Pillar Chemistry. Part 4.† Palladium(II)–2,2′-Bipyridyl,–1,10-Phenanthroline, and–2,9-Dimethyl-1,10-phenanthroline Complex Pillars in α-Zirconium Phosphate

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Palladium(II) can be exchanged into the layered composites α-$Zr(HPO_4)_2(bipy)_{0.25}\cdot1.5H_2O$ (bipy = 2,2′-bipyridyl), α-$Zr(HPO_4)_2(phen)_{0.50}\cdot2H_2O$ (phen = 1,10-phenanthroline), and α-$Zr(HPO_4)_2(dmphen)_{0.50}\cdot2.5H_2O$ (dmphen = 2,9-dimethyl-1,10-phenanthroline) to give new palladium(II) amine complex–pillared materials. In all three cases, both 1 : 2 and 1 : 1 Pd^{II} : amine complexes are formed between the layers. Pillared materials with an interlayer distance as high as 17.3 Å can be obtained. Thus, using such *in situ* preparation methods, it is possible to prepare pillared materials with pore dimensions approaching those found in zeolite Y. Electronic spectral evidence for the presence of different geometries for the pillars is described (square planar for bipy and phen, but five-co-ordinate for both 1 : 2 and 1 : 1 dmphen pillared materials). All the materials exchange further metal ions, Co^{2+}, Ni^{2+}, and Cu^{2+}, to high loading levels, a demonstration that they are indeed pillared. Evidence is presented which shows that uptake of Cu^{2+} occurs at different rates for the 1 : 1 and 1 : 2 complex–pillared materials, *i.e.* the cavities have different sizes and therefore different accessibilities. In addition, spectroscopic probing (visible–near u.v. and e.s.r.) of these cavity-exchanged ions clearly demonstrates that the new cavities formed have geometries different from those present in the parent α-$Zr(HPO_4)_2\cdot H_2O$.

Interest in the insertion of ions or molecules between the layers of layered materials in order to prop the layers apart and produce new porous solids is increasing.[1] Much current work is centred on clays because of their ready accessibility and potential in petrochemical catalytic processes.[2] Layered phosphates also provide benign (*i.e.* thermally and chemically stable) solids capable of manipulation by 'soft' chemical methods. The well known ion exchanger α-$Zr(HPO_4)_2\cdot H_2O$[3] has been particularly useful in preparing new pillared materials because it is easily swelled[4] and is of known crystal structure.[5]

We have recently shown that first-row transition-metal complexes can be used to pillar α-$Zr(HPO_4)_2(EtOH)_2$. The pillars are formed *in situ* by metal-ion exchange, which is followed by co-ordination to the intercalated aromatic amine in α-$Zr(HPO_4)_2(bipy)_{0.25}\cdot1.5H_2O$ (bipy = 2,2′-bipyridyl),[6] α-$Zr(HPO_4)_2(phen)_{0.50}\cdot2H_2O$ (phen = 1,10-phenanthroline),[7] and α-$Zr(HPO_4)_2(dmphen)_{0.50}\cdot2.5H_2O$ (dmphen = 2,9-dimethyl-1,10-phenanthroline).[8] The ions Co^{2+}, Ni^{2+}, and Cu^{2+} were used as spectroscopic probes for the interlayer co-ordination chemistry. Examples of 'moving solids',[6] matrix-induced distortion of the pillar complex formed as compared with crystallographically known Cu^{2+}–phen complexes,[7] and partial elution of amine (dmphen) during metal-ion uptake[8] were uncovered during the work.

The present paper describes materials formed by exchanging Pd^{2+} with the same organic–inorganic composites. It was expected that the known tendency of Pd^{II} to give square-planar[9] (and more rarely five-co-ordinate) complexes rather than six-co-ordinate ones would lead to pillared materials with properties different from those found previously. This is indeed found to be the case.

Experimental

The starting materials α-$Zr(HPO_4)_2(bipy)_{0.25}\cdot1.5H_2O$ (d_{002} = 10.9 Å), α-$Zr(HPO_4)_2(phen)_{0.50}\cdot2H_2O$ (d_{002} = 13.58 Å), and α-$Zr(HPO_4)_2(dmphen)_{0.50}\cdot2.5H_2O$ (d_{002} = 14.6 Å) were prepared as detailed in the references.

Palladium(II) chloride was a Fluka purissimum product and was used as received. All other products were commercial products of the highest purity available. Batch methods were used, as before,[6,7] to follow metal-ion uptake. At 25 °C, Pd^{2+} is taken up only very slowly by all three materials, so that all experiments involved suspensions thermostatted at 50 °C.

The Pd^{2+}-containing solution was prepared by dissolving $PdCl_2$ (250 mg) in 10 cm^3 of 0.1 mol dm^{-3} HCl and then making up to volume (500 cm^3) with water. This solution was then adjusted to pH 2.6 with HCl.

Pd^{2+}-*Uptake Curves.*—A series of samples of 0.5 mmol of the amine intercalate was contacted with a stock solution of Pd^{2+} such that $[Pd^{2+}]:[\overline{amine}] = 1$ (as in ion-exchange usage, the bar above the metal ion or amine signifies the solid state; thus $[\overline{amine}]$ = [intercalated amine]). At set time intervals, the solid was filtered off and the supernatant analysed for Pd^{2+} and pH. The plots of uptake of Pd^{2+} *vs.* time for the three materials are shown in Figure 1.

Co-ordination of Pd^{2+}.—In parallel experiments, a series of batches was prepared in which 0.5 mmol of amine-intercalated solid was contacted with increasing amounts of stock Pd^{2+}-containing solution, such that $[Pd^{2+}]:[\overline{amine}]$ ranged from 0.1 to 1.0. Samples were left at 50 °C for the time required for co-ordination to go to completion (*i.e.* for the d_{002} reflection of the new expanded phase to be maximised). For dmphen, a further batch was prepared and used, having $[Pd^{2+}]:[\overline{dmphen}] = 1.4$.

In both kinds of experiments, *X*-ray diffractograms were registered for both wet and air-dried solids.

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† Part 3 is ref. 8.

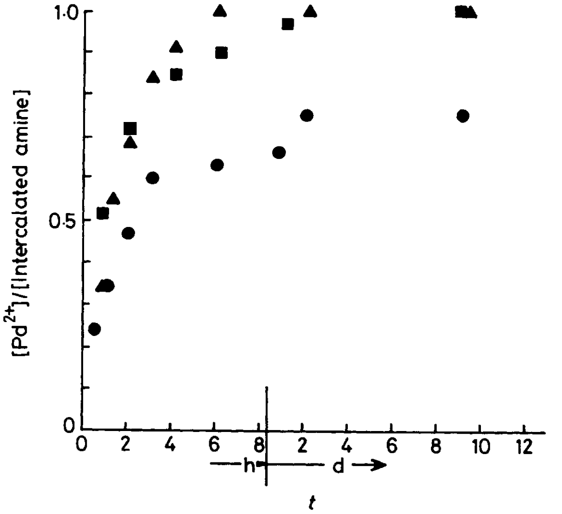


Figure 1. Ion exchange of Pd^{2+} by amines intercalated in α-$Zr(HPO_4)_2$: (■) bipy, (●) phen, and (▲) dmphen

Chemical Analysis and Physical Measurements.—Metal-ion contents were found by atomic absorption spectrometry with a Varian Techtron model 1100 instrument. Water and organic ligand contents of solids were determined by thermogravimetry (t.g.) and differential thermal analysis (d.t.a.) (ignition to constant weight in an airflow with a Mettler 2000C simultaneous thermal analyser; heating rate 5 °C min^{-1}).

A Philips diffractometer was used for monitoring phase changes. Both the d_{002} reflection and its harmonics were used for confirming that the layer structure was always retained, and the much weaker reflections between $2\theta = 15$ and 50° characteristic of the α-type structure were examined. Nickel-filtered Cu-K_α radiation was used; the 2θ values are believed accurate to 0.05°.

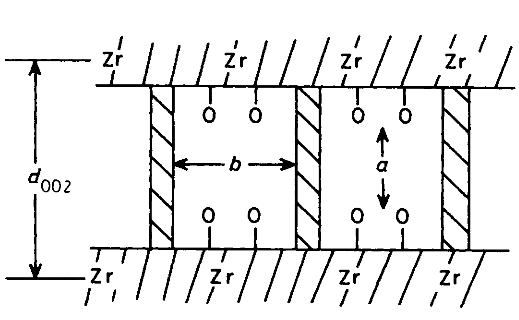
Electronic reflectance and e.s.r. spectra were obtained using instrumentation described previously.[7]

Results and Discussion

Pd^{2+} *Uptake Kinetics.*—The rates of uptake of Pd^{2+} are much slower in all three cases than found in the analogous cases of Co^{2+}, Ni^{2+}, and Cu^{2+}. In one case, that of α-$Zr(HPO_4)_2(phen)_{0.50}\cdot 2H_2O$, complete uptake to give $[\overline{Pd^{2+}}] : [\overline{amine}] = 1$ is never attained, even after very long contact times.

In both bipy and dmphen intercalates, the Pd^{2+} uptake is relatively rapid during the first 4 h, with levels of typically $[\overline{Pd^{2+}}]:[\overline{amine}] = 0.8$—0.9 being attained. Subsequently, the dmphen intercalate reaches full exchange, after a further 2 h, whereas for bipy the remaining Pd^{2+} in solution is taken up only after a further 2 d (see Figure 1). Similarly, the phen intercalate also takes up Pd^{2+} from solution quite rapidly during the first 3 h of contact (although more slowly than the other two materials) to reach $[\overline{Pd^{2+}}]:[\overline{phen}] = 0.6$. There is then an abrupt change in the exchange kinetics, and a plateau is reached after 2 d, no further Pd^{2+} being exchanged even after contact for a further 10 d.

It is noteworthy that the uptake kinetics of Pd^{2+} do not simply follow the order of increasing pillar height: bipy (4.6 Å) < phen (7.28 Å) < dmphen (8.28 Å). Particularly striking is the fact that the exchange kinetics are very similar for bipy and dmphen, despite the higher pillar density in the latter. This neatly demonstrates the critical balance of interlayer steric factors leading to modulation of the cavity dimensions *a* and *b* in the intercalated amine solids (see Scheme and ref. 6).



Scheme.

Co-ordination-induced Phase Changes.—When solids were withdrawn at the initial part of the plot of Pd^{2+} uptake with time, their *X*-ray diffraction patterns were found to be identical to those of the starting intercalated amine phase, *i.e.* only solid solutions of Pd^{2+} in the latter were given. Thus, withdrawing the dmphen intercalate at $[\overline{Pd^{2+}}] : [\overline{dmphen}] = 0.32$, *i.e.* after contacting for 45 min, gave no change in *X*-ray diffraction pattern, despite the fact that the uptake of Pd^{2+} is the most rapid for intercalated dmphen. Similarly, the phen-intercalated solid at $[\overline{Pd^{2+}}]:[\overline{phen}] = 0.24$ (*i.e.* after contact for 30 min) also proved to be a solid solution of Pd^{2+} in α-$Zr(HPO_4)_2(phen)_{0.50}\cdot 2H_2O$. Further along the uptake curve, mixed phases were obtained, *e.g.* solid solutions of Pd^{2+} in the starting phase + a new expanded phase. These observations demonstrate that the uptake of Pd^{2+} by each material and its subsequent co-ordination to the intercalated amine so as to form a complex pillar are well separated processes.

Only the bipy-intercalated material provided evidence for relatively rapid formation of an expanded complex–pillared material. The solid removed after contact for 30 min (*i.e.* at $[\overline{Pd^{2+}}]:[\overline{bipy}] = 0.30$) clearly shows the growth of an expanded phase when *X*-ray diffraction patterns are taken over a period of 25 min (Figure 2). However, in contrast to what was found for the analogous (although faster) reaction with Cu^{2+}, a second process then intervenes after 1 h. Peak a [d_{002} of starting α-$Zr(HPO_4)_2(bipy)_{0.25}\cdot 1.5H_2O$] then increases at the expense of peak b, which in turn disappears to be replaced by a third peak, c, at $d_{002} = 12.61$ Å. Analysis of the thermodynamically stable final solids shows that $d_{002} = 13.38$ Å, *i.e.* peak b, corresponds to a complex pillar with $[\overline{Pd^{2+}}]:[\overline{bipy}] = 1.2$, whereas that at $d_{002} = 12.61$ Å corresponds to a 1:1 complex pillar. The changes in *X*-ray diffraction pattern in Figure 2 may then be imputed to initial co-ordination of the Pd^{2+} to form a 1:2 complex pillar which then dissociates to a 1:1 complex + bipy. The implication is that the interlayer environment must allow considerable mobility because the bipy in the starting material is very spaced out [1 bipy per 4 $Zr(HPO_4)_2$ basal units].

The final solids obtained using increasing quantities of Pd^{2+} are shown as plots of 2θ (4—15°) *vs.* $[\overline{Pd^{2+}}]:[\overline{amine}]$ in Figures 3—5. Each *X*-ray diffraction pattern at a particular $[\overline{Pd^{2+}}]:[\overline{amine}]$ represents the limit obtained after the contact time required to reach solid-state equilibrium. Thus, for bipy, a contact time of 2 d was sufficient, whereas for dmphen 2 d (always at 50 °C) proved sufficient up to $[\overline{Pd^{2+}}]:[\overline{dmphen}] = 0.6$, but even 9 d at $[\overline{Pd^{2+}}]:[\overline{dmphen}] = 1$ was not sufficient to give the pure phase with $d_{002} = 14.10$ Å. Complete removal of the intermediate 1:2 ($d_{002} = 17.3$ Å) phase was attained only by using $[\overline{Pd^{2+}}]:[\overline{dmphen}] = 1.40$. Because of this, the final phase is not completely pure, but contains Pd^{2+} in solid solution, as well as a small amount of α-$ZrPd(PO_4)_2\cdot nH_2O$, $d_{002} = 9.4$ Å.

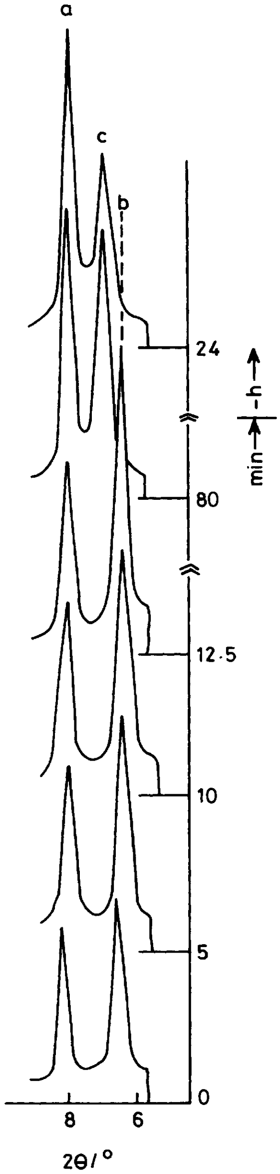


Figure 2. Changes in the d_{002} reflection *vs.* time for [Pd^{2+}]:[bipy] = 0.5. Peak a is the d_{002} reflection of α-$Zr(HPO_4)_2(bipy)_{0.25}\cdot1.5H_2O$, peak b that of α-$ZrH_{1.75}Pd_{0.125}(bipy)_{0.25}(PO_4)_2\cdot2.5H_2O$, and peak c that of α-$ZrH_{1.5}[Pd(bipy)(OH_2)]_{0.25}(PO_4)_2\cdot2.5H_2O$

Co-ordination of Pd^{2+} to intercalated bipy gives rise to two pure phases, one formed at [Pd^{2+}]:[bipy] = 0.50, having d_{002} = 13.38 Å, and the other at [Pd^{2+}]:[bipy] = 1, with d_{002} = 12.61 Å (Figure 3). The relative instability of the complex pillars having [Pd^{2+}]:[amine] = 1.2 is neatly underlined by the plots for phen (Figure 4). The intermediate 1:2 complex pillared phase cannot be obtained completely pure because the 1:1 phase begins to grow in even at [Pd^{2+}]:[phen] = 0.24. Further, the final 1:1 phase could never be obtained completely pure because the starting phen did not take up sufficient Pd^{2+}. The final material obtained is therefore a mixture of 1:1 complex–pillared phase and 1:2 complex–pillared phase, as written in extended form in Table 1.

The most complicated case is dmphen, for which there is evidence of a second intermediate, having d_{002} = 14.7 Å, at [Pd^{2+}]:[dmphen] = 0.40. This phase then gives way to a pure phase with [Pd^{2+}]:[dmphen] = 1:2, d_{002} = 17.3 Å, and a high-intensity 'd_{004}' reflection. As co-ordination of Pd^{2+} continues, a final phase having d_{002} = 14.10 Å appears, although a ratio of [Pd^{2+}]:[dmphen] = 1.40 had to be used in order entirely to remove intermediates (see Figure 5).

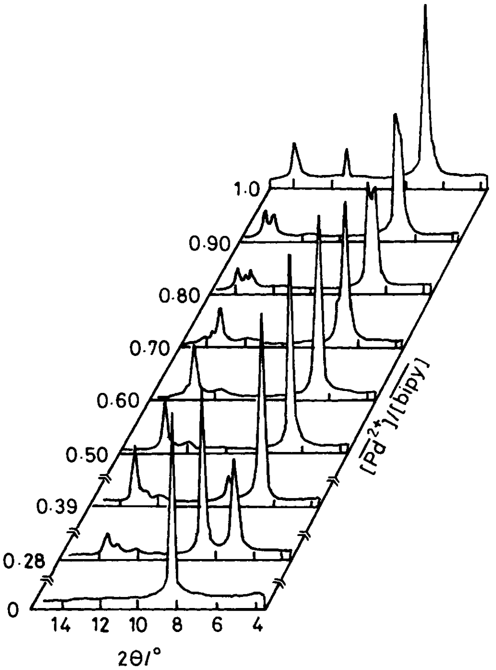


Figure 3. *X*-Ray diffraction patterns of phase changes during co-ordination of Pd^{2+} to amine in α-$Zr(HPO_4)_2(bipy)_{0.25}\cdot1.5H_2O$

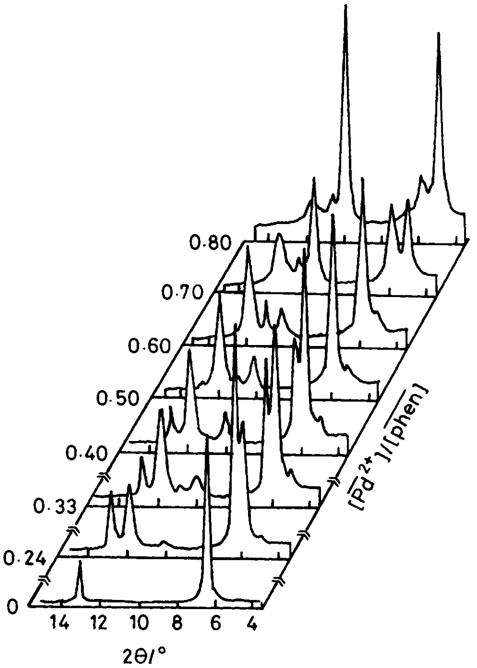


Figure 4. *X*-Ray diffraction patterns as in Figure 3 but for α-$Zr(HPO_4)_2(phen)_{0.50}\cdot2H_2O$

Table 1. Analysis of materials[a]

Material	d_{002}[b]/Å	Ligand/%	Water[c]/% Cavity	Water[c]/% Co-ordinated	Pd/%
α-$ZrH_{1.75}Pd_{0.125}(bipy)_{0.25}(PO_4)_2{\cdot}2.5H_2O$	13.38	10.2 (10.25)	12.25 (11.85)		3.45 (3.50)
α-$ZrH_{1.5}[Pd(bipy)(OH_2)]_{0.25}(PO_4)_2{\cdot}2.5H_2O$	12.61	9.80 (9.80)	11.05 (11.30)	1.30 (1.30)	6.70 (6.70)
α-$ZrH_{1.5}[Pd(phen)_2]_{0.25}(PO_4)_2{\cdot}3H_2O$	14.47	19.75 (19.85)	11.2 (11.9)		5.95 (5.85)
α-$ZrH_{1.2}[Pd(OH_2)_3]_{0.40}(phen)_{0.5}(PO_4)_2{\cdot}2.3H_2O$[d]	17.31	18.7	8.60	4.40	9.50
α-$ZrH_{1.5}[Pd(dmphen)_2(OH_2)]_{0.25}(PO_4)_2{\cdot}2H_2O$	17.31	22.95 (22.95)	7.65 (7.95)	1.20 (1.00)	5.85 (5.85)
α-$ZrH_{0.6}[Pd(OH_2)_3]_{0.2}[Pd(dmphen)(OH_2)_2]_{0.5}(PO_4)_2{\cdot}3H_2O$	14.10	19.15 (19.15)	9.95 (9.95)	5.15 (5.30)	13.7 (13.7)

[a] Calculated values are given in parentheses. [b] Of fresh product. [c] As determined from t.g. (see Figure 6). [d] Not fully exchanged.

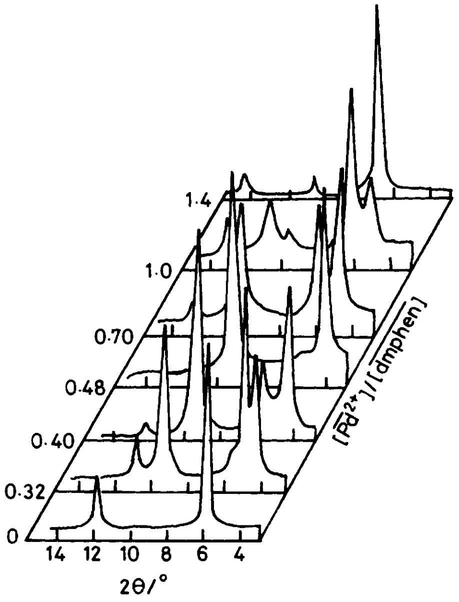


Figure 5. *X*-Ray diffraction patterns as in Figure 3 but for α-$Zr(HPO_4)_2(dmphen)_{0.50}{\cdot}2.5H_2O$

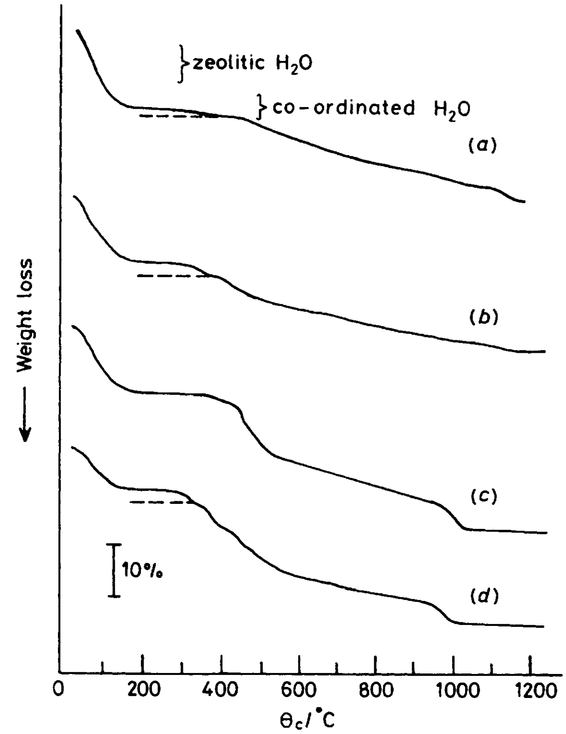


Figure 6. T.g. analyses of final Pd^{2+}-complex-pillared materials: (*a*) α-$ZrH_{1.75}Pd_{0.125}(bipy)_{0.25}(PO_4)_2{\cdot}2.5H_2O$, (*b*) α-$ZrH_{1.5}[Pd(bipy)(OH_2)]_{0.25}(PO_4)_2{\cdot}2.5H_2O$, (*c*) α-$ZrH_{1.5}[Pd(phen)_2]_{0.25}(PO_4)_2{\cdot}3H_2O$, and (*d*) α-$ZrH_{1.2}[Pd(OH_2)_3]_{0.4}(phen)_{0.5}(PO_4)_2{\cdot}2.3H_2O$

Local Pillar Geometry.—The *X*-ray diffraction evidence of Figures 3—5 indicates that Pd^{2+} co-ordinates to the amine ligand to form a complex pillar in each case. Direct evidence for this should in principle be immediately available from the electronic reflectance spectra of the solids because it is well known that PdO_4, PdN_2O_2, and PdN_4 chromophores give *d–d* bands in very different energy ranges. For example, $[Pd(OH_2)_4]^{2+}$, $[Pd(en)(OH_2)_2]^{2+}$, and $[Pd(en)_2]^{2+}$ (en = ethylenediamine) give major peaks at 26 000, 28 000, and 35 000 cm^{-1} (in that order).[10] In practice, high-energy amine π–π^* bands complicate a simple geometry assignment, as also does the recently discovered tendency of Pd^{2+} to give long-bonded $Pd \cdots N$ distances even with strong donors such as phen.[11] (This means that it cannot simply be assumed that *cis*-PdO_2N_2 is given in the case of, *e.g.* a 1:1 complex.) Caveats apart, the spectra of the materials containing Pd^{2+}, bipy, and phen are indicative that a grossly square-planar geometry is always present (see Figure 7). For example, the spectrum of α-$Zr_{1.5}[Pd(bipy)(OH_2)]_{0.25}(PO_4)_2{\cdot}2.5H_2O$ is characterised by a low-intensity shoulder at 26 000 cm^{-1}, followed by an intense double peak centred at 31 000 cm^{-1}; the latter we impute to *d–d* transitions of a PdN_2O_2 chromophore. Similar reasoning applies to the 1:2 bipy and phen complex pillars, although considerable masking by ligand π–π^* transitions occurs.

Conversely, the electronic spectra of the dmphen complex pillars are very different to those known for bidentate N–N ligands. In both 1:2 and 1:1 cases, very low-energy bands are observed. The latter gives a clear shoulder at 23 250 cm^{-1} {the further shoulder at 26 000 cm^{-1} is due to an impurity of the 1:2 complex pillar; it is not present in the pillared material $ZrH_{0.6}[Pd(OH_2)_3]_{0.2}[Pd(dmphen)(OH_2)_2]_{0.5}(PO_4)_2{\cdot}3H_2O]$}. According to Furlani,[12] a shift to lower energy of ν_1 (deriving from the $d_{x^2-y^2} \longrightarrow d_{z^2}$ transition in axial ligand fields) accompanied by an increase in intensity is diagnostic of a square-based pyramidal (s.p.) geometry, which would accord with the spectrum in Figure 7(*d*). However, it does not rationalise the Pd^{2+} *d–d* spectrum of the 1:2 form, which gives two clear bands, at 19 000 and 25 950 cm^{-1} together with an unclear shoulder at 28 200 cm^{-1}; ν_1 is at much lower energy than for any other Pd(N–N) complex known. This fact and the intensity sequence $\nu_2 > \nu_1$ suggest an assignment to a trigonal-bipyramidal (t.b.p.) Pd^{2+}-containing pillar [see also the *d–d* band assignment for a 'tripod' ligand tris(*o*-diphenylphosphinophenyl)arsine with a pseudo-t.b.p. geometry: 19 000 and 22 600 cm^{-1} ($^1E' \longleftarrow A_1$); 29 800 cm^{-1} ($^1E'' \longleftarrow {}^1A'_1$)[13]. The high $\nu_2 - \nu_1$ splitting of *ca.* 7 000 cm^{-1} suggests that the trigonal bipyramid present is distorted. Further, removal of the co-ordinated water for the 1:2 complex pillar leads to distinct changes in spectra: ν_1 decreases in energy and increases in intensity and ν_2 decreases in intensity. These changes are in the direction expected for t.b.p. $\longrightarrow$ s.p. distortions.

Thus, formation of the Pd^{2+}-containing pillar can give a geometry which is different from those found in Pd–phen complexes, although it is difficult to rationalise the differences in interlayer distances that this gives rise to. Particularly striking is the fact that the ratio $[\overline{Pd^{2+}}]:[\overline{\text{dmphen}}]$ = 1:2 gives a material with the same interlayer distance, 17.3 Å, as the 1:1 Pd–phen pillared material, and the ratio $[\overline{Pd^{2+}}]:[\overline{\text{dmphen}}]$ = 1:1 gives a material with d_{002} = 14.10 Å.

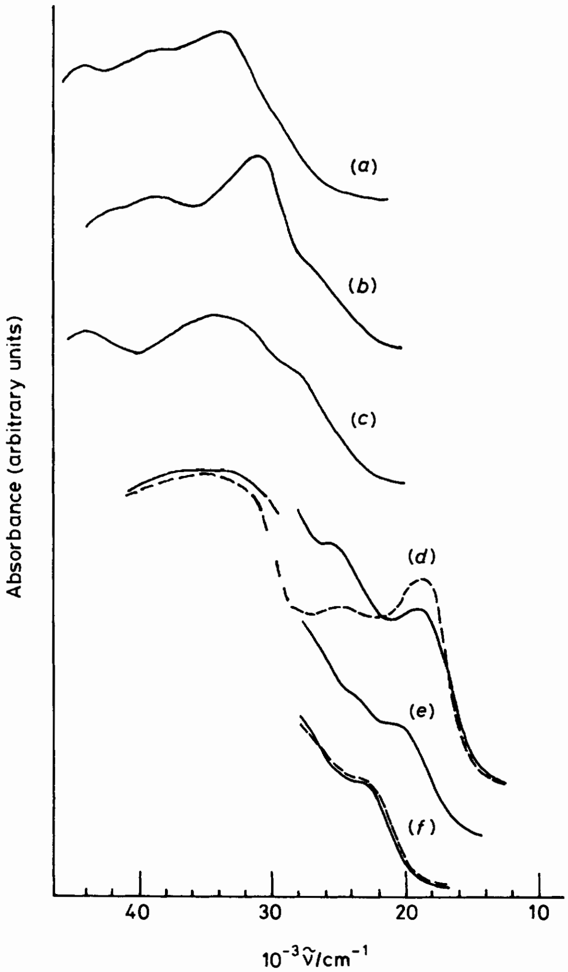


Figure 7. Electronic spectra (as reflectance) of Pd^{2+}–complex pillared materials: (*a*) α-$ZrH_{1.75}Pd_{0.125}(bipy)_{0.25}(PO_4)_2{\cdot}2.5H_2O$, (*b*) α-$ZrH_{1.5}[Pd(bipy)(OH_2)]_{0.25}(PO_4)_2{\cdot}2.5H_2O$, (*c*) α-$ZrH_{1.5}[Pd(phen)_2]_{0.25}(PO_4)_2{\cdot}3H_2O$, (*d*) α-$ZrH_{1.5}[Pd(dmphen)_2(OH_2)]_{0.25}(PO_4)_2{\cdot}2H_2O$, (*e*) Pd^{2+}-exchanged material between (*d*) and (*f*), and (*f*) α-$ZrH_{0.6}[Pd(OH_2)_3]_{0.2}[Pd(dmphen)(OH_2)_2]_{0.50}(PO_4)_2{\cdot}3H_2O$. (——) As prepared, (- - -) after heating at 250 °C for 2 h

Clearly, there is a favoured phen-type site in the zirconium phosphate matrix.

Pillar Stability and Cavity Characteristics.—Do the Pd^{2+}–amine complex pillared materials described effectively work as pillaring agents, *i.e.* are the cavities formed after pillaring available for further exchange or uptake of other molecules? Figure 8 shows a comparison between the ion-exchange behaviour towards Cu^{2+} of the pillared materials with $[\overline{Pd^{2+}}]:[\overline{\text{bipy}}]$ = 1:1 and 1:2. Both materials initially take up Cu^{2+} very rapidly, reaching 30—40% exchange of Cu^{2+} after contact for only 10 min. (Which immediately removes any doubt as to whether the uptake is merely on the surface or in the interlayer region: surface uptakes of transition-metal ions in zirconium phosphates are of the order 0.3—0.4%.) The uptake then slows down considerably and some 4 d are necessary before 60—70% loading of Cu^{2+} is reached. Both the kinetics and final loading are different, the 1:2 pillared material taking up Cu^{2+} faster than does the 1:1. This is in accord with the presence of a higher free height (*a* in Scheme) in the former than in the latter and also with a lower pillar density in the 1:2 case. Formation of a 1:2 pillar implies that there is one pillar per eight basal units in the zirconium phosphate structure, whereas a 1:1 pillar implies the presence of one pillar per four basal units.

For Cu^{2+} this picture seems valid because the pillar is retained in both cases, although d_{002} changes to 12.89 Å for the 1:1 pillar. However, there is marked amorphisation in the 1:2 pillared material, even though the interlayer does not change. Indeed, on exchanging Co^{2+} and Ni^{2+} the 1:2 material gives entirely amorphous products, whereas the 1:1 analogue remains pillared, giving well crystalline solid solutions in both cases and up to high loading levels. Despite the problem caused by lower stability of the 1:2 pillar, the results underline one advantage of phosphates with respect to clays as regards pillaring. With Na^+-exchanged gelwite and hectorite, pillaring with large hydroxy pillars, such as $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$

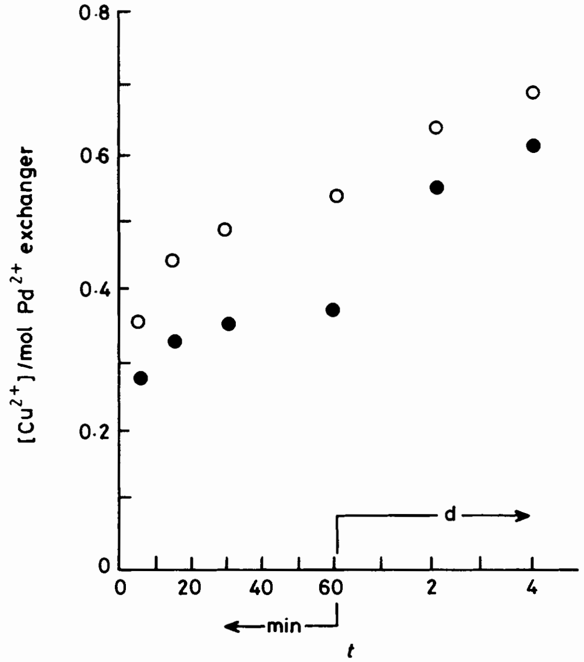


Figure 8. Ion exchange of Cu^{2+} by α-$ZrH_{1.75}Pd_{0.125}(bipy)_{0.25}(PO_4)_2{\cdot}2.5H_2O$ (○) and α-$ZrH_{1.5}[Pd(bipy)(OH_2)]_{0.25}(PO_4)_2{\cdot}2.5\ H_2O$ (●)

and $[Zr_4(OH)_{14}(H_2O)_{10}]^{2+}$, followed by calcination to give polyoxy-pillars leads to materials with protons in the intralayer region, *i.e.* not accessible to cation exchange.[14]

Similarly, the pillared material with $[Pd^{2+}]:[phen] = 1:2$ gave well crystalline solid-state solutions for all three metal ions (*i.e.* Co^{2+}, Ni^{2+}, and Cu^{2+}) and to quite high loadings. In contrast, the 1:2 dmphen pillared materials are not stable to uptake of further transition metal ions.

The parent material α-$Zr(HPO_4)_2 \cdot H_2O$ has such a low

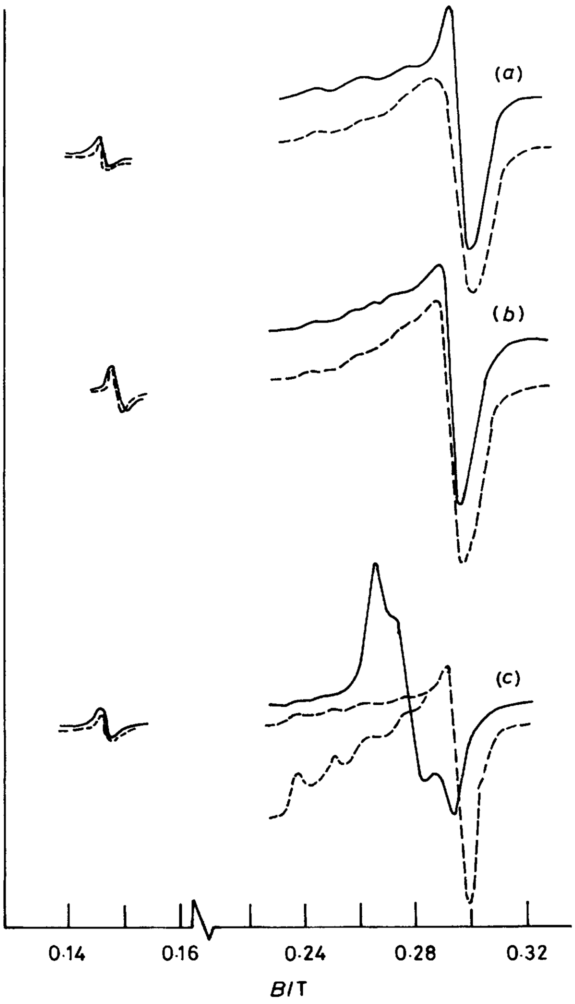


Figure 9. E.s.r. spectra of Cu^{2+}-exchanged (5% w/w) pillared materials: (*a*) α-$ZrH_{1.75}Pd_{0.125}(bipy)_{0.25}(PO_4)_2 \cdot 2.5H_2O$, (*b*) α-$ZrH_{1.5}[Pd(phen)_2]_{0.25}(PO_4)_2 \cdot 3H_2O$, and (*c*) α-$ZrH_{1.5}[Pd(bipy)(OH_2)]_{0.25}(PO_4)_2 \cdot 2.5H_2O$. (——) As prepared, (– – –) after heating at 150 °C for 1.5 h

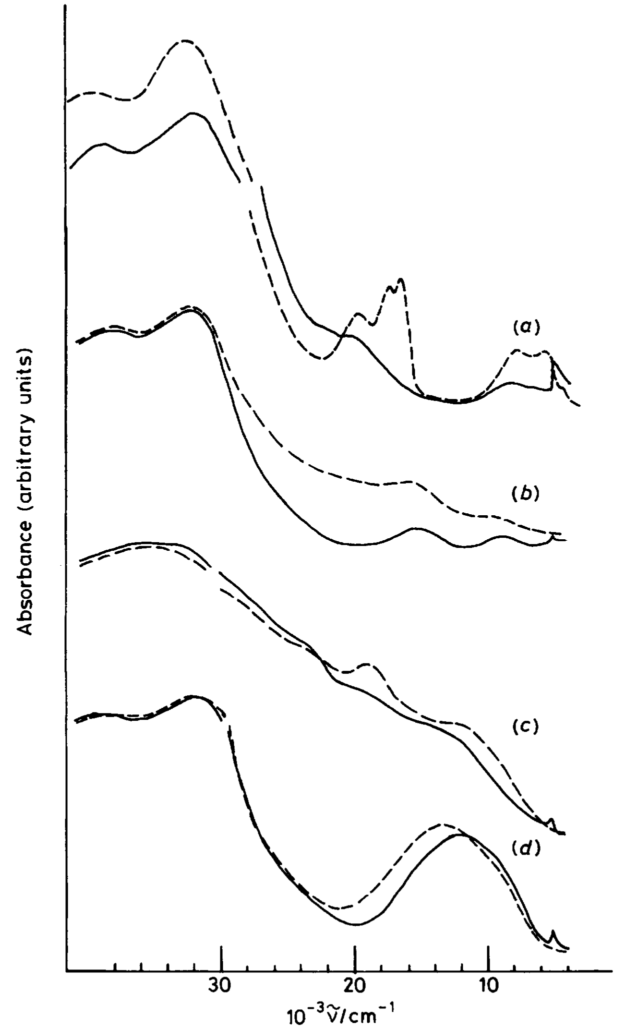


Figure 10. Electronic spectra (as reflectance) of Co^{2+}, Ni^{2+}, and Cu^{2+} exchanged into the Pd^{2+}–complex pillared materials: (*a*) α-$ZrH_{0.7}Co_{0.55}Pd_{0.1}(bipy)_{0.25}(PO_4)_2 \cdot H_2O$, (*b*) α-$ZrH_{0.7}[Pd(bipy)]_{0.25}[Ni(OH_2)_{2.5}]_{0.4} \cdot 2.8H_2O$, (*c*) α-$ZrPd_{0.24}Cu_{0.76}(dmphen)_{0.36}(PO_4)_2 \cdot 3.2H_2O$, and (*d*) α-$ZrH_{0.26}Cu_{0.62}Pd_{0.24}(bipy)_{0.25}(PO_4)_2 \cdot nH_2O$. (——) As prepared, (– – –) after heating at 120 °C for 2 h

Table 2. E.s.r. parameters; 5% Cu^{2+} (nominal)

Material		$g_{\parallel}$	$g_{\perp}$	$10^4A_{\parallel}/cm^{-1}$
α-$ZrH_{1.75}Pd_{0.125}(bipy)_{0.25}(PO_4)_2 \cdot 2.5H_2O$	as prepared	2.261	2.069	184.7
	150 °C, 1.5 h	2.255	2.079_9	184.2
α-$ZrH_{1.5}[Pd(bipy)(OH_2)]_{0.25}(PO_4)_2 \cdot 2.5H_2O$	as prepared	2.297 g_1	2.196 g_2	2.077 g_3
	150 °C, 1.5 h	2.366	2.068	157.4
α-$ZrH_{1.5}[Pd(phen)_2]_{0.25}(PO_4)_2 \cdot 3H_2O$	as prepared	2.344	2.079	175.1
	150 °C, 1.5 h	2.280	2.083	

interlayer distance that it can be treated as a pseudo-zeolite structure, in which each cavity can hold a single bivalent transition metal ion.[15] When pillared to the relatively high free heights found here, the cavities are no longer so 'closed' and different co-ordination geometries than found in the parent are expected. Is there evidence for this from the electronic reflectance and e.s.r. spectra (necessarily of low-loaded Cu^{2+}-exchanged materials)? First, for the pillared material with $[\overline{\mathrm{Pd}^{2+}}]:[\overline{\mathrm{bipy}}] = 1:2$ the $A_{\parallel}$ value is typical of a CuN_2O_2 (presumably with two O axial) chromophore, nicely fitting the evidence for bipy dispersed in the solid state in this case. Conversely, in the pillared material with $[\overline{\mathrm{Pd}^{2+}}]:[\overline{\mathrm{bipy}}] = 1:1$ the Cu^{2+} is clearly in an all-O cavity (see Table 2 and Figure 9). However, even at such low loadings, the materials show half-field lines at *ca.* 1 500 G (0.15 T), characteristic of the presence of dimers,[16] which is further supported by the magnetically exchanged type signal [Figure 9(*b*)] present in the as-prepared 5% Cu^{2+}–$[\overline{\mathrm{Pd}^{2+}}]:[\overline{\mathrm{bipy}}] = 1:1$ pillared material. The reflectance spectra of the as-prepared material and after removal of cavity water may be ascribed to an all-O environment (no change in interlayer distance nor in the u.v.–visible spectra of Pd^{2+} on exchange of Cu^{2+} in the cavities).

For all the bipy and phen pillared materials the broad band at 12 000 cm^{-1} with the unclear shoulder at *ca.* 9 000 cm^{-1} simply shifts to 13 300 cm^{-1} on cavity dehydration. Both *d–d* bands and the e.s.r. spectra show that in these cases there are no large geometry changes as compared with the tetragonal CuO_4 + 2O hydrated species.[17] Nevertheless, there is some difference in cavity as compared with the parent α-$Zr(HPO_4)_2 \cdot H_2O$ (both fully and partially exchanged) because removal of cavity water gives copper(II) *d–d* bands shifted to higher energy in the case of the Pd^{2+}–bipy and –phen pillared materials (although not in those of the dmphen analogue).

From well known correlations of tetragonality *vs.* *d–d* band energy[17] this means that the Cu^{2+} is in a more elongated tetragonal geometry after anchoring to oxygen atoms from the cavity phosphates. Similarly, Ni^{2+} in as-prepared materials is in a pseudo-octahedral clearly NiO_6 environment ($\nu_1 = 10Dq = 8\,700$ cm^{-1}). However, when cavity water is removed, the *d–d* spectrum changes to one different from that given by Ni^{2+} loaded into α-$Zr(HPO_4)_2 \cdot H_2O$ itself.[18] The u.v.–visible spectrum is complex, but band energies (see Figure 10) are in agreement with the presence of more than one site. In similar vein, Co^{2+} occupies a pseudo-octahedral site in as-prepared materials (both 1:1 and 1:2) which change, reversibly, to pseudo-tetrahedral ones on removal of cavity water.

Conclusions

Palladium(II) forms both 1:1 and 1:2 amine complexes *via* ion exchange followed by co-ordination to the intercalated amine in α-$Zr(HPO_4)_2(bipy)_{0.25} \cdot 1.5H_2O$, α-$Zr(HPO_4)_2(phen)_{0.50} \cdot 2H_2O$, and α-$Zr(HPO_4)_2(dmphen)_{0.50} \cdot 2.5H_2O$. This is a further demonstration that the co-ordination chemistry in a constrained space is different from that found in complexes formed in solution (1:2 Pd^{2+}–phen complexes do not exist).

Using these methods, materials with pillar heights of *ca.* 11 Å can be obtained, *i.e.* with hole dimensions even larger than those found in zeolite Y. More importantly, the cavities formed allow ready access to other metal ions (Cu^{2+}, Co^{2+}, and Ni^{2+}). On dehydration, these cavities provide co-ordination sites different to those found in the parent α-$Zr(HPO_4)_2 \cdot H_2O$. The chemical reactions occurring in such cavities are under investigation.

References

1 J. M. Thomas, *Nature (London)*, 1986, **322**, 500; R. M. Barrer, *J. Inclusion Phenomena*, 1986, **4**, 109.

2 E. P. Giannelis and T. J. Pinnavaia, *Inorg. Chem.*, 1985, **24**, 3602 and refs. therein; M. L. Occelli and D. H. Finseth, *J. Catal.*, 1986, **99**, 316 and refs. therein.

3 A. Clearfield, in 'Inorganic Ion-Exchange Materials,' ed. A. Clearfield, CRC Press, Boca Raton, Florida, 1982, ch. 1; G. Alberti and U. Costantino, in 'Intercalation Chemistry,' eds. M. S. Wittingham and A. J. Jacobson, Academic Press, New York, 1982, ch. 5.

4 U. Costantino, *J. Chem. Soc., Dalton Trans.*, 1979, 402.

5 J. M. Troup and A. Clearfield, *Inorg. Chem.*, 1977, **16**, 3311; A. Clearfield, W. L. Duax, A. S. Medina, G. D. Smith, and J. R. Thomas, *J. Phys. Chem.*, 1969, **73**, 342.

6 C. Ferragina, A. La Ginestra, M. A. Massucci, P. Patrono, and A. A. G. Tomlinson, *J. Phys. Chem.*, 1985, **89**, 4762.

7 C. Ferragina, A. La Ginestra, M. A. Massucci, P. Patrono, and A. A. G. Tomlinson, *J. Chem. Soc., Dalton Trans.*, 1986, 265.

8 C. Ferragina, A. La Ginestra, M. A. Massucci, P. Patrono, and A. A. G. Tomlinson, *Mater. Res. Bull.*, 1987, **22**, 29.

9 L. Rasmussen and C. K. Jørgensen, *Acta Chem. Scand.*, 1968, **32**, 2313.

10 L. Rasmussen and C. K. Jørgensen, *Inorg. Chim. Acta*, 1969, **3**, 547.

11 Z. Taira and S. Yamazaki, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 649.

12 C. Furlani, *Coord. Chem. Rev.*, 1968, **3**, 141.

13 M. J. Norgett, J. H. M. Thornley, and L. M. Vananzi, *J. Chem. Soc. A*, 1967, 540.

14 D. T. B. Tennakoon, W. Jones, and J. M. Thomas, *J. Chem. Soc., Faraday Trans. 1*, 1986, 3081.

15 L. Alagna and A. A. G. Tomlinson, *J. Chem. Soc., Faraday Trans. 1*, 1982, 3009.

16 S. S. Eaton, K. M. More, B. M. Sawant, and G. M. Eaton, *J. Am. Chem. Soc.*, 1983, **105**, 6560.

17 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, **5**, 143.

18 L. Alagna, A. A. G. Tomlinson, C. Ferragina, and A. La Ginestra, *J. Chem. Soc., Dalton Trans.*, 1981, 2376.

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