Zirconium Polyimine Phosphonates, a New Class of Remarkable Complexing Agents

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Recently we reported on layered zirconium polyether phosphates and phosphonates.[1,2] These compounds are of two types. Monophosphates (or phosphonates) of general composition Zr-$[O_3PO(CH_2CH_2O)_n–H]_2$ swell in water, and when n exceeds 9 they exfoliate. They can incorporate electrolytes into the polyether chains and become ionic conductors. If phosphate groups are present on both ends of the polyether chain, the chains cross-link the layers so that only limited swelling occurs. However, these cross-linked products readily incorporate transition metal species in a somewhat crown ether-like manner. We now report some details of the preparation of zirconium polyimine compounds which are analogous to those for the polyethers. These compounds exhibit remarkable complexing behavior for anionic species or for cation–anion pairs.

The compounds prepared were mainly phosphonates because the P–C bond is more stable to hydrolytic cleavage than the P–O bond of phosphates. Both mono- and diphosphonic acids of polyamines were synthesized. The general procedure[3] involves reaction of a polyamine, $NH_2(CH_2CH_2NH)_n–H$, with (chloromethyl)phosphonic acid, $ClCH_2PO_3H_2$, in basic solution. Use of an excess of phosphonic acid yields diphosphonic acids.

The phosphonic acids were dissolved in dilute HCl (~1 M), and a dilute solution (~0.01 M) of zirconyl chloride was added. The mixtures were refluxed for times ranging up to 24 h and the solids recovered, washed, and dried at 70 °C. Mixed derivatives in which a portion of the aminophosphonic acid was replaced by either phosphate or phosphite ions were prepared from solutions containing mixtures of phosphonic acid with either H_3PO_4 or H_3PO_3. With addition of the smaller phosphate and phosphite ligands, precipitation occurred very rapidly and the products were less crystalline even though refluxing was continued for 10–24 h. The products were characterized by elemental analysis and IR, NMR, and TGA procedures.[4]

Table 1. Representative Interlayer Spacings of Zirconium Polyimine Phosphonates or Phosphates of General Composition $Zr(O_3PR)_x(O_3PR')_{2-x}$

R	R'	X	basal spacing (Å)
$-CH_2NHCH_2CH_2NH_2$		2	17.1
$-CH_2NHCH_2CH_2NH_2$	$-OH$	1.7–1.8	16.3
$-CH_2NHCH_2CH_2NH_2$	$-OH$	0.63	14.5
$CH_2(NHCH_2CH_2)_2NH_2$		2	21.8
$CH_2(NHCH_2CH_2)_3NH_2$		2	27.6
$O-CH_2CH_2NH_2$		2	12.7
$O-CH_2CH_2NHCH_2CH_2NH_2$		2	21.0
$-CH_2NHCH_2CH_2NHCH_2PO_3{}^a$		1	14.3
$-CH_2NHCH_2CH_2NHCH_2PO_3{}^a$	$-OH$	0.5	amorphous
$-CH_2NH(CH_2CH_2NH)_2CH_2PO_3$		1	17.7
$-CH_2NH(CH_2CH_2NH)_3CH_2PO_3$		1	19.2

^{a} The diphosphonates conform to the general formula $Zr(O_2P-R)_x(O_3PR')_{2-2x}$.

Table 1 lists the interlayer spacings of some representative bis(monophosphonates) and diphosphonates. The interlayer spacing of the monophosphonates depends upon the degree of protonation and drying conditions. Protonation of the amino groups results in colloidal dispersion of the layers, presumably as single exfoliated layers. In the protonated condition, the aminophosphonates are anion exchangers. Previously, Dines et al.[5] reported the preparation of zirconium (pyridylethyl) phosphonate, $Zr(O_3PCH_2CH_2C_5H_4N)_2$. About 0.2 mol of Pd could be complexed by the pyridine groups, and this complex behaved as an active hydrogenation catalyst. Maya[6] prepared $Zr(OH)_{0.64}$-$(O_3PCH_2CH_2NH_3NO_3)_{1.68}$, which he showed to exhibit anion-exchange properties, but no details were given. Rosenthal and Caruso[7] prepared $Zr[O_3(CH_2)_3NH_3]_2Cl_2$ and $Zr[O_3P(CH_2)_3-NH_2]_2(O_3PCH_3)_{1.8}·2H_2O$. They found that the former compound was unreactive and even in the protonated form was not able to exfoliate the layers. However, the mixed derivative was porous and exhibited anion-exchange behavior. In addition, Cu(II) could be incorporated along with its counterion as an amine complex. We had earlier reported[2] a similar reaction with $CuCl_2$.

The monoamine $Zr(O_3PCH_2CH_2NH_2)_2$ dispersed only with difficulty. It had to be thoroughly wet, in the protonated form, and subjected to sonication before colloidal dispersion took place. In contrast, the analogous phosphate $Zr(O_3POCH_2CH_2NH_2)_2$ was difficult to isolate because it formed a clear gel containing up to 95% water. The gel could be broken by rotovaping to concentrate the solid and then adding acetone or other water-soluble organic. This tendency to form gels was general for the phosphates.

The dispersed polyimine phosphonates in the protonated form behave as anion exchangers. Complex and polyvalent anions not only exchange but become encapsulated and form insoluble zirconium polyimine complexes. Among the species so precipitated are $Fe(CN)_6{}^{3-}$, $Fe(CN)_6{}^{4-}$, $PtCl_4{}^{2-}$, and a variety of heteropoly acid anions, including $[PW_{12}O_{40}]^{3-}$, $[PV_2W_{10}O_{40}]^{5-}$, and $[SiW_{12}O_{40}]^{4-}$. Infrared spectra for the two hexacyano

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(3) Von Uhlig, E.; Achilles, W. *J. Prakt. Chem.* **1969**, *311*, 529.
(4) A typical procedure is as follows: A 7.8-g sample (59.8 mmol) of $ClCH_2$-PO_3H_2 was added to 10 mL of water. A solution containing 7.2 g of NaOH dissolved in 33.3 mL of water (5.4M solution) and 14.4 g of ethylenediamine were added to the phosphonic acid solution with brisk stirring. The solution was then refluxed for 4–5 h, cooled, and filtered to remove a small amount of solid which had formed. The pH was then adjusted to 7.5 with 5 M HCl and 200 mL of methanol added. The mixture was kept in a refrigerator overnight and filtered to collect the solid, which was washed with methanol and dried at 60 °C. Yield: 7.7 g (71%). Anal. Calcd for $NH_2CH_2CH_2NHCH_2PO_3H_2·1^1/_2H_2O$ (fw 181.13): C, 19.89; H, 7.79; N, 15.47; P, 17.10. Found: C, 19.41; H, 7.6; N, 15.58; P, 17.78. A 6.88-g sample of [((2-aminoethyl)amino)methyl]-phosphonic (AEAMP) acid (38 mmol), $NH_2CH_2CH_2NHCH_2PO_3$-$H_2·1.5H_2O$, was suspended in 20 mL of water, and 3 mL of concentrated HCl was added with stirring to dissolve the aminophosphonic acid. Then 6.9 g (21.4 mmol) of $ZrOCl_2·8H_2O$ in 60 mL of water was added to the acid solution with stirring. The mixture was refluxed for 24 h and cooled to room temperature. Then 200 mL of ethanol was added to precipitate the product. This mixture was held in the refrigerator overnight and the solid recovered by filtration. It was washed with ethanol and dried at 60 °C. Yield: 6.5 g (70%). Anal. Calcd for Zr-$(O_3PCH_2NHCH_2CH_2NH_2)_{1.8}(HPO_4)_{0.2}·2HCl·1.8H_2O$: C, 13.25; H, 4.53; N, 10.3; P, 11.39; Cl, 14.48; Zr, 18.63. Found: C, 13.27; H, 4.53; N, 10.04; P, 10.69; Cl, 14.68; Zr, 18.0. IR (KBr disk): 3442 (s), 3070 (vs), 2857 (w, sh), 2358 (s), 2330 (w,sh), 1648 (m), 1456 (mw), 1051 (w), 1032 (s), 988 (s), 772 (w), 714 (w), 660 (w), 567 (w), 420 (m). The X-ray powder pattern gave a broad peak at 15.3 Å, (001), and a weaker reflection at 7.6 Å, (002).

(5) Dines, M. B.; Digiacomo, P. M.; Callahan, K. P.; Griffith, P. C.; Lane, R. H.; Cooksey, R. E. In *Chemically Modified Surfaces in Catalysis and Electrocatalysis*; Miller, J. S., Ed.; ACS Symposium Series 192; American Chemical Society, Washington, DC, 1982.
(6) Maya, L. *J. Inorg. Nucl. Chem.* **1981**, *43*, 400.
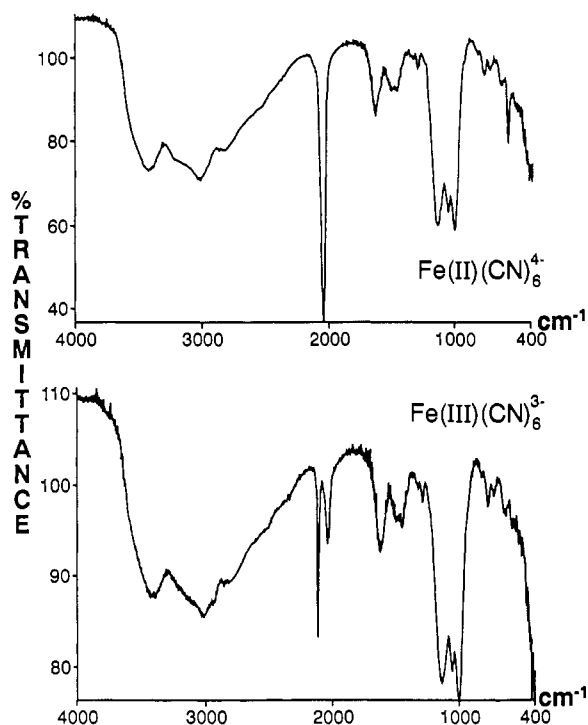(7) Rosenthal, G. L.; Caruso, J. *Inorg. Chem.* **1992**, *31*, 3104.

Figure 1. Infrared spectra for thehexacyanoferrate ions encapulated between the layers of the protonated zirconium polyimine $Zr(O_3PCH_2NHCH_2CH_2NH_2)_{1.74}(HPO_4)_{0.26}$.
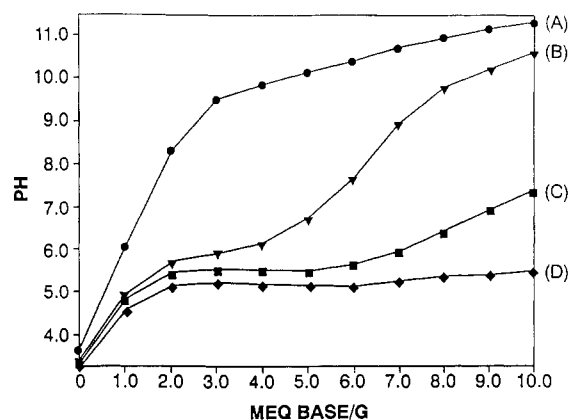

Figure 2. Potentiometric titration curves for (A) $Zr(O_3PCH_2NHCH_2CH_2NHCH_2PO_3)_{0.5}(HPO_4)\cdot HCl$ and the same compound with (B) 0.5 mol of Cu^{2+} added, (C) 1 mol of Cu^{2+} added, and (D) 2 mol of Cu^{2+} added/mol of polyimine.

derivatives are shown in Figure 1. Their compositions were $Zr(O_3PCH_2NHCH_2CH_2NH_2)_{1.74}(HPO_4)_{0.26}[H_4Fe(CN)_6]_{0.523}$- $(HCl)_{0.145}(H_2O)_{4.5}$ for the hexacyanoferrate(II) ion and $Zr(O_3PCH_2NHCH_2CH_2NH_2)_{1.74}(HPO_4)_{0.26}[H_3Fe(CN)_6]_{0.682}$- $(HCl)_{0.05}(H_2O)_{4.7}$ for the hexacyanoferrate(III) ion. It is understood that the protons associated with the cyanoferrate species and HCl are presumably located on the amino groups. Practically all of the original chloride ion present has been displaced by the cyanoferrate anions.

The infrared spectrum for the hexacyanoferrate(II) complex contains a very strong band at 2036 cm^{-1} due to the C–N stretch of the cyano groups, strong water and NH_3^+ bands (3442, 3007, 1620, 1500 cm^{-1}), and P–O stretching bands at 1134, 1046, 994 cm^{-1}. The IR spectrum for the hexacyanoferrate (III) complex is very similar except that it contains two cyanide stretching bands. The one at 2120 cm^{-1} is characteristic of the Fe(III) species whereas the second band at 2036 cm^{-1} indicates that some reduction to Fe(II) has taken place.

A 0.05 M solution of potassium tetrachloroplatinate(II), K_2-$PtCl_4$, was added dropwise to a stirred solution of the zirconium polyimine. With each addition, a precipitate formed, and when precipitation was complete, the complex was stirred for 10 min and collected. Elemental analysis and TGA data gave the formula $Zr(O_3PCH_2NHCH_2CH_2NH_2)_{1.67}(HPO_4)_{0.33}(HPtCl_3)\cdot3.5H_2O$. There were only three Cl$^-$ ions in the platinum chloride or [PtCl$_3$]$^-$ as the anion, with the neutralizing proton being held on the amino groups.

The interlayer spacing, as observed for the (001) X-ray reflection for the hexacyanoferrate(III) complex, was 17.3 Å. This value is only 1.9 Å larger than that of the zirconium [((aminoethyl)amino)methyl]phosphonate complex which has a basal spacing of 15.4 Å when completely dry. This small increase is only possible if the cyano groups protrude between the alkylamino groups. The amino chains are probably tilted at an angle of ~60° to produce the 15.4-Å basal spacing. Thus, the hexacyanoferrate ions would also tilt at the same angle. In order for C≡N groups to fit between the chains, which are 5.3 Å apart, the chains would have to spread apart. That is, they would no longer be inclined at 60° to the layers. One can visualize the

hexacyanoferrate ions lying in a row in one direction but in every other row at right angles to the first. This condition is necessary because the chains are forced apart by intrusion of the hexacyano ions, narrowing the space in the next row. Thus, we would expect that only 0.5 mol of complex ions could fit into such a structure. However 12–17% of the chains are replaced by HPO_4^{2-} groups. Wherever such a smaller group exists, the anions can reside in adjacent rows. Thus, in the case of the hexacyanoferrate anions where 1.74 mol of chains was present, the structure can accommodate $1.74/4 + 0.26 = 0.695$ mol of the anion, as compared to 0.523 and 0.682 mol actually incorporated in the two hexacyanoferrate complexes.

In the chloroplatinate complex the increase in basal spacing was only 1 Å. However, the [PtCl$_3^-$ species, retaining its planar arrangement, can fit between every two chains. Thus, a maximum of 1 mol of this complex may be incorporated, as was actually observed.

The cross-linked polyimines also behave as complexing agents. This behavior is illustrated by the potentiometric titration curves shown in Figure 2. As the protons on the amino groups are neutralized, $CuCl_2$ enters the channels between the polyimine chains. Since phosphate groups are also present, Na$^+$ may also exchange with the phosphate protons. However, as shown by the shape of the curves, increasing amounts of Cu^{2+} are taken by the polyimine. The solid slowly transforms from light green to bright blue in the process. A single band at 710 nm with a very weak shoulder at 660 nm was observed in the UV–visible spectrum. For the compound $Zr(O_3PCH_2NHCH_2CH_2NH_2)_2$, initially the maximum was at 710 nm at low Cu^{2+} content, but as more Cu^{2+} was taken up, the maximum shifted to 680 nm. These results indicate an initial copper (II) complex with one amino group in the aquo–metal coordination sphere shifting to a complex containing two amino groups as the copper ion content increases. Copper can also be extracted from nonaqueous solvents by contact with the polyamine phosphonates.

We have investigated several novel uses of these polyimines. In the dispersed state, they sequester heteropoly and isopoly anions. Thermal or hydrolytic removal of the organic results in novel pillared zirconium phosphates. Combination of the dispersed polyimine with a similarly dispersed colloidal solution of zirconium (sulfophenyl)phosphonates,[7] $Zr(O_3PC_6H_4SO_3H)_2$, results in immediate precipitation of a compound with alternating layers of amine and sulfonate. These reactions will be more fully described in subsequent publications.