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SYNTHESIS AND ION-EXCHANGE PROPERTIES OF ZIRCONIUM BIS-(CARBOXYMETHANEPHOSPHONATE), A NEW ORGANIC–INORGANIC ION EXCHANGER

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SUMMARY

By slowly decomposing zirconium fluoro-complexes in the presence of tri-methylphosphonoacetate, a crystalline compound of formula $Zr(HOOCCH_2PO_3)_2$ has been obtained. Experimental evidence showed this compound to have a layered structure of the α-$Zr(HPO_4)_2 \cdot H_2O$ type. Since the proton of the carboxylic group can be replaced by other cations, this compound behaves as an inorganic–organic ion exchanger with carboxylic groups fixed to the insoluble crystalline inorganic matrix. The titration curve of this compound with 0.100 M (NaCl + NaOH) solutions was investigated. Owing to the potential applications of $Zr(HOOCCH_2PO_3)_2$ in gas or thin-layer chromatography, the ion-exchange properties relative to the functional groups present at the surface of the micro-crystals were also studied.

INTRODUCTION

Zirconium bis(monohydrogenphosphate) monohydrate, α-$Zr(HPO_4)_2 \cdot H_2O$, exhibits a layered structure, each layer consisting of zirconium atoms lying in a plane and bridged through tetrahedral PO_4 groups, located above and below this plane[1]. Three oxygens of each PO_4 group are bonded to three different Zr atoms while the fourth oxygen bears the proton that can be easily replaced by other cations. In a previous paper[2] we reported compounds in which the $\equiv$P–OH tetrahedral groups of $Zr(HPO_4)_2$ are replaced by $\equiv$P–R or $\equiv$P–OR groups (R being an organic radical). In particular, compounds of formulae $Zr(C_6H_5PO_3)_2$, $Zr(HOCH_2PO_3)_2$ and $Zr(C_2H_5OPO_3)_2$ and having a layered structure very similar to that of α-$Zr(HPO_4)_2 \cdot H_2O$ were prepared. Apart from their fundamental aspects, these compounds might constitute a new series of solid supports for gas or thin-layer chromatography and could be used as intercalating agents for polar molecules. If an ionogenic group, such as $-SO_3H$, $-COOH$, $-N(CH_3)_3OH$, etc., is present in the organic radical, the compound could act as an ion exchanger in which the ionogenic groups of organic nature are bonded to an insoluble crystalline inorganic matrix. This compound could be considered as an organic–inorganic ion exchanger.

This paper reports the synthesis and some cation-exchange properties of an

organic–inorganic ion exchanger, zirconium bis(carboxymethane phosphonate), which contains the carboxyl functional group.

EXPERIMENTAL

Chemicals

$ZrOCl_2 \cdot 8H_2O$ was a Merck (Darmstadt, G.F.R.) "pro analysi" product. Trimethylphosphonoacetate, $(CH_3O)_2P(O)CH_2CO_2CH_3$, was supplied by Ega-Chemie (Steinheim, G.F.R.); all other reagents were Carlo Erba (Milan, Italy) RPE products.

Preparation of material

The method[2] of slow decomposition of zirconium fluoro-complexes in the presence of the appropriate phosphonic ester was used. A clear solution, having the composition $[(CH_3O)_2P(O)CH_2CO_2CH_3] = 4$, $[(CH_3O)_2P(O)CH_2CO_2CH_3]/[Zr] = 10$, $[F]/[Zr] = 6$ and $[HCl] = 1$ M, was left to evaporate at 60° in order to decompose the zirconium fluoro-complexes and to hydrolize the ester groups. The volume of the solution was maintained constant by means of a siphon apparatus. The product began to precipitate within 4 days and the precipitation was complete in 10 days. The crystals were washed with distilled water up to pH ≈ 3.5 and stored over P_4O_{10} (the X-ray powder patterns of wet and anhydrous products were identical).

Analytical procedure

Elementary analysis of the crystals was carried out as previously described[2]. The titration curves were performed with the batch procedure by equilibrating, at $25 \pm 1°$, several samples (0.500 g) with 100 ml of 0.100 M (MCl + MOH) solution (M = Li, Na, K). After the equilibration time (7 days), the solids were filtered off and their X-ray diffractograms were recorded, while the liquids were analyzed for their pH′ value and metal ion content. The carboxymethane phosphonate groups produced from the hydrolysis of the compound were analyzed by titrating the supernatant solutions with 0.010 M HCl using a Mettler automatic titrimeter. The number of exchangeable protons present at the surface of the micro-crystals and the surface ion exchange isotherms were obtained as already described[3,4]. Metal cations were determined with a Perkin-Elmer 305 atomic absorption spectrophotometer. Lanthanum was determined colorimetrically after complexation with alizarin red S ($\lambda = 5500$ Å). The densities were measured pycnometrically at $20.0 \pm 0.1°$ using CCl_4 as displacing liquid. X-ray diffraction patterns were taken with a General Electric Diffractometer using Ni-filtered CuK_α radiation.

RESULTS AND DISCUSSION

Chemical analyses showed the compound to be zirconium bis(carboxyme-thanephosphonate), $Zr(HOOCCH_2PO_3)_2$. Experimental analysis data (%, w/w): 27.7% Zr, 18.8% P, 7.3% C, 2.4% H. Calculated data for $Zr(HOOCCH_2PO_3)_2$: 27.9% Zr, 18.7% P, 7.1% C, 2.3% H.

The thermogravimetric analysis of the product, whose X-ray diffraction pattern is reported in Table I, indicated that it begins to decompose at 250°, while the percent weight loss at 1000° agrees well with the proposed formula. Single crystals for X-ray

TABLE I

X-RAY POWDER DIFFRACTION PATTERNS

s = Strong; m = medium; w = weak; v = very.

$d\,(\text{Å})$	
$Zr(HOOCCH_2PO_3)_2$	$Zr(NaOOCCH_2PO_3)_2 \cdot 4H_2O$
11.1 vs	14.4 vs
5.56 s	7.22 s
4.45 w	5.15 w
4.37 w	4.87 m
3.88 m	3.58 w
3.79 w	2.82 w
3.70 w	
3.37 vw	
3.32 vw	
3.16 vw	
3.09 vw	
3.02 w	
2.77 w	
2.65 w	

structural determination were not obtained but some experimental evidence, such as the shape of the crystals (hexagonal platelets), the intercalation of amines[5] and the determination of the parameter n (number of formula units contained in a square centimetre of layer), suggests that this compound has a layered structure very similar to that of α-Zr(HPO₄)₂·H₂O.

As discussed in ref. 6, the parameter n is easily obtained from the relation $n = \varrho d/M$, where ϱ is the density (g/cm³), d the inter-layer distance, in cm, and M the formula weight of the compound. The n value of compounds having a layered structure of the α-type[6] was found to range from $6.8 \cdot 10^{-10}$ to $6.9 \cdot 10^{-10}$ moles/cm²; the n value calculated for Zr(HOOCCH₂PO₃)₂ is $n = 2.31 \times 11.1 \cdot 10^{-8}/367.2 = 6.95 \cdot 10^{-10}$ and this gives strong support to the hypothesis of a α-layered structure for Zr(HOOCCH₂PO₃)₂. In this case the structure of Zr(HOOCCH₂PO₃)₂ should be similar to that of α-Zr(HPO₄)₂·H₂O with the $\equiv$P–OH groups replaced by $\equiv$P–CH₂–COOH. Now, since the distance between adjacent phosphorus atoms in the x–y plane is 5.3 Å (Fig. 1a), there is not room enough for the –CH₂–COOH groups of two adjacent inorganic layers to be inter-penetrated. A double film of organic groups is thus expected to be present between the inorganic layers, as shown schematically in Fig. 2.

The inter-layer distance may be estimated taking into account the length of two $\equiv$P–CH₂–COOH groups and assuming that the distance of the plane of the phosphorus atoms from the plane of zirconium atoms is 1.6 Å, as in α-Zr(HPO₄)₂·H₂O[7] (Fig. 1b). The experimental value of 11.1 Å (found by X-ray measurements) is in good agreement with the estimated value (ranging from 10.8 to 11.6 Å according to the mutual position of terminal –OH groups). The forces holding the layers are Van der Waals forces or hydrogen bonds between adjacent –COOH groups.

This compound may be considered as an example of an inorganic–organic cation exchanger because the proton of the carboxylic group, bonded to an insoluble inorganic matrix, can be replaced by other cations. Furthermore, because of its
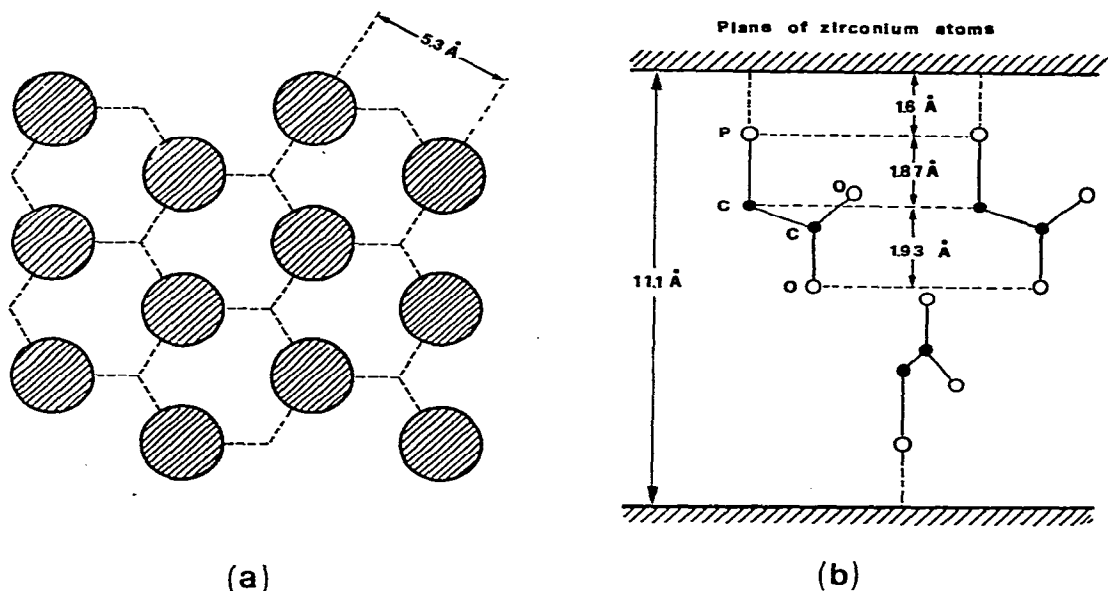
(a)   (b)

Fig. 1. (a) Idealized position of the phosphorus atoms in $Zr(HOOCCH_2PO_3)_2$, viewed in a plane parallel to the layers and passing through the baricentres of the atoms. (b) Schematic representation of the P–CH$_2$–COOH groups in $Zr(HOOCCH_2PO_3)_2$. Hydrogen atoms are not shown.
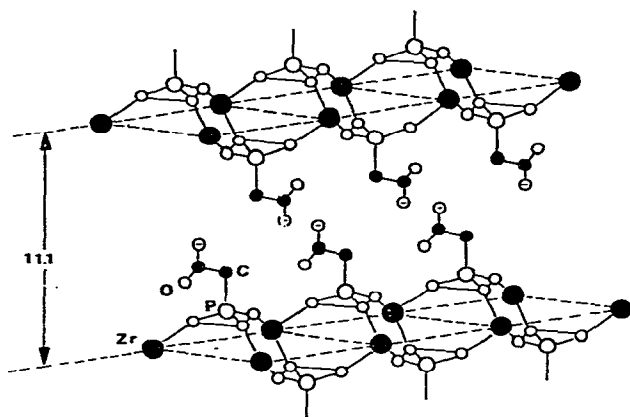

Fig. 2. Idealized crystal structure of zirconium bis(carboxymethanephosphonate). The minus sign refers to oxygens carrying the fixed negative charges.

layered structure, $Zr(HOOCCH_2PO_3)_2$ may be considered an organic–inorganic intercalating agent for polar molecules. Preliminary experiments showed that n-alkylamines can be intercalated[5].

Fig. 3 shows the titration curve of $Zr(HOOCCH_2PO_3)_2$ with 0.100 M (NaCl + NaOH) solutions. In the same figure the Na$^+$-uptake curves, as well as the mmoles of phosphonate groups released to the solution at the various pH values, are reported. From the sodium uptake and from the mmoles of phosphonate released to the solution at pH 7.3, we can derive an experimental ion-exchange capacity of 4.80 + 0.6 =
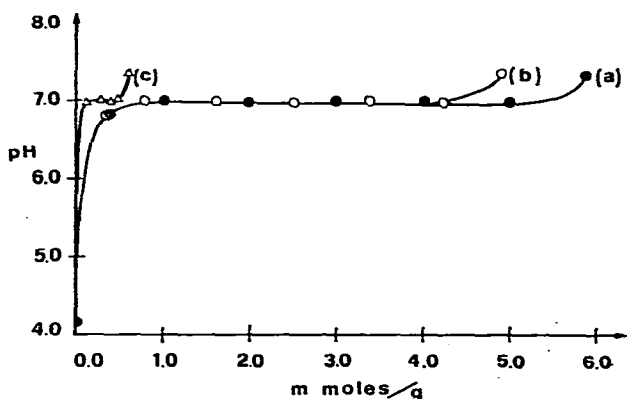
Fig. 3. H^+/Na^+ ion-exchange process on $Zr(HOOCCH_2PO_3)_2$, titrated with $0.100\ M$ (NaCl + NaOH) solution at $25 \pm 1°$ (batch procedure). Curves: a, NaOH added; b, sodium ion uptake; c, phosphonate groups released.

5.40 mequiv./g, a value close to 5.45 mequiv./g, the theoretical ion-exchange capacity calculated assuming two exchangeable hydrogen ions per formula weight of exchanger.

The exchange occurs in a single step at pH $\approx$ 7 and, apart from the small hydrolysis, it leads to the formation of the phase $Zr(NaOOCCH_2PO_3)_2 \cdot 4H_2O$, whose X-ray diffraction pattern is reported in Table I.

X-ray analyses of samples, having increasing Na^+-conversion, showed that the process occurs discontinuously via two phases, $Zr(HOOCCH_2PO_3)_2$ ($d = 11.1$ Å) and $Zr(NaOOCCH_2PO_3)_2 \cdot 4H_2O$ ($d = 14.4$ Å), one transforming into the other as the exchange proceeds. The ion-exchange process can thus be schematically written (neglecting the solubility of the ingoing sodium ion in the already formed phases) as:

$$Zr(HOOCCH_2PO_3)_2 + 2Na^+ + 2OH^- + 2H_2O \rightarrow Zr(NaOOCCH_2PO_3)_2 \cdot 4H_2O$$
$$(d = 11.1\ \text{Å}) \qquad\qquad\qquad\qquad\qquad\qquad (d = 14.4\ \text{Å})$$
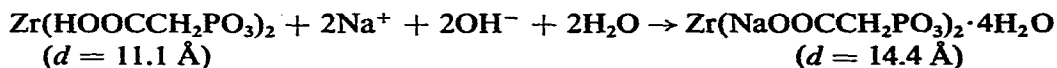
This behaviour is very similar to that found in the exchange mechanism of α-$Zr(HPO_4)_2 \cdot H_2O$ and of other layered inorganic exchangers[8], and it is further support for the layered structure of this material.

Attempts to convert $Zr(HOOCCH_2PO_3)_2$ into the lithium or potassium forms led to highly hydrolyzed materials. In our opinion this is due to steric hindrance to the diffusion of cations having large crystalline or hydrated ionic radii within the layers of exchanger. In fact, the greater the steric hindrance, the higher must be the pH of the supernatant solutions at which the protons of the exchanger are replaced. Now, if the pH becomes too high, the exchanger is strongly hydrolyzed and the hydrolysis prevents the study of the ion-exchange process. On the other hand, the steric hindrance to the diffusion of counter-ions within the layers of $Zr(HOOCCH_2PO_3)_2$ permits the replacement of the exchangeable protons present at the surface of the micro-crystals without exchanging the inner ones. Thus, the ion-exchange properties relative to the surface of the micro-crystals of this exchanger can be easily investigated. Such an investigation is useful for the potential applications of $Zr(HOOCCH_2PO_3)_2$ in thin-layer or column chromatography and it gives informa-

tion on the selectivity of the surface carboxylic acid groups towards various cations.

A method to determine the number of surface fixed charges per gram of α-$Zr(HPO_4)_2 \cdot H_2O$ has been previously developed[3]. Following the same procedure, the surface ion-exchange capacity of $Zr(HOOCCH_2PO_3)_2$ has been determined by bringing in contact 1 g of exchanger with 25 ml of 0.5 N $BaCl_2$ solution. A value of 13.4 μequiv. per gram of micro-crystals was found. It must be noted that this value depends on the particle size of the material and thus it may change for the different preparations.

The ion-exchange properties, relative to the surface of zirconium phosphate micro-crystals, towards mono-, di- and trivalent cations have been investigated[3,4]. Owing to the weakly acidic character of the carboxylic group, it was found that hydrogen ions are so strongly preferred to alkali metal ions that no appreciable exchange takes place in acidic media. The selectivity increases, as expected, with increasing charge of the cations. It was thus possible to determine the H^+/M^{z+} ion-exchange isotherms for Mg^{2+}, Cu^{2+}, Ba^{2+} and La^{3+} (Fig. 4). The selectivity also increases with increasing crystalline radius of the cations. As already found for α-$Zr(HPO_4)_2 \cdot H_2O$, the surface isotherms are sigmoidal. This means that the surface selectivity of the exchanger towards these cations decreases as they progressively replace the protons at the surface of the micro-crystals. The shape of the isotherms may be related to the arrangement of the surface fixed charges. In a perfect crystal, this arrangement should be similar to that found for α-$Zr(HPO_4)_2 \cdot H_2O$ which, in turn, is similar to the arrangement of the phosphorus atoms in Fig. 1a. The fixed charges are therefore arranged in an hexagonal array and the distance between adjacent charges should be 5.3Å. Thus, as discussed in a previous paper concerning the surface isotherms of α-Zr-$(HPO_4)_2 \cdot H_2O$[4], the sigmoidal isotherms may be due to the difficulty of accommodating two large hydrated counter-ions in adjacent positions. The surface ion-exchange isotherms of α-$Zr(HPO_4)_2 \cdot H_2O$ and $Zr(HOOCCH_2PO_3)_2$ are neverless very similar. Only the H^+/Cu^{2+} isotherm is appreciably different and this indicates that the interaction of Cu^{2+} with $\equiv P-O^-$ and $\equiv P-CH_2-COO^-$ groups is substantially different.
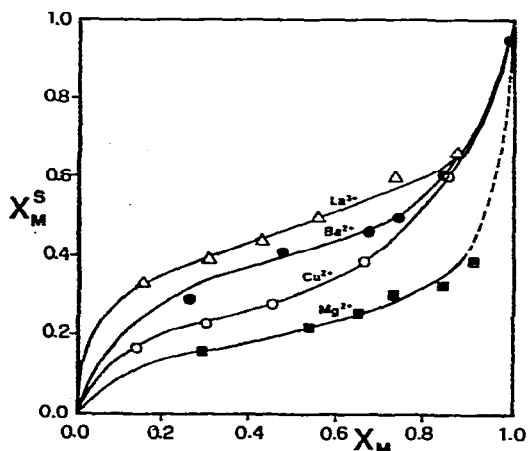

Fig. 4. H^+/M^{z+} ion-exchange isotherms for the surface of $Zr(HOOCCH_2PO_3)_2$ micro-crystals. X_M = Equivalent ionic fraction of M^{z+} in solution; X_M^s = μequiv. of M^{z+} exchanged at the surface of the exchanger divided by its surface ion-exchange capacity (13.4 μequiv./g); $C = 5 \cdot 10^{-4} N$; 25 $\pm$ 1°.

CONCLUSIONS

The results indicate that the synthesis of inorganic–organic ion exchangers, in which the inorganic matrix has a structure similar to that of the layers of α-Zr(HPO$_4$)$_2 \cdot$H$_2$O, is possible. With a suitable choice of different phosphonic acids (or esters) and also by replacing the zirconium with other tetravalent metals, several other inorganic–organic ion exchangers could be prepared. In our opinion, the only restrictions upon these syntheses are in the nature of the phosphonic groups involved. Three oxygens of these groups must be able to bind the tetravalent metal atoms; furthermore, in order to obtain a layered compound with an α-type structure, the organic radical bonded to the phosphorus atom must have a Van der Waals cross-section diameter lower than the distance between two tetravalent metal atoms in the plane [5.3 Å in α-Zr(HPO$_4$)$_2 \cdot$H$_2$O].

Finally, the stability of the phosphonic acids must also be taken into account. Attempts to prepare compounds having the phospho–amine bond failed owing to the high rate of hydrolysis of the $\equiv$P–NH$_2$ groups. From a practical point of view the organic–inorganic ion exchangers could be of great interest as solid supports for chromatographic separations and, in this connection, chromatographic experiments on thin layers of Zr(HOOCCH₂PO₃)₂ should be performed. Moreover, taking into account that some salt forms of α-zirconium phosphate have been successfully employed as solid supports for gas chromatographic separations of polar organic molecules[9], a study of the sorption at the surface of inorganic–organic crystals would be of interest.

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