Inorganica Chimica Acta, 201 (1992) 207–212

Preparation and some properties of Zr phosphate hypophosphite and Zr phosphate dimethylphosphinate with γ-layered structure

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(Received March 30, 1992; revised June 8, 1992)

Abstract

It was found that the interlayer dihydrogen phosphate of γ-Zr phosphate, other than by $O_2P(OH)R$ groups, can be totally or partially replaced by O_2PR_2 groups ($R=H$ or organic radical). The preparations of two new compounds having composition $ZrPO_4 \cdot O_2PH_2$ (interlayer distance = 8.84 Å) and $ZrPO_4 \cdot [O_2P(OH)_2]_{0.33}$-$[O_2P(CH_3)_2]_{0.67}$ (int. dist. = 10.33 Å) are reported and discussed. The compounds were characterized by X-ray powder diffraction and thermogravimetric analysis, as well as, after dissolution, by chemical and NMR analysis. The formulation of the γ-layered compounds can be now generalized as $ZrPO_4(O_2PR'R'')_{1-x}(O_2PR'''R'''')_x \cdot nS$, where the various R can be H, OH or an organic radical while S is a solvent in the interlayer region. Some considerations on their structure and their ion-exchange properties are also reported.

Introduction

Different from α-zirconium phosphate (α-ZP), where all the phosphate groups are bonded with three oxygens to three different Zr atoms [1, 2], in the γ-Zr phosphate (γ-ZrP) 50% of the phosphate groups are bonded with four oxygens to four different Zr atoms, while the remaining 50% are bonded only with two oxygens to two different Zr atoms [3–5]. Thus, although the anhydrous forms of these compounds have the same composition, $ZrH_2P_2O_8$, they must be formulated as α-$Zr(O_3POH)_2$ and γ-$ZrPO_4 \cdot O_2P(OH)_2$, respectively. It is evident that the prefixes α and γ of the previous literature, when it was believed that the differences between α- and γ-ZrP were essentially due to a different stacking of the layers [1, 6], could now no longer be necessary. However, we still maintain in this paper these prefixes as a short and simple identification of the two compounds so as to avoid confusion with the previous literature.

It is now also evident that pure M(IV) phosphonates with the γ-layered structure cannot exist [5]; in fact, only three oxygens are present in the phosphonic acids, so that only layered α-$M(IV)(O_3PR)_2$ or pillared α-$M(IV)(O_3P\text{-}R\text{-}PO_3)$ can be formed with these acids. However, if the $O_2P(OH)_2$ groups present in the interlayer region are totally or partially exchanged with $O_2P(OH)R$ groups, mixed phosphate–phosphonate γ-layered compounds of composition $M(IV)PO_4$-$[O_2P(OH)_2]_{1-x}[O_2P(OH)R]_x \cdot nH_2O$, where $R=H$ or an organic radical, can be prepared. Therefore the previous literature on the preparation of γ-derivatives [7, 8] has recently been reinterpreted in the light of the new knowledge and various γ-Zr phosphate phosphonates have been obtained and characterized [9, 10].

On the other hand, while M(IV) hypophosphite or phosphinates with α-layered structure cannot be formed (only two oxygens are available), such a possibility exists for mixed γ-layered compounds.

To confirm that these γ-derivatives can really be obtained, an investigation into the preparation of two new γ-layered compounds, $ZrPO_4[O_2P(OH)_2]_{1-x}$-$[O_2PH_2]_x \cdot nH_2O$ and $ZrPO_4[O_2P(OH)_2]_{1-x}[O_2P(CH_3)_2]_x \cdot nH_2O$, was performed.

A preliminary characterization of these compounds, as well as some consideration of their structure, are reported and discussed.

Experimental

Reagents and materials

Except for zirconyl chloride octohydrate (E. Merck) and dimethylphosphinic acid ($(CH_3)_2PO_2H$, Riedel De Haen AG), all other chemicals were C. Erba RPE grade.

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The hypophosphorous acid, H_3PO_2, was prepared by passing, under a nitrogen atmosphere, a saturated (~ 0.75 M) solution of calcium hypophosphite through a cation exchange column containing Amberlite IR120.

The γ-ZrP was prepared as reported earlier [11].

Instrumental

The X-ray powder diffraction patterns of the samples were recorded according to the step scanning procedure (step size = 0.03°) with a computerized Philips PW 1710 diffractometer, using Ni filtered Cu $K\alpha$ radiation. The weight loss curves were obtained under an oxygen atmosphere with a heating rate of 2 °C/min using a Stanton Redcroft thermal analyser (STA780 series).

The relative proportions of H_2PO_4, H_2PO_2 or $(CH_3)_2PO_2$ in the products investigated were obtained by the liquid state ^{31}P NMR analysis with a Bruker AC200 instrument, after dissolving 0.05 g of the sample in a little conc. hydrofluoric acid (≈ 0.5 ml) and dimethyl sulfoxide–D_2O as solvent. The shifts of the signals of orthophosphoric, hypophosphorous and dimethylphosphinic acids were 2.9, 15.3 and 60.7 ppm, respectively. The shifts are relative to 85% D_3PO_4 in D_2O, with a positive sign indicating a shift to lower field.

The longitudinal relaxation time constants (T_1) were measured using the non-selective inversion recovery method. The measurements were performed at 25 °C directly in the solutions to be analysed. Since the T_1 values were greatly affected by the relative proportions of HF, dimethyl sulfoxide and D_2O present in the sample solutions, a range of values for each kind of phosphorus was found: T_1 $(H_3\mathit{P}O_4) = 1.0$–2.2 s; T_1 $(H_3\mathit{P}O_2) = 0.5$–1.3 s; T_1 $[(CH_3)_2\mathit{P}O_2] = 0.9$–$2.0$ s.

To ensure quantitative area measurements, a delay five times larger than the maximum T_1 was employed between consecutive acquisitions.

Ion-exchange procedure

The ion exchange experiments were performed by titrating 200 mg of the sample, suspended in 40 ml 0.1 N NaCl, with 0.1 N NaOH solution under a constant stream of nitrogen, using a Mettler DK autotitrator.

Results and discussion

Preparation of γ-zirconium phosphate hypophosphite

Preliminary attempts to replace the interlayer $H_2PO_4^-$ groups of γ-ZrP by the $H_2PO_2^-$ groups of calcium hypophosphite or of hypophosphorous acid by topotactic reactions were carried out over a wide range of experimental conditions: concentrations were varied between 0.1–1.5 M, temperatures between 20 and 90 °C and contact times between 6 h and 28 days. With calcium hypophosphite, partially exchanged zirconium phosphate hypophosphite and/or zirconium phosphate phosphite hypophosphite or their mixtures were always formed. From these attempts, it was concluded that the best results could be obtained if pure hypophosphorous acid was used instead of its calcium salt. In this case there is not the inconvenience previously found for phosphonic acids [5–9] that α-derivatives may be formed at high acid concentrations. However high concentrations, although possible, are not necessary since it was found that the rate of the topotactic reaction already proceeds satisfactory at concentrations >1 M. It was also found that, to avoid the possible oxidation of the hypophosphite to phosphite, it was better to operate at temperatures lower than 50 °C under a nitrogen atmosphere. However, if the temperature was too low (e.g. room temperature) the crystalline γ-ZrP phase was gradually converted to an amorphous product which, after heating at about 45 °C for 7–10 days in the mother waters, finally gave the full exchanged Zr phosphate hypophosphite with a good degree of crystallinity. On the basis of these observations, the topotactic reaction was directly carried out at 45 °C with good results.

A typical method of preparation of γ-Zr phosphate hypophosphite (ZrPhP) is as follows. About 100 ml of freshly prepared 1.5 M H_3PO_2 solution were taken, under nitrogen, in a plastic bottle. Nitrogen gas was passed through the solution for about 10 min, then a weighed amount (1 g) of γ-ZrP was added and the bottle immediately stoppered air-tight. The mixture was heated for about 20 days in a thermostatic water bath at 45 °C. The product was separated and washed several times until the pH of the wash solution became higher than 4. It was then left in ambient conditions overnight and conditioned over P_4O_{10}. Some samples were also conditioned over saturated $BaCl_2$ solution (90% relative humidity).

Preparation of γ-Zr phosphate dimethylphosphinate

This derivative, hereafter abbreviated as ZrPDP, was obtained on heating 1 g γ-ZrP with 0.5 M $(CH_3)_2PO_2H$ to about dryness for about 20 days. The product was separated and conditioned as above.

Characterization

The liquid state ^{31}P NMR spectra of ZrPhP gave a phosphate to hypophosphite ratio equal to 1, suggesting that all the interlayer H_2PO_4 groups of γ-ZrP have been replaced by the H_2PO_2 groups to give a compound of composition $ZrPO_4 \cdot H_2PO_2$ (*MW* = 251).

The thermogravimetric curve in an oxygen atmosphere of a sample of ZrPhP conditioned over P_4O_{10} is shown in Fig. 1, curve a. The thermal decomposition of ZrPhP in air or oxygen atmospheres is complicated by the

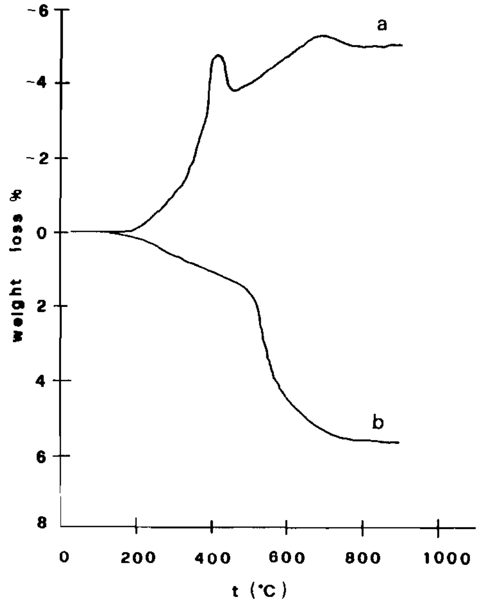


Fig. 1. Thermogravimetric curves of γ-zirconium phosphate hypophosphite (curve a) and γ-zirconium phosphate dimethylphosphinate (curve b) previously conditioned over P_4O_{10}.

gradual oxidation of the hypophosphite groups accompanied by concomitant loss of water due to the condensation of hydroxyl groups. Taking into account that the final compound, as indicated by XRD analysis, is cubic ZrP_2O_7, the overall process can be written as

$$ZrPO_4 \cdot H_2PO_2 + O_2 \longrightarrow ZrP_2O_7 + H_2O$$

The theoretical weight gain for the overall pyrolysis reactions is 5.28%, which is very close to the experimental value, 5.0%. From the thermogravimetric curve it is also possible to see that oxidation has an appreciable rate only at temperatures higher than 100 °C. This is in agreement with the fact that, at room temperature, the γ-Zr phosphate hypophosphite was found to be stable for a long time, e.g. a sample of ZrPhP did not show any change in its XRD pattern or in the phosphate–hypophosphite ratio (NMR analysis) even 45 days after its preparation.

It is of interest to note that the first step of the pyrolysis seems to be the oxidation of the hypophosphite to the phosphite group; in fact, by heating a sample of ZrPhP in an oxygen atmosphere for 3 h at 300 °C, a product with interlayer distance $d = 9.2$ Å and X-ray pattern similar to the anhydrous γ-zirconium phosphate phosphite, $ZrPO_4 \cdot H_2PO_3$, was formed.

Finally, it was found that ZrPhP remains practically anhydrous even when conditioned at high relative humidity, e.g. the water content of ZrPhP at 90% of relative humidity was only 0.2 mol H_2O/mol Zr. Furthermore this small amount of water is also hardly retained and can be almost completely removed at about 60–70 °C or when the product is conditioned over P_4O_{10} at room temperature. It can be concluded that ZrPhP, because of its lack of hydrophilic groups in the interlayer region, is essentially a hydrophobic compound.

The X-ray powder diffraction pattern of ZrPhP is given in Table 1, column 1. From the first reflection, an interlayer distance of 8.84 Å could be assigned to this compound. The interlayer distance did not change with conditioning at various relative humidities or heating the sample for 3 h at 150 °C.

As concerns ZrPDP, NMR analysis showed that only 2/3 of the interlayer H_2PO_4 groups of γ-ZrP were replaced by $(CH_3)_2PO_2$ groups to form a mixed compound of composition $ZrPO_4(H_2PO_4)_{0.33}[(CH_3)_2PO_2]_{0.67}$ ($MW = 280.5$).

The thermogravimetric curve in an oxygen atmosphere of a sample of ZrPDP conditioned over P_4O_{10} is shown in Fig. 1, curve b.

The weight loss (1.9%) in the temperature range 200–520 °C can be ascribed to the condensation of hydroxyl groups of the H_2PO_4 ion in the interlayer region (theoretical 2.11%). At higher temperatures the oxidation of methyl phosphinic groups took place followed by the condensation to cubic pyrophosphate

TABLE 1. X-ray powder diffraction patterns of $ZrPO_4 \cdot O_2PH_2$ and $ZrPO_4[O_2P(OH)_2]_{0.33}[O_2P(CH_3)_2]_{0.67}$ conditioned over P_4O_{10}

$ZrPO_4 \cdot O_2PH_2$		$ZrPO_4[O_2P(OH)_2]_{0.33}[O_2P(CH_3)_2]_{0.67}$	
d (Å)	$I/I_0 \times 100$	*d* (Å)	$I/I_0 \times 1$
8.84	100	10.33	100
5.29	80	5.60	23
4.59	68	5.24	1
3.77	8	4.82	7
3.42	66	4.11	2
3.29	76	3.90	3
3.08	13	3.78	32
3.04	24	3.50	1
2.97	6	3.32	11
2.696	10	3.28	5
2.590	2	3.16	4
2.409	14	2.94	2
2.378	15	2.71	4
2.307	3	2.684	7
2.135	11	2.620	2
2.097	7	2.486	5
2.038	4	2.360	2
1.992	12	2.159	3
1.850	8	2.140	3
1.767	5	2.030	2
1.708	4	1.955	2
1.674	12	1.812	2
1.665	12	1.799	2
1.652	10	1.763	3
1.555	6	1.705	1
		1.635	2
		1.627	1
		1.609	3

$$ZrPO_4\cdot(H_2PO_4)_{0.33}[(CH_3)_2PO_2]_{0.67}\xrightarrow{200\text{–}520\ ^\circ C}$$
$$ZrPO_4(H_2P_2O_7)_{0.17}[(CH_3)_2PO_2)]_{0.67}\xrightarrow{520\text{–}900\ ^\circ C}ZrP_2O_7$$

The formation of cubic pyrophosphate has also been confirmed by XRD. Note that the calculated overall weight loss from 200 to 900 °C (5.52%) agrees well with the experimental value (5.6%).

Similarly to what was found for ZrPhP, only a small amount of water is taken up even at high relative humidity (0.2 mol/FW ZrPDP at 90% r.h.). The compound, because of the presence of methyl groups in the interlayer region, is therefore essentially hydrophobic, and the small amount of water present could be associated to the residual H_2PO_4 hydrophilic groups.

The XRD pattern of ZrPDP conditioned over P_4O_{10} is reported in Table 1, column 2. A similar pattern was also obtained for a sample conditioned at 90% r.h.; only the first interlayer distance was increased a little (from 10.44 to 10.57 Å), while all other '*d*' values remained practically unaltered.

Structural aspects

Previous investigations demonstrated that the *a* and *b* parameters of the unit cell of γ-$ZrPO_4H_2PO_4\cdot 2H_2O$ remain essentially unaltered for the topotactic exchange of the interlayer H_2PO_4 groups with other groups such as HPO_2OH or $C_6H_5PO_2OH$ [10]; only the interlayer distance was found to be dependent on the RPO_2R' groups present in the interlayer region. Useful models can be therefore made with the aid of a computer simply introducing into it the structural data of the γ-layer (taken from refs. 4 and 11) and replacing H_2PO_4 with the investigated RPO_2R' group.

In the present case, no steric hindrance in the interlayer region is expected to occur for the replacement of H_2PO_4 with the smaller H_2PO_2 groups. The experimental replacement of 100% is therefore in agreement with such an expectation.

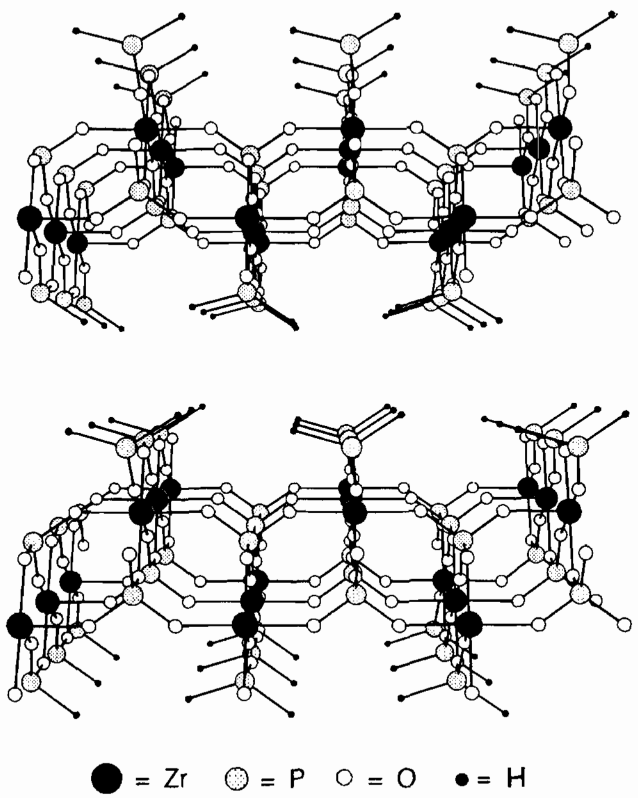


Fig. 2. A schematic model of the structure of two adjacent layers of $ZrPO_4\cdot H_2PO_2$.

A schematic model of the structure of two adjacent layers of $ZrPO_4\cdot H_2PO_2$ is shown in Fig. 2. The case is different for the replacement of H_2PO_4 with larger groups such as $O_2P(CH_3)_2$. A schematic representation of two portions of a layer of ZrPDP, viewed perpendicular to the *a* and *b* axes, respectively, is reported in Fig. 3. Note that there is enough room along the *a* axis for the accommodation of adjacent methyl groups. A certain steric hindrance, due to the presence of two methyl groups bonded to the tetrahedral phosphorous, has instead to be expected along the *b* axis. Only a partial replacement of the interlayer H_2PO_4 initially present in the interlayer region should therefore be possible, in agreement with NMR analysis of the product obtained. Note however that the *x* value in partially exchanged compounds, $ZrPO_4\cdot[O_2P(OH)_2]_{1-x}[O_2P(CH_3)_2]_x$, should decrease with increasing steric hindrance of the R group; however this decrease seems to be discontinuous because the same value, $x=0.67$, was also obtained with $(O_2POHC_6H_5)$ [9] and $(O_2POHC_6H_{11})$ [10]. Note that the steric hindrance is also expected to depend on the nature of the RPO_2R' groups initially present in the interlayer region. In particular, *x* is expected to reach the maximum value for compounds in which R and/or R' are the smallest possible, that is hydrogen. We are therefore now examining the steric effects in mixed γ-derivatives in which the initial interlayer groups are H_2PO_2 or CH_3PO_2H.

Finally it can be noted that, in agreement with the expected steric hindrance, a very slow rate of the topotactic reaction was found. Note that renewing the solutions during the preparations did not alter the interlayer distance or the composition of the product, indicating that the full replacement of the interlayer H_2PO_4 groups is not possible.

Ion-exchange properties

Due to the absence of acid groups in the interlayer region of ZrPhP, its cation-exchange capacity should be zero. The experimental titration curve of ZrPhP

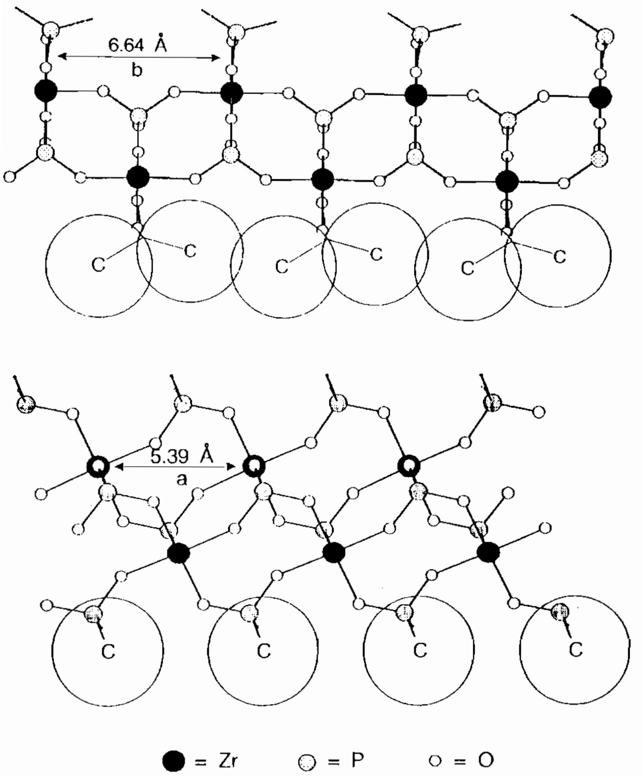


Fig. 3. A schematic representation of two portions of a layer of γ-zirconium phosphate dimethylphosphinate viewed perpendicular to the *b* and *a* axes, upper and lower, respectively. A radius of 2 Å was assumed for the methyl group.

(Fig. 4) indeed shows that no Na uptake occurs at acid pH values. However, taking into account that phosphate, phosphonate and phosphinate monovalent anions can easily interchange each other in the interlayer region of γ-layered compounds, the replacements of $O_2PH_2^-$ anions with OH^- cannot be excluded, especially at high pH values.

Preliminary investigations seem to confirm that a semicrystalline $ZrPO_4(OH \cdot H_2O)nH_2O$ (int. dist. $=12$ Å) is indeed formed when a sample of ZrPhP is titrated with an automatic titrator at $pH_{stat}=10$.

Since other mono- or polyvalent anions could be also exchanged, the possibility of using γ-ZrP or its organic derivatives as anion-exchangers is therefore presently being investigated in our laboratory.

Conclusions

The possibility of introducing PO_2R_2 or even mixtures of PO_2RR' groups in the interlayer region of γ-ZrP (and probably of other γ-layered compounds) opens the way for the preparation of a large number of new layered inorgano–organic compounds in which the properties can be largely modified in the desired direction by a proper choice of the nature of the R radical.

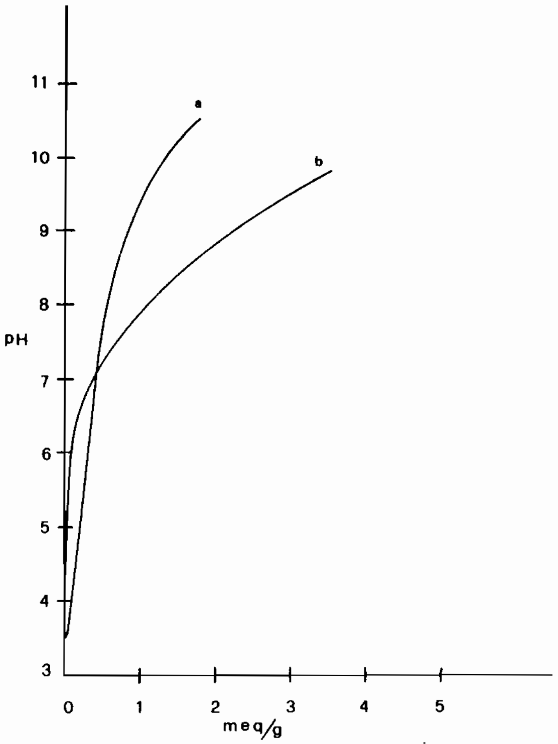
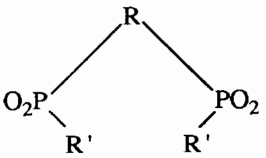


Fig. 4. Titration curve of ZrPhP (curve a) and ZrPDP (curve b) with 0.1 N NaOH in the presence of 0.1 N added NaCl.

The formulation of the γ-layered compounds can be now generalized as $ZrPO_4(O_2PR'R'')_{1-x}(O_2PR'''R'''')_x \cdot nS$, where the various R can be H, OH or an organic radical while S is a solvent in the interlayer region.

New ion-exchangers, intercalating agents, catalysts and ionic conductors could be obtained and even pillared compounds are, in principle, possible if divalent groups such as



(R = divalent organic radical; R' = H, OH) can be inserted in the interlayer region to join adjacent layers.

Acknowledgements

This work has been supported by MURST (40%). One of the authors (R. K. Biswas) is grateful to the TWAS-Italian Awards Scheme for a Fellowship and to the University of Rajshahi for granting study-leave.

References

1 A. Clearfield, *Inorganic Ion-Exchange Materials,* CRC, Boca Raton, FL, 1981.

2 G. Alberti, *Acc. Chem. Res., 11* (1978) 163.

3 N. J. Clayden, *J. Chem. Soc., Dalton Trans.,* (1987) 1877.

4 A. Norlurd Christensen, E. Krogh Andersen, I. G. Krogh Andersen, G. Alberti, N. Nielsen and M. S. Lehmann, *Acta Chem. Scand., 44* (1990) 865.

5 G. Alberti, U. Costantino, R. Vivani and R. K. Biswas, *React. Polym., 17* (1992) 245.

6 A. Clearfield, R. H. Blessing and J. A. Stynes, *J. Inorg. Nucl. Chem., 30* (1968) 22495.

7 S. Yamanaka, K. Sakamoto and M. Hattori, *J. Phys. Chem., 88* (1984) 2067, and refs. therein.

8 S. Yamanaka, K. Yamasaka and M. Hattori, *J. Nucl. Chem., 43* (1981) 1659.

9 G. Alberti, R. Vivani, R. K. Biswas and S. Murcia Mascaros, *React. Polym.,* in press.

10 G. Alberti, M. Casciola, R. Vivani and R. K. Biswas, *Inorg. Chem.,* submitted for publication.

11 G. Alberti, M. G. Bernasconi and M. Casciola, *React. Polym., 11* (1989) 865.