuN_2O_2 and CuN_4,[15] a clear distinction between the two does not appear possible.) However, the reasons for the anomalously low $A_{\parallel}$ value for the material annealed at low temperature are not known.

The assignment of a pseudo-tetrahedral geometry is further supported by the presence of a low-energy shoulder in the electronic reflectance spectrum, at *ca.* 9 000 cm^{-1}.[16] Although the steric requirements of the bulky phen molecule can often lead to some out-of-plane distortion in copper(II) complexes, to our knowledge this is the first observation of a pseudo-tetrahedral geometry, and can be attributed to the constraints of the interlayer region.

Pseudo-octahedral species are clearly present in the hydrated cobalt(II) analogue, although as found for the bipy case[2] a clear distinction between CoN_2O_4 and CoO_6 chromophores cannot be made because of band overlap. However, a distinct shoulder at *ca.* 8 000 cm^{-1} suggests that the latter (*i.e.* cavity) species is also present, as well as the former.[17] On dehydration, the spectrum is characteristic of a tetrahedral moiety, band energies being in agreement with a CoN_2O_2 formulation. (The band at 20 000 cm^{-1} is very high for pseudo-tetrahedral CoN_2O_2 and may be due to the second site.)

The *d–d* spectrum of the hydrated Ni^{2+}-containing material (Figure 9) is of interest because the bands at 9 200, 13 200, and 19 000 cm^{-1} have their counterparts only in model *trans*-NiN_4O_2 complexes.[18] (The shoulder at *ca.* 25 000 cm^{-1} is presumably due to the cavity-co-ordinated moiety.) Given that for steric reasons bis(phen) complexes of Ni^{2+} always adopt a *cis* geometry, this convincingly illustrates how intercalation co-ordination chemistry differs from that in solution.

Cavity-exchanged Materials.—Both α-$ZrH_{1.6}[Cu(phen)_2]_{0.20}(PO_4)_2{\cdot}3H_2O$ and α-$ZrH[Cu(phen)]_{0.50}(PO_4)_2{\cdot}3H_2O$ exchange further Cu^{2+}, and also Ag^+ and Pd^{2+}, to give solid solutions. This demonstrates that pillaring has been successful and that, despite the large size of the pillars, access of further species to the interlayer region is not blocked.

Conclusions

We have shown that if the layers of α-$Zr(HPO_4)_2{\cdot}H_2O$ are first pre-swelled, even large species such as $[Cu(phen)_2]^{2+}$ or phen itself can be intercalated. The available evidence indicates that the former remains intact on intercalation and that the latter does not intercalate flat between the layers. The steric requirements of the cavity (combined with those of the phen itself) give rise to distorted sites for Cu^{2+} and Ni^{2+} not observed in solution co-ordination chemistry.

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