Cobaltocene Intercalates of Zirconium Hydrogen Phosphate

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Summary Intercalation compounds of zirconium hydrogen phosphate with cobaltocenium cations have been prepared by direct reaction of cobaltocene with zirconium hydrogen phosphate and by ion exchange reactions of cobaltocenium solutions with zirconium hydrogen phosphate.

Intercalation compounds of organometallic guests in layered inorganic hosts have thus far been mainly restricted to compounds with transition metal dichalcogenide hosts. The first reported compounds of this type are the cobaltocene intercalates of the layered transition metal disulphides.[1] Further work has extended and defined the range of metallocene-like organometallics that are suitable as guests in those hosts.[2] Recently metallocene intercalates of the layered oxychloride FeOCl have been reported.[3] Zirconium hydrogen phosphate is a layered solid that has been extensively studied as a cation exchange material.[4] It provides a host lattice of the framework type, distinctly different from the nearly close-packed lattices of the transition metal disulphides. We now report that the zirconium hydrogen phosphate lattice can incorporate cobaltocenium cation in its interlamellar space to form a new type of organometallic intercalation compound.

α-Zirconium hydrogen phosphate, $Zr(HPO_4)_2\cdot H_2O$, reacts with 0·5 equiv. of cobaltocene in toluene solution at 100—120 °C to form an intercalation compound. The microcrystalline product exhibits a complex *X*-ray diffraction pattern that is distinct from that of the starting material. The first three lines of an (001) series of the type commonly observed in layered compounds are clearly distinguishable and indicate a layer spacing of 12·0 Å. We assume that the intralayer structure of the macro-anionic zirconium phosphate layers is maintained. This assumption is supported by the reversibility of the intercalation reaction (*vide infra*). $Zr(HPO_4)_2\cdot H_2O$ has a layer spacing of 7·6 Å;[5] thus the intercalation of cobaltocene increases the separation of the zirconium phosphate layers by 4·4 Å In the layered transition metal disulphides, intercalation of cobaltocene expands the lattice by *ca.* 5·6 Å. The lower lattice expansion observed here can be explained by the expulsion of water from the interlamellar space of the zirconium phosphate (van der Waals' radius of H_2O = 2·8 Å) and by the difference between the nesting of the cobaltocene and that of the water in the ridges on the interlamellar surface formed by the phosphate hydroxy-groups. The proposed structure is represented schematically in the Figure.

The cobaltocene is intercalated as cobaltocenium cation. The reaction can be represented by equation (1). The

$$Zr(HPO_4)_2\cdot H_2O + 0\cdot5\ Co(C_5H_5)_2 \longrightarrow Zr(Co(C_5H_5)_2)_{0\cdot5}H_{1\cdot5}(PO_4)_2 + 0\cdot25\ H_2 + H_2O \qquad (1)$$

composition of the cobaltocene–zirconium hydrogen phosphate intercalate was confirmed by elemental analysis [$ZrP_2O_8C_5H_{6\cdot5}Co_{0\cdot5}$: found (calc.): P, 15·91 (16·42); C, 14·40 (15·9); H, 1·8 (1·7); Co, 7·1 (7·8)]. The zirconium hydrogen phosphate acts as a proton source to oxidize the neutral cobaltocene, by analogy to the oxidation of cobaltocene by aqueous acids. The presence of cobaltocenium ions in the intercalation compound was demonstrated by its pale yellow-green colour. The cobaltocenium ion can be removed from the zirconium phosphate lattice by washing the intercalation compound with 2 M HCl. A mixture of the α-phase and a highly hydrated phase (layer spacing = 10·7 Å) of zirconium hydrogen phosphate is produced as the solid product of this regeneration reaction. Similar observations have been made by Alberti *et al.*, when $ZrNaH(PO_4)_2$ is regenerated by acid.[6]

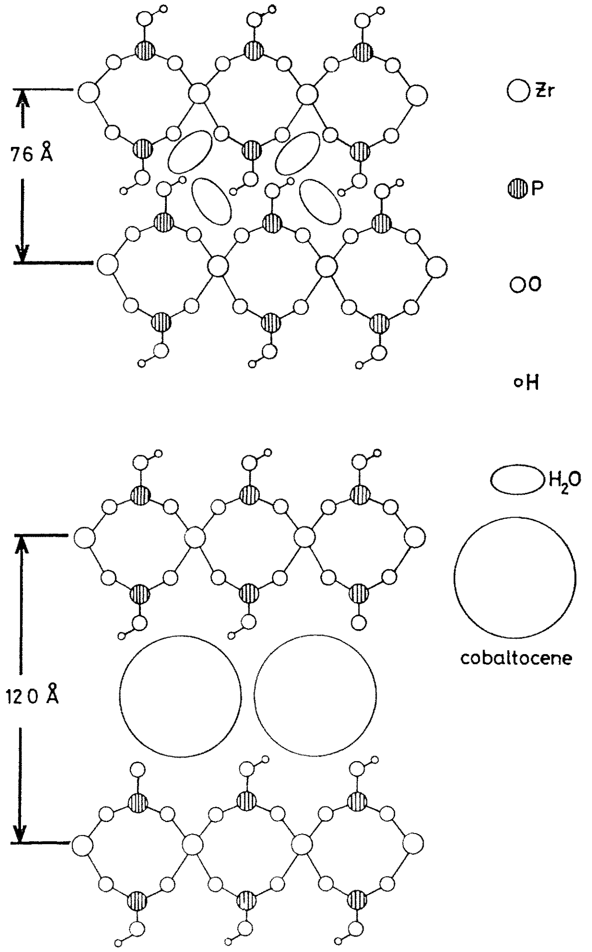

Figure. Schematic representation of α-$Zr(HPO_4)_2\cdot H_2O$ (top) and its cobaltocene intercalation compound (below).

As expected from equation (1), zirconium hydrogen phosphate also reacts with solutions of cobaltocenium cation in an ion exchange manner. The extent of the reaction and the layer spacing of the resulting intercalation compounds are dependent upon the solvent, the pH of the solution, and on the phase of the zirconium hydrogen phosphate. Highly crystalline α-zirconium hydrogen phosphate does not exchange its protons for cobaltocenium ions efficiently at room temperature. However, γ-zirconium hydrogen phosphate,[7] γ-$Zr(HPO_4)_2\cdot 2H_2O$, reacts with an aqueous solution of cobaltocenium hydroxide to give an intercalated product with layer spacing of 16·2 Å. The elemental analyses indicate incorporation of 0·4 equiv. of cobaltocenium and about 3 equiv. of H_2O. The structure can be represented by an intercalated layer of cobaltocenium cations propping apart the γ-zirconium phosphate layers. The difference between the observed layer spacing, 16·2 Å, and that of β-zirconium hydrogen phosphate [the dehydrated form of γ-$Zr(HPO_4)_2\cdot 2H_2O$] is 6·9 Å which corresponds with the van der Waals' size of a cobaltocenium cation along its C_5 axis, 6·8 Å. It has recently been recognized[8] that the actual intralayer structures of the zirconium hydrogen phosphate macro-anionic layers are different in the α- and γ-phases. While the detailed structure of the γ-phase has not yet been elucidated, the packing of the zirconium and phosphorous polyhedra is more dense in the γ-phase than in the α-phase An understanding of the structure of the cobaltocene intercalate of γ-zirconium hydrogen phosphate must await knowledge of the structure of the starting phase

Hydrogen uranyl phosphate, HUO_2PO_4 $2H_2O$, another layered acid phosphate of a different structure type, also incorporates 0 5 equiv of cobaltocene upon direct reaction in toluene at 110 °C to yield an intercalated product with a layer expansion of 3·9 Å

The technical assistance of J Picone is gratefully acknowledged

(*Received*, 17*th September* 1979, *Com* 992)

[1] M B Dines, *Science*, 1975, **188**, 1210

[2] W B Davies, M L H Green and A J Jacobson *J C S Chem Comm* , 1976, 781 R P Clement, W B Davies, K A Ford, M L H Green, and A J Jacobson, *Inorg Chem* , 1978, **17**, 2754

[3] T R Halbert and J Scanlon, *Materials Res Bull* , 1979, **14**, 415

[4] G Alberti *Accounts Chem Res* , 1978, **11**, 163 and references therein

[5] A Clearfield and G D Smith, *Inorg Chem* , 1969, **8** 431

[6] G Alberti U Costantino, and J S Gill, *J Inorg Nuclear Chem* 1976, **38**, 1733

[7] A Clearfield, R H Blessing and J A Stynes, *J Inorg Nuclear Chem* 1968 **30** 2249

[8] S Yamanaka and M Tanaka, *J Inorg Nuclear Chem* 1979, **41**, 45 G Alberti, U Costantino, and M L Giovagnotti, *ibid* , p 643