Amino Acid Derivatives of Layered Zirconium Phosphates – α-Zirconium L-(+)-Serinephosphate and Zirconium L-(+)-Serinephosphate Phosphates

Umberto Costantino*, Morena Nocchetti, Fabio Marmottini, and Riccardo Vivani

Dipartimento di Chimica, Università di Perugia,
Via Elce di Sotto 8, I-06123 Perugia, Italy
Fax: (internat.) + 39-75/5855566
E-mail: ucost@unipg.it

Received April 20, 1998

Keywords: Layered compounds / Zirconium / Amino acids / Zirconium L-(+)-serinephosphates / Intercalation

A layered derivative of α-zirconium phosphate containing L-(+)-serine covalently attached to the inorganic layer has been prepared by allowing Zr fluoro complexes to decompose in the presence of L-(+)-phosphoserine. On the basis of thermogravimetric weight loss and C,H,N elemental analyses, the layered compound obtained has been formulated as $Zr[HOOCCH(NH_2)CH_2OPO_3]_2$. The X-ray powder diffraction pattern has been indexed with a monoclinic cell (a = 5.3737 Å, b = 9.3231 Å, c = 14.510 Å, β = 96.99°, Z = 2). FT-IR absorption spectra show that the serine groups attached to the inorganic layers are present as zwitterions. Thermal decomposition commences at ca. 250 °C and occurs in two steps: the first is due to a decarboxylation reaction, with the formation of the amino derivative $Zr(NH_2CH_2CH_2OPO_3)_2$, while the second is associated with pyrolysis of the organic moiety, leading to ZrP_2O_7. Despite the presence of the amino acid function in the interlayer region, the compound does not show intercalation ability towards cations or anions or polar species. However, compounds with a certain degree of microporosity and possessing ion-exchange and adsorption properties have been obtained by replacing some of the phosphoserine groups of the compound by HPO_4 groups, to produce the mixed layered derivatives $Zr[HOOCCH(NH_2)CH_2OPO_3]_{2-x}(HPO_4)_x$.

In 1978, Alberti and co-workers showed that it is possible to anchor organic functions to the layers of α-zirconium phosphate [α-$Zr(HOPO_3)_2$] by allowing fluorozirconium complexes to decompose in the presence of organophosphoric or -phosphonic acids[1]. As the complexing agent is slowly removed (i.e. as HF), layered zirconium organophosphates or -phosphonates of the general formulae $Zr(ROPO_3)_2$ or $Zr(RPO_3)_2$ (where R is the organic moiety) with structures similar to that of the inorganic analogue are obtained. This method has attracted the attention of many researchers since a large number of layered compounds with different properties and functionalities can be obtained simply by changing the nature of the R groups[2]. The sole limitation to synthesis is that only groups with a cross-section equal to or less than 24 $Å^2$ can be used, which corresponds to the free area around each POH group present on the surface of the layers of the parent α-$Zr(HOPO_3)_2$[3]. However, more voluminous groups may be attached to the α-layers if their dimensions are compensated for by introducing small groups R′ (e.g. H, OH, CH_3) so as to obtain compounds of the formula $Zr(RPO_3)_{2-x}(R'PO_3)_x$[4].

To date, many organic derivatives bearing different functional groups (alkyl, aryl, carboxylic acid, aldehydic, amino, etc.) and even macrocyclic ligands have been prepared and investigated[5][6][7][8][9]. However, only a few papers on layered derivatives bearing the amino acid function can be found in the literature[10][11], despite the fact this functional group is of interest with regard to its amphoteric character and in view of its ability to coordinatively bind transition metal ions.

We report herein on the results of an investigation of the layered compounds obtained by precipitating Zr^{IV} with L-(+)-phosphoserine or with a mixture of L-(+)-phosphoserine and phosphoric acid. The aim of the work was not only to prepare new derivatives incorporating the amino acid function but also to obtain new stationary phases for chiral recognition, by anchoring chiral groups to a stable and insoluble inorganic backbone.

Results

Preparation and Characterization of α-Zirconium L-(+)-Serinephosphate

Figure 1 shows a computer-generated model of the phosphoserine molecule. The cross-section, evaluated at the level of the amino acid group, is very near to 24 $Å^2$, the maximum permissible value for the preparation of stoichiometric zirconium organophosphates. However, before starting the synthetic procedures, experiments were carried out to assess the stability of the ester bond of phosphoserine in acidic media at 60°C, by recording ^{31}P-NMR spectra of such solutions at regular intervals. The hydrolysis of phosphoserine (0.2 M) in HCl (0.4 M) at this temperature was found to be a very slow process, the amount of phosphates in solution after 3 days accounting for less than 3% of the total phosphorus content (Figure 2). This result indicates that phosphoserine is sufficiently stable to be employed un-

  1434–1948/98/1010–1447 $ 17.50+.50/0

der the synthesis conditions. Nevertheless, precipitates obtained following the procedure described in the experimental section, collected after 1−3 days, were found to contain increasing amounts of phosphates (from 5 to 10% of the total phosphorus content). In order to reduce the presence of phosphates in the precipitate, the rate of precipitation was increased by bubbling wet nitrogen into the reaction vessel. Under these conditions, the solid collected after 12 h did not contain appreciable amounts of phosphates. The X-ray powder diffraction (XRPD) pattern of the wet sample was almost identical to that of a sample dried over phosphorus pentoxide and further characterization was performed on the latter sample.

Figure 1. Ball-and-stick model of L-(+)-phosphoserine

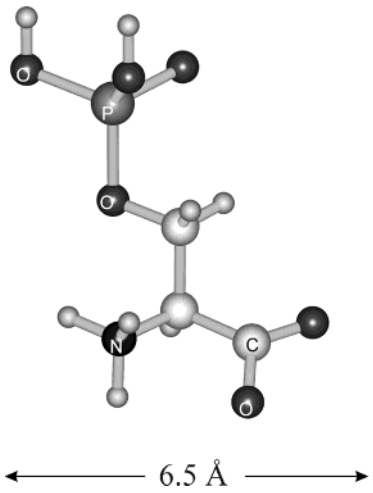


Figure 3 shows the thermogravimetric (TG) and differential thermal analysis (DTA) curves obtained at a heating rate of 5°C/min under oxygen. No appreciable loss is seen up to about 250°C, suggesting the absence of water of crystallization. Thermal decomposition starts at about 250°C and occurs in two steps. The first is very sharp and corresponds to the loss of 20% of the initial weight, while the second occurs over a much broader temperature range and leads to the formation of cubic ZrP_2O_7, as shown by the XRPD spectrum of a sample heated at 900°C. The total weight loss amounts to 42.1%, which is almost identical to that calculated (42.2%) for the following thermal decomposition:

$$Zr[HOOC-CH(NH_2)CH_2OPO_3]_2 + 5\ O_2 \rightarrow ZrP_2O_7 + 2\ NH_3 + 3\ H_2O + 6\ CO_2$$

Results of C,H,N elemental analyses were consistent to within 5% of the stoichiometry derived from TG data. Percentage weights calculated on the basis of the above formula and found values were: C 15.7, H 2.6, N 6.1, and C 15.2, H 2.8, N 5.8, respectively.

Figure 4 depicts the XRPD pattern obtained using the stepwise scanning procedure. The pattern was indexed, using the TREOR program[12], on the basis of a monoclinic cell with parameters a = 5.3737 Å, b = 9.3231 Å, c = 14.510 Å, β = 96.99°, $M(18)$ = 23, $F(18)$ = 30. Assuming

Figure 2. ^{31}P-NMR spectra of a sample of 0.2 M phosphoserine in 0.4 M HCl, using D_2O as solvent, maintained at 60°C for 30 min (spectrum a) and 3 d (spectrum b); peak labels are expressed in Hz

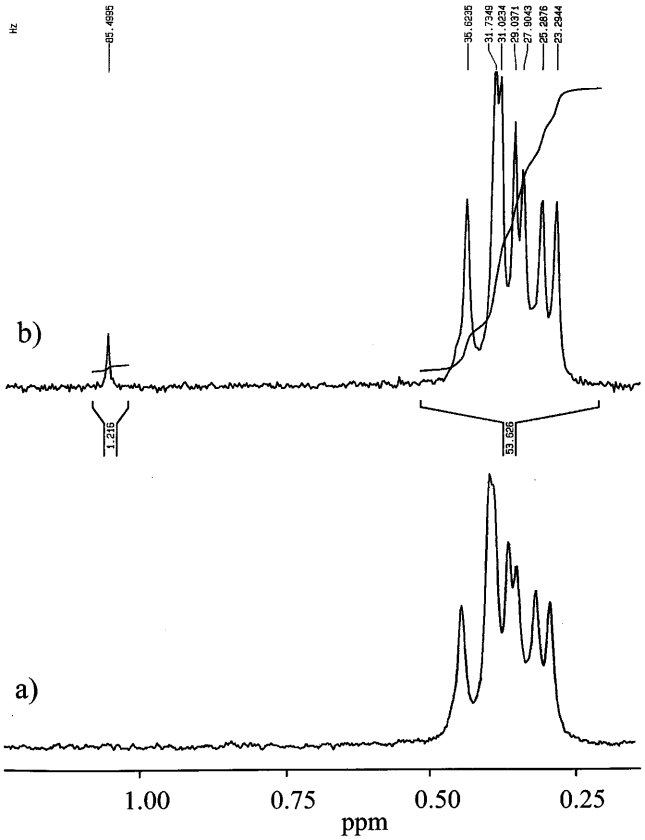
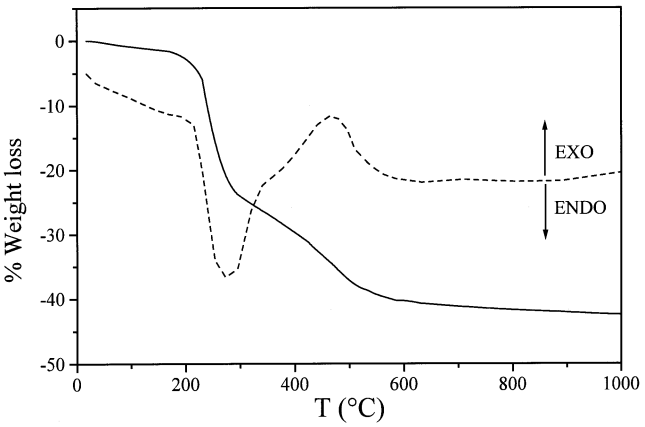


Figure 3. TG (solid line) and DTA (dotted line) curves of zirconium L-(+)-serinephosphate previously equilibrated over P_4O_{10}; heating rate 5°C/min, O_2 flow 30 ml/min



the presence of two formula weights in the unit cell volume (V = 721.5 Å^3), the calculated density (2.10 g cm^{-3}) is very near to the measured density (2.11 g cm^{-3}).

The XRPD pattern of the zirconium serinephosphate is typical of that of layered zirconium phosphate or phosphonates, with a strong first reflection (see Figure 4) corresponding to an interlayer distance (d) of 14.40 Å. Information about the type of layered structure can be obtained by determining the number (n) of moles of compound per

Figure 4. XRPD patterns of zirconium L-(+)-serinephosphate

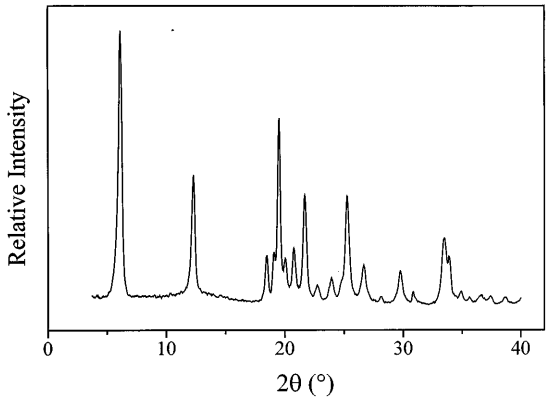
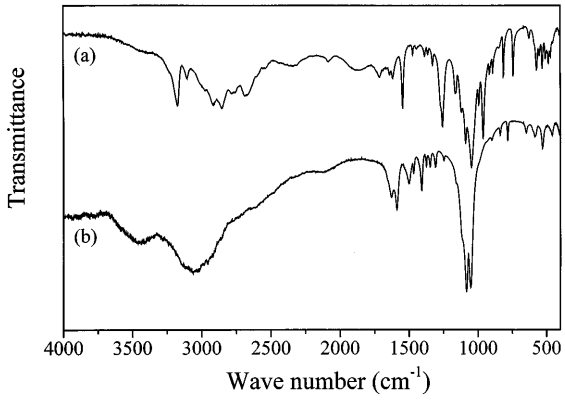


Figure 5. FT-IR absorption spectra of (a) L-(+)-phosphoserine, (b) zirconium L-(+)-serinephosphate

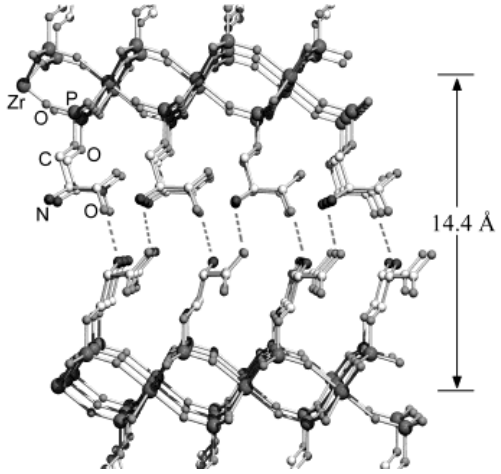


unit area of layer. This number is calculated from the ratio density × interlayer distance/formula weight, and is characteristic of the type of layer structure, being $6.8 \cdot 10^{-10}$ and $9.3 \cdot 10^{-10}$ mol cm^{-2} for the α- and γ-type compounds, respectively[13]. The *n* parameter of zirconium serinephosphate, calculated from the density of 2.11 g/cm^3, the interlayer distance of 14.40 Å, and the formula weight of 457.2 Da (from TG data), is $6.6 \cdot 10^{-10}$ mol cm^{-2}. This result is indicative of an α-type layer structure, where each layer consists of a planar arrangement of zirconium atoms bridged by the oxygen atoms of the phosphate groups, which are located alternatively above and below the zirconium plane. The *a* and *b* axes of the monoclinic cell lie in a plane parallel to the Zr atom plane and the area $a \times b/2$ corresponds to the free area around each phosphorus atom. This free area amounts to 25.1 Å^2, a value slightly higher than the 24 Å^2 typical for α-Zr(HPO$_4$)$_2$[3], probably because of the presence of the serine group bonded to the phosphate.

Further structural information was derived from a comparison of the IR absorption spectra of solid phosphoserine and zirconium serinephosphate (see Figure 5, spectra a and b, respectively). Both spectra show the typical bands of the protonated amino group and of the ionized carboxyl group. The region 1800−1300 cm^{-1} is particularly significant. The phosphoserine spectrum shows the typical amino acid I and II bands due to NH_3^+ deformations at 1640 and 1620 cm^{-1}, and the asymmetric stretching of the COO^- group at 1548 cm^{-1}. Furthermore, the absorption of the undissociated COOH group at 1717 cm^{-1} indicates that not all phosphoserine molecules are present as zwitterions. This absorption is absent in the zirconium serinephosphate spectrum (Figure 5, spectrum b). In addition, the I and II bands attributable to NH_3^+ deformation are split and shifted to lower wavenumbers (1628 and 1590 cm^{-1}), probably due to the hydrogen bonds being weaker in the layered compound. A similar shift is observed for the asymmetric stretching of the COO^- group (1501 cm^{-1})[14]. At higher wavenumbers (3700−3500 cm^{-1}), the zirconium serinephosphate spectrum shows a broad band, probably due to some water adsorbed on the surface microcrystals. Indeed, TG data do not show any bulk water loss. At lower wavenumbers, in the region 1300−800 cm^{-1}, the zirconium serinephosphate spectrum shows a complex system of bands attributable to the phosphate groups.

In conclusion, the data collected indicate that zirconium L-(+)-serinephosphate has a layered structure of the α-type, similar to that shown in Figure 6. This model representation was obtained by applying the Hyperchem MM+ force field (a modified version of the Allinger's original data set[15]) to a set of L-(+)-phosphoserine molecules to obtain a monolayer that fits the phosphate site distribution on each side of the inorganic matrix, which is assumed to be almost identical to that in α-Zr(HOPO$_3$)$_2$. It is interesting to note that when the layers are brought together, a hydrogen atom of the ammonium groups resides at such a distance from the oxygen atom of the carboxylic groups (2.6 Å) that allows the formation of hydrogen bonds. The layer−layer interactions are dominated by ionic and hydrogen bonds and the interlayer distance obtained from the model is similar to that measured from XRPD patterns.

Figure 6. Computer-generated model showing the packing of two layers of zirconium L-(+)-serinephosphate; the possible hydrogen bonds are indicated



Once the empirical formula and the structural model had been established, it seemed of interest to reconsider the thermal decomposition process, since the TG data (see Figure 3) showed that, at about 250°C, the first sharp weight

loss (20% of the initial weight) was near to that (19.3%) calculated for the following process:

$$Zr[HOOCCH(NH_2)CH_2OPO_3]_2 \rightarrow Zr(NH_2CH_2CH_2OPO_3)_2 + 2\ CO_2$$

Further evidence for this reaction was gained by collecting XRPD spectra of zirconium serinephosphate maintained at different temperatures (see Figure 7), and by performing evolution gas analysis (EGA) on a sample heated to 900°C (see Figure 8). Both these experiments gave clear evidence that a clean decarboxylation reaction occurs. It can be seen from Figure 7 that the *d* value does not change up to about 200°C, but decreases from 14.4 Å to 12.1 Å at 250°C. At higher temperatures, the XRPD patterns become more and more disordered. It is interesting to note that the phase at 250°C has an interlayer distance similar to that of zirconium 2-aminoethylphosphonate (11.3 Å)[16]. Furthermore, the EGA profile (see Figure 8) shows a marked increase of the CO_2 partial pressure in the 250−300°C temperature range.

Figure 7. XRPD patterns of zirconium L-(+)-serinephosphate maintained at the indicated temperature

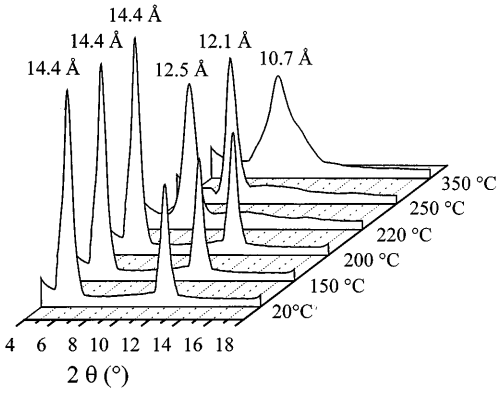
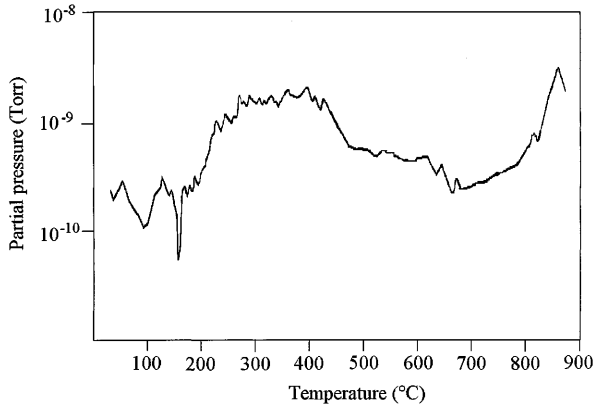


Figure 8. CO_2 partial pressure as a function of temperature in evolution gas analysis of zirconium L-(+)-serinephosphate



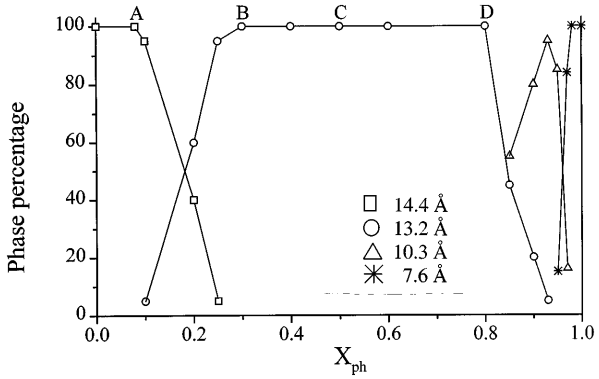
Considering the proposed structure, this new layered compound might be expected to behave as an amphoteric ion-exchange material, capable of taking up cations, anions and even neutral salts from solutions. Moreover, it could also be expected to act as an intercalating agent of polar molecules. Unfortunately, despite the numerous attempts made, the compound was found to be incapable of intercalating neutral species (alkanols, ethyleneglycol, propylamine, glycine), nor could it be titrated with NaOH or HCl solutions.

The lack of intercalation is probably due to the strong layer−layer interactions arising from the long-range ionic bonds between the zwitterions anchored to the surface of the layers, as well as from the network of interlamellar hydrogen bonds. The layer separation necessary for the insertion of the guest species seems to require a very high activation energy. However, it was observed that precipitates obtained after 3 days of precipitation time, which contained a small number of hydrogen phosphate groups, showed some exchange properties toward sodium ions. Therefore, zirconium serinephosphates in which some of the phosphoserine groups are replaced by phosphate groups were prepared, and their ion-exchange behaviour was investigated.

Preparation and Characterization of Zirconium L-(+)-Serinephosphate Phosphates

Several samples of zirconium serinephosphate phosphate, containing increasing amounts of phosphate groups, were prepared using the HF procedure[17] (see Experimental Section) starting from solutions with increasing mole fraction Xph = phosphoric acid/phosphoserine + phosphoric acid. The general trend shown by the system is summarized in Figure 9, where the approximate percentage composition of the phases obtained, identified by their interlayer distances, is plotted against the Xph in the precipitating solution. The percentage of a given phase was estimated from the intensity of the relevant first reflection in the XRPD powder pattern, which is assumed to be roughly proportional to the amount of that phase.

Figure 9. Percentage of the phases obtained in the system Zr(IV)/L-(+)-serinephosphate/phosphoric acid as a function of the molar fraction Xph (see text) in the precipitating solution



The system is discontinuous: initially, up to Xph ≈ 0.1, some phosphates replace an equivalent amount of serinephosphate groups in zirconium serinephosphate (14.4 Å) with slight modification of the XRPD patterns. When the maximum solubility of O_3POH groups in this latter phase is reached (the solid contains an average of one phosphate in every five groups), formation of a new phase with an

interlayer distance of 13.2 Å begins and the phase transition 14.4 → 13.2 Å is completed at Xph ≈ 0.3. The solids precipitated in the range 0.3 ≤ Xph ≤ 0.8 maintain about the same interlayer distance. Concomitantly, their phosphate content increases from one phosphate in every three groups to the idealized composition of two phosphates in every three groups.

A further increase in Xph produces another immiscible phase with a higher phosphate content and an interlayer distance of 10.3 Å, together with pure α-$Zr(HOPO_3)_2$ (interlayer distance 7.6 Å). It proved impossible to isolate the 10.3 Å phase in pure form. However, the spacing of 10.3 Å would be that expected for a mixed compound[18], in which a layer of serinephosphate containing phosphate groups regularly alternates with a layer containing only phosphates, i.e. (13.2 Å + 7.6 Å)/2 = 10.4 Å.

Some representative samples of the mixed compounds obtained by varying the Xph in solution (those marked with a capital letter in Figure 9) were characterized by thermal analysis, as well as by C, N elemental analysis in order to establish their empirical formulae. Figure 10 shows the weight-loss curves of the samples, previously conditioned at room temp. and 75% relative humidity, and the results of C, N elemental analyses. When heated at 1000°C, all samples show the typical XRPD pattern of cubic ZrP_2O_7. Assuming that all the zirconium and phosphorus present was transformed into zirconium pyrophosphate, and taking into account the experimental percentage weight loss, the formula weights were calculated at room temp. Furthermore, the results of C,N elemental analyses allow the determination of the number of moles of phosphoserine per formula weight, while the percentage weight losses at 150°C allow determination of the number of moles of water of hydration. The empirical formula of the mixed compounds can be written as $Zr[HOOCCH(NH_2)CH_2OPO_3]_{2-x}$-$[HOPO_3]_x \cdot n\ H_2O$. Table 1 shows the values of x and n for the samples examined, together with the interlayer distance taken from the XRPD patterns depicted in Figure 11. In addition, Table 1 includes the no. of mmol of exchangeable protons bound to the carboxylic and phosphate groups per gram of compound, calculated on the basis of the empirical formula. To assess their ion-exchange capacity, the samples were titrated with an NaOH solution in the presence of added NaCl. The potentiometric titration curves, shown in Figure 12, give experimental ion-exchange capacities very near to those that would be expected if only the protons of the P−OH groups were replaced by the sodium ions. Furthermore, the titration curves do not show any well-defined ion-exchange plateau, as though the Na^+ uptake process occurs without the phase transitions usually associated with ion-exchange processes in layered metal(IV) phosphates[19]. The XRPD patterns of the samples obtained after titration indicate that the uptake process occurs without appreciable alteration of the interlayer distance. It seems that the serinephosphate groups act as pillars, determining the interlayer distance, and that the ionogenic phosphate groups are randomly inserted between these pillars. Hence, the incoming sodium ions find sufficient space to be accommodated without an increase of the interlayer distance. In this context, it was of interest to examine the surface properties of the mixed compounds in comparison with those of the original zirconium serinephosphate.

Figure 10. Percent weight loss as a function of the temperature of the indicated samples previously equilibrated at 75% relative humidity at room temp. Heating rate 5°C/min, air flow; the C,N elemental analysis (percent by weight) of the same samples is reported in the inset

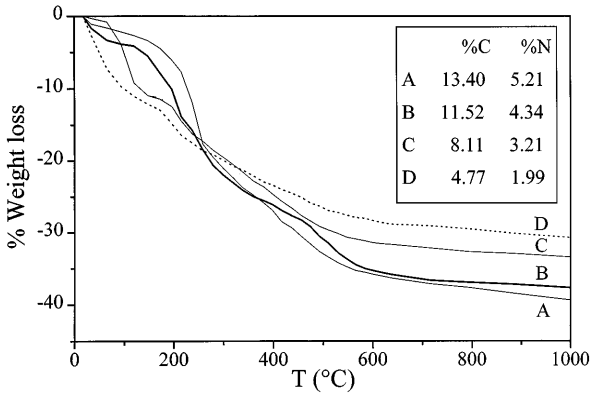


Figure 11. XRPD patterns of samples A and C (see text)

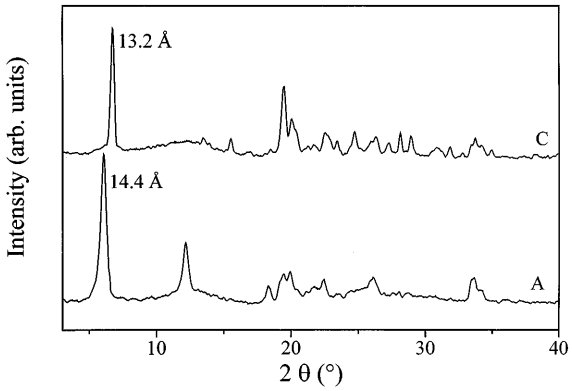
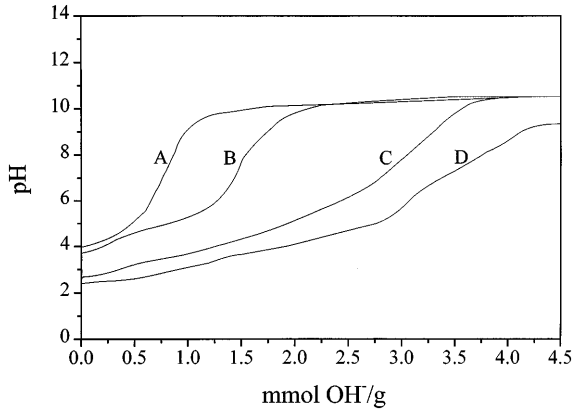


Table 1. Composition, interlayer distance, and calculated ion-exchange capacity of the two ionogenic groups of zirconium serinephosphate phosphates, obtained at the indicated values of mole fraction of phosphoric acid in solution (Xph)

Sample	Xph	$Zr[HOOCCH(NH_2)CH_2OPO_3]_{2-x}(HPO_4)_x \cdot n\ H_2O$ x	n	d [Å]	mmol H^+ [−COOH]/g	mmol H^+ [−POH]/g
A	0.1	0.36	0.65	14.4	3.75	0.823
B	0.25	0.60	1.14	13.2	3.29	1.41
C	0.5	1.1	2.05	13.2	2.26	2.76
D	0.8	1.4	2.62	13.2	1.57	3.66

N_2 adsorption isotherms of zirconium serinephosphate and of samples A and C were recorded. B.E.T. analysis of the isotherms gives specific surface areas of 5.5, 10.6, and 54.5 m^2/g, respectively. It seems that the replacement of serinephosphate groups by phosphates produces an increase in the specific surface area of the solids and the high surface area of sample C may be attributed to the presence of some microporosity in the interlayer region.

Figure 12. Potentiometric titration curves of the indicated samples with a 0.1 M NaOH solution in the presence of 0.1 M NaCl as added salt



Conclusion

As noted by Clearfield in a recent monograph[7], one of the most exciting aspects of the chemistry of metal(IV) phosphates and phosphonates is the possibility of manipulating the inorganic layered backbone by "soft chemistry" procedures, so as to design materials with specific properties. The work reported herein shows that it is possible to anchor an amino acid function bearing a chiral centre to the α-layer. The α-zirconium serinephosphate obtained does not show the expected ion-exchange or intercalation properties. However, the interlayer region becomes accessible to sodium ions upon replacing some serinephosphate groups by phosphate groups. The zirconium serinephosphate phosphates obtained merit further study, e.g. with regard to investigation of their ion-exchange and intercalation properties with the aim of producing exfoliation of the layered microcrystals. Furthermore, new chiral stationary phases may be obtained by deposition of the exfoliated materials onto suitable supports. This may represent an alternative method to that suggested by Malluk and coworkers[20] based on the intercalation of a chiral receptor in the original α-zirconium phosphate.

Financial support of the *Consiglio Nazionale delle Ricerche* and of the *Ministero Università e Ricerca Scientifica e Tecnologica* is gratefully acknowledged.

Experimental Section

Materials: L-(+)-Phosphoserine (2-amino-3-phosphatylpropanoic acid) was purchased from Sigma and used as received. $ZrOCl_2 \cdot 8\ H_2O$ was a Merck product; all other chemicals were Carlo Erba RP-ACS reagents. – Zirconium serinephosphate and zirconium serinephosphate phosphates were prepared using the method of slow decomposition of zirconium fluoro complexes[3] in the presence of an aqueous solution of phosphoric acid and/or phosphoserine. The preparation conditions were as follows: molar ratio $Zr^{IV}/HF = 6$, molar ratio $P/Zr^{IV} = 3$, phosphoserine and/or phosphoric acid concentration 0.2 M, temperature of precipitation 60°C, time of precipitation 1–4 d. After precipitation, the microcrystals were separated from the solution, washed with distilled water up to pH ≈ 4, and finally dried at room temperature over a saturated NaCl solution (relative humidity ca. 75%) or over phosphorus pentoxide.

Instrumentation: The X-ray powder diffraction (XRPD) patterns of the samples were recorded by the stepwise scanning procedure (increment: $2\Theta = 0.02°$, time per step: 5 s) with a computer-controlled Philips PW 1710 diffractometer, using Ni-filtered Cu-K_α radiation. The XRPD patterns at different temperatures were obtained with an A. Paar HTK diffraction camera. – TG and DTA analyses were performed with a Stanton Redcroft thermal analyser (STA 781), with a heating rate of 5°C/min under an air or O_2 flow. This apparatus coupled with a Fisons mass spectrometer was used to obtain EGA curves. – N_2 adsorption and desorption isotherms were recorded with a Carlo Erba Sorptomatic 1800 apparatus. – C,H,N, elemental analyses were carried out with a Carlo Erba Model 1106 Analyser. Densities were determined pycnometrically at 20°C, using CCl_4 as the displacement liquid. – The molar ratios phosphate/serinephosphate in the products investigated were also estimated by liquid-state ^{31}P-NMR analysis with a Bruker AC 200 instrument, after dissolving 0.05 g of the sample in a small volume of conc. HF (ca. 0.5 ml) and D_2O as solvent. – The ion-exchange experiments were performed with a Mettler DK automatic titrator operating in equilibrium-point mode, by titrating 200 mg of the sample, suspended in 40 ml of 0.1 M NaCl solution, with 0.1 M NaOH solution under an N_2 stream.

[1] G. Alberti, U. Costantino, S. Allulli, N. Tomassini, *J. Inorg. Nucl. Chem.* **1978**, *40*, 1113.
[2] [2a] L. Maya, *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 207. – [2b] M. B. Dines, P. M. Di Giacomo, *Inorg. Chem.* **1981**, *20*, 92. – [2c] M. B. Dines, P. C. Griffith, *Polyhedron* **1982**, *1*, 62. – [2d] Ortiz-Avila, A. Clearfield, *Inorg. Chem.* **1985**, *24*, 1773.
[3] J. M. Troup, A. Clearfield, *Inorg. Chem.* **1977**, *16*, 3311.
[4] [4a] M. B. Dines, P. M. Di Giacomo, K. P. Callahan, P. C. Griffith, R. H. Lane, R. E. Cooksey in *Chemically Modified Surfaces in Catalysis and Electrocatalysis*, vol. 192 (Ed.: J. S. Miller), ACS Symposium Series, Washington DC, **1982**, chapter 12. – [4b] G.Alberti, U. Costantino, J. Kornyei, M. L. Luciani Giovagnotti, *React. Polym.* **1985**, *4*, 1.
[5] G. Alberti, M. Casciola, U. Costantino, R. Vivani, *Adv. Mater.* **1996**, *8*, 291.
[6] G. Alberti in *Solid-State Supramolecular Chemistry: Two- and Three-Dimensional Inorganic Networks* (Eds.: G. Alberti, T. Bein), vol. 7 of the series *Comprehensive Supramolecular Chemistry* (Ed.: J. M. Lehn), Pergamon, Elsevier Science, Oxford, **1996**, chapter 5.
[7] A. Clearfield in *Progress in Inorganic Chemistry*, vol. 47 (Ed.: K. D. Karlin), John Wiley & Sons, New York, **1998**, 371–508.
[8] E. Brunet, M. Huelva, R. Vazquez, O. Juanes, J. C. Rodriguez-Ubis, *Chem. Eur. J.* **1996**, *2*, 1578.
[9] G. Alberti, L. Boccali, C. Dionigi, R. Vivani, V. I. Kalchenko, L. I. Atamas, *Supramol. Chem.* **1996**, *7*, 129.
[10] E. Jaimez, G. B. Hix, R. C. T. Slade, *J. Mater. Chem.* **1997**, *7*, 475.
[11] D. M. Poojary, B. Zhang, A. Clearfield, *Angew. Chem.* **1994**, *106*, 2420; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2324.
[12] P. E. Werner, L. Eriksson, M. Westdhal, *J. Appl. Crystallogr.* **1985**, *18*, 367.
[13] G. Alberti, U. Costantino, M. L. Luciani Giovagnotti, *J. Inorg. Nucl. Chem.* **1979**, *41*, 643.
[14] F. S. Parker, *Applications of Infrared Spectroscopy in Biochemistry, Biology, and Medicine*, Plenum Press, New York, **1971**, chapter 9.
[15] N. L. Allinger, *J. Am. Chem. Soc.* **1977**, *99*, 8127.
[16] M. Casciola, U. Costantino, A. Peraio, T. Rega, *Solid State Ionics* **1995**, *77*, 229.
[17] G. Alberti, E. Torracca, *J. Inorg. Nucl. Chem.* **1968**, *30*, 317.
[18] G. Alberti, U. Costantino, G. Perego, *J. Solid State Chem.* **1986**, *63*, 455.
[19] G. Alberti, *Acc. Chem. Res.* **1978**, *11*, 163.
[20] G. Cao, M. E. Garcia, M. Alcalà, L. F. Burgess, T. E. Mallouk, *J. Am. Chem. Soc.* **1992**, *114*, 7574.

[98114]