Diffusion of Large Amine Ligands into Layered α-$Zr(HPO_4)_2{\cdot}H_2O$. Access to a Solid-state Co-ordination Chemistry

Carla Ferragina,[a] Maria Massucci,[a] Aldo La Ginestra,[a] Pasquale Patrono,[a] and Anthony A. G. Tomlinson*[b]
[a]I.M.A.I. and [b] I.T.S.E., Area della Ricerca di Roma del C.N.R., C.P.10, Monterotondo Stazione, 00016 Roma, Italy

2,2′-Bipyridyl and 1,10-phenanthroline can be diffused between the layers of pre-swelled α-$Zr(HPO_4)_2{\cdot}2H_2O$ to give the materials α-$Zr(HPO_4)_2[bipy]_{0.25}{\cdot}1.5H_2O$ and α-$Zr(HPO_4)_2[phen]_{0.5}{\cdot}2H_2O$; metal ions co-ordinate preferentially to the stage I dispersed ligand with *in situ* formation of complex pillars.

Supported complexes are basically of two kinds: those in which the metal ion bonds directly to the matrix,[1] and those where it co-ordinates to a ligand itself attached to a matrix (*e.g.* silica, alumina, *etc.*)[2]. We have found that a relatively bulky amine can be dispersed into a layered material and the 'ligand-pillared' phase thus formed preferentially co-ordinates transition metal ions *in situ*. These constitute a third class: organic–inorganic composite supports.

Contacting α-$Zr(HPO_4)_2{\cdot}H_2O$ or α-$Zr(NaPO_4)(HPO_4){\cdot}5H_2O$ with 10^{-2}—10^{-3} mol dm^{-3} solutions of bipy (2,2′-bipyridyl) or phen (1,10-phenanthroline) in water–ethanol (1 : 1) leads to materials with only low (<3% molar) loading levels (presumably because of steric effects). Conversely, when the metastable alcohol phases, *e.g.* α-$Zr(PO_4)_2$-[2EtOH],[3] are contacted with the same solutions, the layer swelling caused by intercalation of the alcohol (known to form a bilayer between the layers[3]) is sufficient to allow almost immediate uptake of organic amine. Maximum uptake of the amine is reached after 24 h contacting time and after filtering off and drying in air the materials analysed† as α-$Zr(HPO_4)_2[bipyl]_{0.25}{\cdot}1.5H_2O$ and α-$Zr(HPO_4)_2[phen]_{0.25}{\cdot}2H_2O$. No further ligand could be diffused. Both materials are pure stage I phases, but show very different interlayer distances: 10.9 (bipy) and 13.58 Å (phen). Neither amine lies flat between the layers (an interlayer distance of *ca.* 9.6 Å would be expected were the amines flat). Dreiding

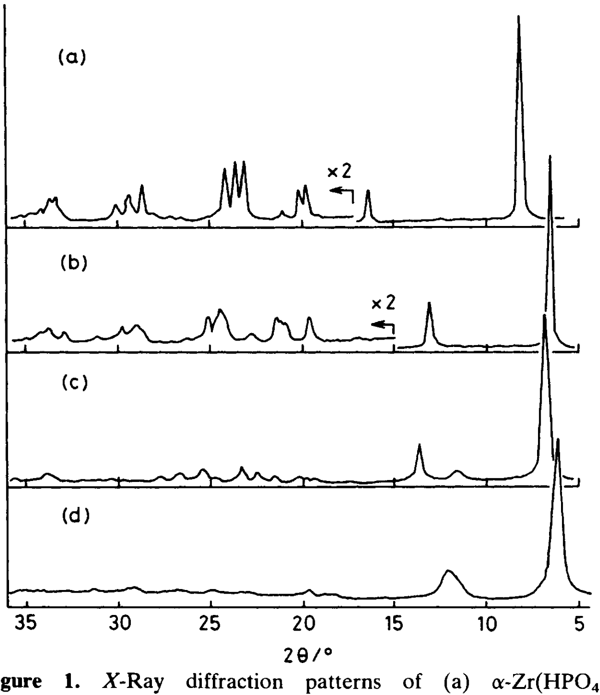

Figure 1. *X*-Ray diffraction patterns of (a) α-$Zr(HPO_4)_2$-$[bipy]_{0.25}{\cdot}1.5H_2O$; (b) α-$Zr(HPO_4)_2[phen]_{0.5}{\cdot}2H_2O$; (c) α-$ZrH_{1.5}[Cu(bipy)]_{0.25}(PO_4)_2{\cdot}3.15H_2O$; (d) α-$ZrH[Cu(phen)]_{0.5}(PO_4)_2{\cdot}2H_2O$. The predominant low-angle d_{002} reflexion is characteristic of stage I behaviour, *i.e.* the amine ligand is ordered throughout each layer of the material.

---

† Satisfactory analyses (*via* thermogravimetry, monitoring of absorption spectra of supernatants during uptake, and metal analyses after calcination of materials) were obtained for all materials.

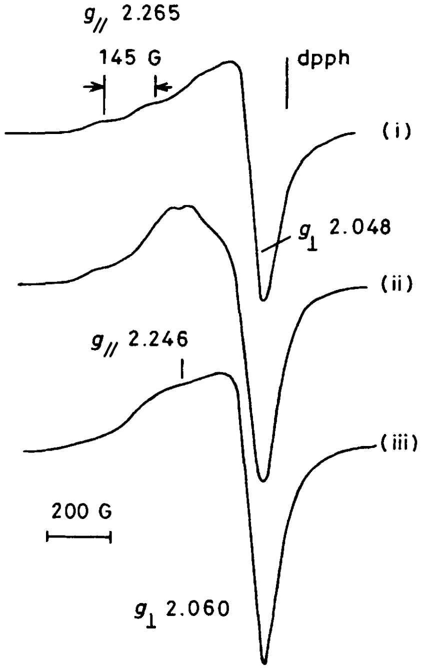

Figure 2. E.s.r. spectra: (i) 2% $\mathrm{Cu^{2+}}$-exchanged α-$\mathrm{Zr(PO_4)_2}$-[phen]$_{0.5}$·$\mathrm{H_2O}$; (ii) α-ZrH[Cu(phen)]$_{0.5}$$\mathrm{(PO_4)_2}$·$\mathrm{2H_2O}$; (iii) as for (ii), after heating material at 140 °C for 2 h. dpph = diphenylpicrylhydrazyl.

models indicate that the bipy is somewhat sidewise slanted to the layers, whereas phen is almost vertical. The former would give a larger coverage of the basal units of the parent α-$\mathrm{Zr(HPO_4)_2}$·$\mathrm{H_2O}$ structure than would the latter, which accounts for the difference in maximum loading levels. The water molecules are zeolitic in type (ready removal at 110 °C), are readily regained (within minutes), and their removal does not cause the structure to collapse.

These solid-state dispersed ligands co-ordinate metal ions. A solution of $\mathrm{Cu^{2+}}$ [10^{-3} mol dm^{-3} $\mathrm{Cu(OAc)_2}$] in contact with them (1 : 1 molar ratio, referred to ligand) is completely taken up (bipy: 24 min; phen: 7 days) giving bright blue materials analysing as α-$\mathrm{ZrH_{1.5}}$[Cu(bipy)]$_{0.25}$$\mathrm{(PO_4)_2}$·$\mathrm{3.15H_2O}$ (A) and α-ZrH[Cu(phen)]$_{0.5}$$\mathrm{(PO_4)_2}$·$\mathrm{2H_2O}$ (B). Co-ordination causes reorientation of the ligand between the layers: d_{002}(A) = 13.05 Å; d_{002}(B) = 15.2 Å. Powder diffraction patterns for the phen and bipy species, with and without $\mathrm{Cu^{2+}}$, are in Figure 1, The presence of fine structure in the e.s.r.spectra characteristic of N-co-ordination (Figure 2) demonstrates that the $\mathrm{Cu^{2+}}$ is indeed co-ordinated to the amine in both cases,[4] and not simply exchanged into the cavities formed by the ligand-pillaring. The same is found for the $\mathrm{Co^{2+}}$ and $\mathrm{Ni^{2+}}$ analogues. For α-$\mathrm{ZrH_{1.5}}$[Ni(bipy)]$_{0.25}$$\mathrm{(PO_4)_2}$·$\mathrm{3.15H_2O}$, the electronic spectrum is characteristic of a *cis*-$\mathrm{NiN_2O_4}$ chromophore (ν_1 9 100 and 10 750; ν_2 16 500; ν_3 26 500 cm^{-1}).[5]

On dehydration, the metal ion anchors more strongly to both ligand and matrix, giving (P–O)$_n$M(N–N) moieties. The number *n* is variable, presumably because of contraints on the metal ion due to ligand orientation within the layer and the influence this has on availability of matrix oxygen atoms. In α-$\mathrm{ZrH_{1.5}}$[Co(bipy)]$_{0.25}$ $\mathrm{(PO_4)_2}$, the $\mathrm{Co^{2+}}$ is tetrahedral in gross geometry (electronic spectrum: ν_2 5 750, 7 250, and 8 850; ν_3 16 080, 17 700, and 20 200 cm^{-1}). Conversely, the $\mathrm{Cu^{2+}}$ analogue adopts a tetragonal octahedral metal ion geometry. The rigidity of phen within the layers imposes a distorted tetrahedral geometry on the (matrix + ligand)-co-ordinated $\mathrm{Cu^{2+}}$ in α-ZrH[Cu(phen)]$_{0.5}$$\mathrm{(PO_4)_2}$ (see Figure 2), as deduced from the very low $A_{//}$ value of *ca.* 35 G.[4]

The layer swelling technique for inserting large molecules into α-$\mathrm{Zr(HPO_4)_2}$·$\mathrm{H_2O}$ and similar materials is general in application, and the solid-state dispersed ligand species obtained can be used for developing an intercalation co-ordination chemistry.

Received, 30th May 1984; Com. 631

References

1 T. J. Thomas, D. E. Hucul, and A. Brenner, in 'Chemically Modified Surfaces in Catalysis and Electrocatalysis,' ACS Symposium Series, 1982, Vol. 192, p. 267.

2 D. C. Bailey and S. H. Langer, *Chem. Rev.*, 1981, **81**, 109.

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

4 J. Foley, S. Tyagi, and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1984, 1; D. Attanasio, A. A. G. Tomlinson, and L. Alagna, *J. Chem. Soc., Chem. Commun.*, 1977, 618.

5 Compare with metal-ion exchanged parent α-$\mathrm{Zr(PO_4)_2.H_2O}$: L. Alagna, A. A. G. Tomlinson, C. Ferragina, and A. La Ginestra, *J. Chem. Soc., Dalton Trans.*, 1981, 2376.