A Simple Route to Amide-functionalized Tetravalent Metal Phosphonates. Interlayer Amidation of an Ethylenediammonium Exchanged Form of Zirconium Carboxyethylphosphonate

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A simple route to layered tetravalent metal phosphonates containing amide linkages is demonstrated by a model reaction in which the ethylenediammonium ion exchanged form of layered zirconium carboxyethylphosphonate is converted into the amide derivative by thermal condensation.

Layered phosphates and phosphonates of tetravalent metal ions such as Zr^{4+} afford a variety of organic derivatives.[1-7] One approach to such compounds is to replace the interlayer HPO_4^{2-} groups of γ-zirconium phosphate with various organophosphoric ester ions, as reported by Yamanaka.[2] Another method, first reported by Alberti *et al.*,[3] is based on the direct reaction of tetravalent metal ions with phosphonic or organophosphoric acids. Recently, this method was extended by Burwell and Thompson[6] to prepare amide- and ester-functionalized zirconium phosphonates *via* amine and alcohol intercalation reactions of the acyl chloride compound of layered zirconium phosphonate derived from its carboxylic acid form.

In this communication we demonstrate a simple route to such amide-functionalized derivatives of tetravalent metal phosphonates by a model reaction in which the ethylenediammonium ion exchanged product of zirconium carboxyethylphosphonate is thermally condensed into its amide form.

The zirconium carboxyethylphosphonate sample, **1**, was prepared in a manner similar to that of Alberti *et al.*[3] and its composition was determined thermogravimetrically as $Zr(O_3PC_2H_4CO_2H)_{1.67}(HPO_4)_{0.33}$. The phosphonate was mixed with an aqueous solution of ethylenediamine at various ratios of amine to Zr and the mixture was stirred at 25 °C for 12 d. This equilibration time was selected after preliminary experiments had shown invariant pH for longer times. The resulting mixtures were centrifuged, fully washed with water, and freeze-dried. The pH of the supernatants was measured by a TOA model TSC-10A autotitrator. Thermogravimetry was carried out at a heating rate of 10 °C min^{-1} in air. Powder X-ray diffraction (XRD) measurements were made with Cu-Kα radiation using tetradecan-1-ol as an external standard. Infrared absorption spectra were measured by the KBr-pellet method using a Hitachi model 270–30 spectrometer.

The powder XRD diffraction patterns of **1** and its reaction products with ethylenediamine are characterized by the major peaks at 2θ *ca.* 5.4–6.8° attributable to the (002) reflections, along with their second and/or third order reflections, as shown in Fig. 1. The XRD data indicate that at a ratio amine:Zr of 1.0:1, the host compound **1** (interlayer spacing 12.9 Å) was fully converted into an intercalated solid with an interlayer spacing of 16.3 Å. This intercalated solid is denoted as **2**. At higher addition levels, partial decomposition of **1** occurred and the reaction products yielded a mixture of ZrP_2O_7 and ZrO_2 upon heating to 1000 °C. The IR spectrum of **2** (Fig. 2) showed a broad band associated with the CO_2^- group near 1680 cm^{-1}, replacing the 1710 cm^{-1} peak due to the C=O stretching of the CO_2H group observed for **1**. This indicates that ethylenediamine is intercalated by **1** in such a way that the protons of the interlayer CO_2H groups are replaced by the terminal NH_3^+ cations.

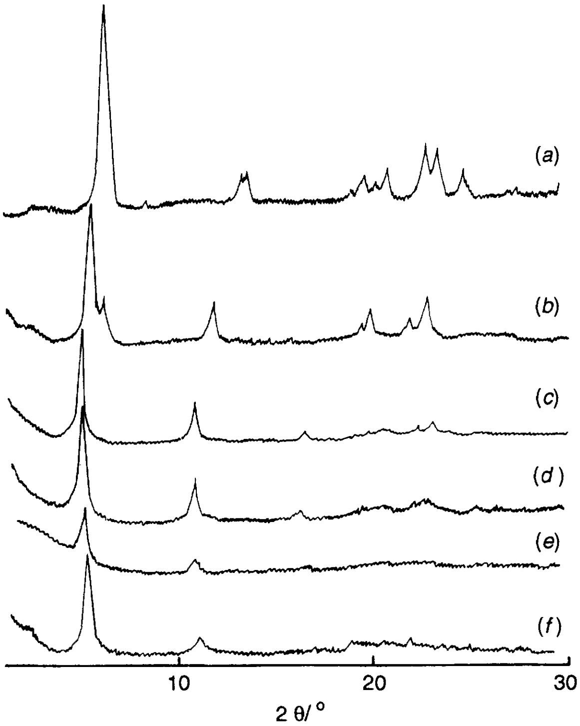


Fig. 1 X-Ray diffraction patterns of **1** (*a*), **1** treated with ethylenediamine at a ratio amine:Zr of 0.5 (*b*), 1.0 (*c*), 2.0 (*d*), 3.0 (*e*) and 3 (*f*) (Cu-Kα radiation)

The thermogravimetric curve for **2** indicated that three steps occurred over the temperature range 0–700 °C, as shown in Fig. 3. The first weight loss at below 100 °C is due to the desorption of water. The third weight loss, in common with **1**, commencing at 300 °C, is primarily attributable to a loss of the interlayer organic moiety and partly to the condensation of the residual hydrogen phosphate groups. Burwell and Thompson[7] also observed a distinct weight loss at temperatures below 220 °C for the hexylammonium intercalate of $Zr(O_3PCH_2CH_2CO_2H)_2$ and attributed the loss to the deintercalation and evaporation of the hexylamine guest.[7] The second weight loss at temperatures between 150 and 250 °C for **2**, on the other hand, was found to be due to a different mechanism, as described below.

Combination of the thermogravimetric data for **1** and **2** led to a proposed composition $Zr(O_3PCH_2CH_2CO_2H)_{1.67}$-$(HPO_4)_{0.33}(H_2NCH_2CH_2NH_2)_{0.52}\cdot0.61H_2O$ for **2**. Heating the intercalated solid **2** at 210 °C for 1 h resulted in the conversion of the CO_2^- band characteristic of **2** into so-called amide-I and -II bands at 1655 and 1560 cm^{-1} respectively (Fig. 2). These two amide bands are similar to those at 1646 and 1548 cm^{-1} observed for alkylamide intercalation compounds of zirconium phosphonate derived from the acyl chloride form.[7] It is thus obvious that the interlayer ionic-bonded $-CO_2^-NH_3^+$-group in **2** is condensed into a covalently bonded -CONH- form by heating to *ca.* 200 °C. This interlayer amidation was confirmed by observation (by IR) that the intercalated solid (**2**) was reconverted into **1** upon contact with 0.1 mol dm^{-3} aqueous hydrochloric acid solution, whereas the 210 °C-pyrolysed product, **3**, was unchanged by the same treatment (Fig. 2). The thermogravimetric curve for **3** showed only one weight loss (Fig. 3). Combination of the thermogravimetric data for **1** and **3** indicated the composition $Zr(O_3PCH_2CH_2CO_2H)_{0.65}$-$(HPO_4)_{0.33}(O_3PCH_2CH_2CONHCH_2CH_2NHCOCH_2CH_2$-$PO_3)_{0.51}\cdot0.44H_2O$ for **3**. The composition data for **2** and **3** indicate that almost all the $-CO_2^-NH_3^+$- groups in **2** are converted into the -CONH- form by thermal condensation, in accord with the IR observations for **3**. The XRD pattern of **3** also showed a reduced interlayer spacing relative to **2** (from 16.3 to 15.7 Å), due to the amidation (Fig. 1).

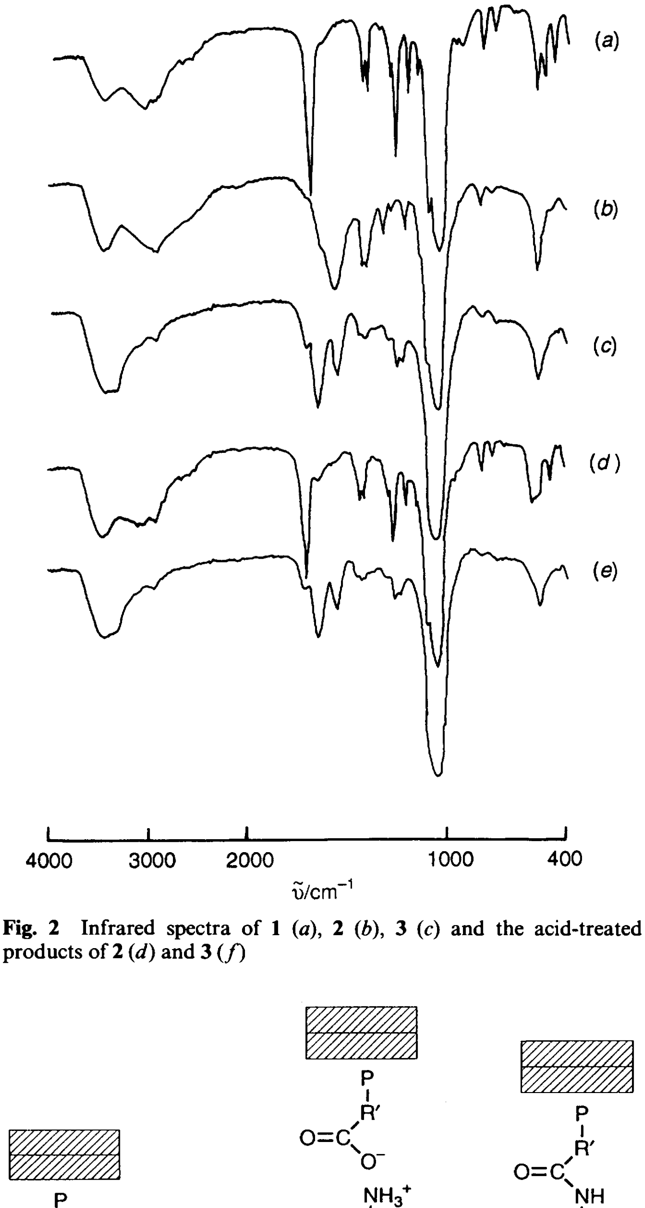
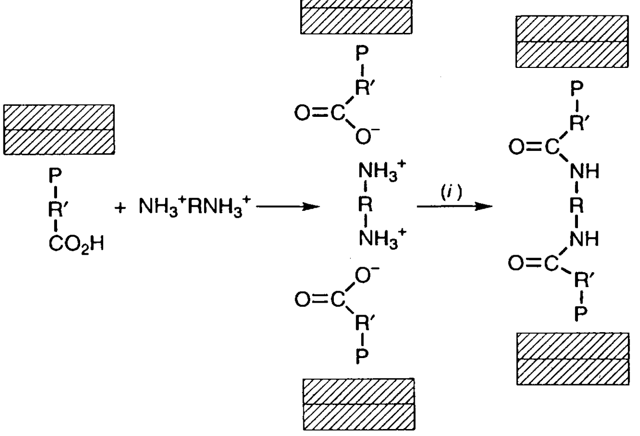


Fig. 2 Infrared spectra of **1** (*a*), **2** (*b*), **3** (*c*) and the acid-treated products of **2** (*d*) and **3** (*f*)



Scheme 1 A proposed route to introduce organic functionalities R into the carboxylated form of tetravalent metal phosphonates *via* thermal condensation; (*i*) $-H_2O$, heat

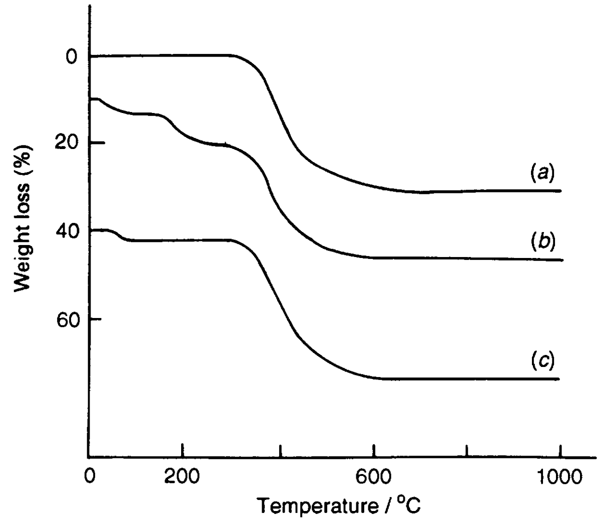


Fig. 3 Thermagravimetric curves for **1** (*a*), **2** (*b*) and **3** (*c*) with a heating rate of 10 °C min^{-1} in air. The vertical scales for (*b*) and (*c*) are shifted by 10 and 40%, respectively

The above intercalation and interlayer amidation processes in the **1**-ethylenediamine system were reproducible. A simple route to amide derivatives of tetravalent metal phosphonates from their carboxylic acid forms without preparatory conversion of the carboxylic acid groups into acyl chlorides, is shown in Scheme 1. Whether the two ammonium termini bind to the same phosphonate layer or to any two adjacent layers will be discussed elsewhere.

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