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Poly(metal methylphenylphosphinates) from Metal Chloride Solutions in Methyl Methylphenylphosphinate*

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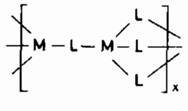
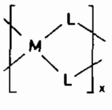
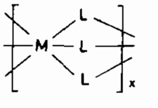
The family of complexes known as poly(metal phosphinates) consists of metal ions linked in a linear chainlike fashion by diorganophosphinato bridges [2]. Structures involving single-, double- or triple-phosphinato bridges, such as I–III, have been established for these complexes (L = RR′POO$^-$; R,R′ = alkyl or aryl) [2–8], while more complicated polymeric structures, with cross-linked linear units of type I or II, have been postulated for some ML_2 complexes [9]. Inorganic polymers of the preceding types, and especially Cr^{3+} complexes, can be used for the production of coherent films with interesting mechanical properties [10]. For this particular application, special synthetic techniques were developed for poly(metal phosphinate) powders that can be extruded into film [11, 12].



I



II



III

Essentially, the methods of preparation of M(OOPR′R)$_n$ complexes are based on the reaction of a metal salt (*e.g.*, chloride, carbonate, acetate) or carbonyl with the diorganophosphinic acid or its sodium salt in aqueous or organic media [2, 9, 11–17]. However, it was also demonstrated that thermal decomposition of the 1:2 adduct of $CoCl_2$ with ethyl diethylphosphinate ($(C_2H_5O)(C_2H_5)_2P{=}O$) leads eventually to the formation of $Co(OOP(C_2H_5)_2)_2$ [18].

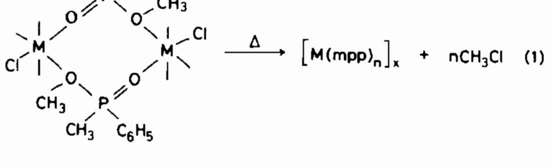
These laboratories have quite extensively studied the corresponding poly(metal phosphonates) and poly(metal phosphates) (*i.e.*, M(OOP(OR′)R)$_n$ and M(OOP(OR)$_2$)$_n$, respectively) [19–22]. These complexes were conveniently prepared in practically quantitative yields, by heating solutions of metal chlorides in an excess of a neutral phosphonate or phosphate alkylester [19–24]. We were interested in preparing and characterizing the corresponding poly(metal phosphinates), and especially those with metal ions that have not been isolated or studied previously (*e.g.*, Sc^{3+}, Y^{3+}, Ln^{3+}, Ti^{3+}, V^{3+}, Th^{4+}, U^{4+}, Ga^{3+}, In^{3+}). We employed the synthetic method used for the polymeric phosphonate or phosphate complexes [19–22], *i.e.*: A solution of a metal chloride in excess methyl methylphenylphosphinate was heated at gradually increasing temperatures, until precipitation occurred. In twenty six cases investigated so far, the yield of the poly(metal methylphenylphosphinate) ([M(mpp)$_n$]$_x$) precipitated was practically quantitative (~100% of the theoretical). The temperature of precipitation varied in the 50–220 °C range, depending on the metal ion used. By carefully controlling the rate of temperature increase (1–2° per min), we were able to obtain precipitates consisting of free-flowing powders, with approximately uniform particle size distribution. Whenever the temperature of the metal chloride solution in methyl methylphenylphosphinate was increased at a rapid rate, the precipitates were apparently higher polymers, consisting of membrane- or rubber-like materials.

The formation of [M(mpp)$_n$]$_x$ complexes presumably proceeds by a series of reactions, *i.e.*, formation of the MCl_n adduct with the neutral ester (mmpp) (IV), with the ligand acting as unidentate (P=O oxygen-bonded) [19–23, 25]; involvement of the methoxy oxygen of mmpp in coordination to a neighboring metal ion, resulting in the formation of a mmpp-bridged intermediate, such as V, at elevated temperatures; and, finally, elimination of CH_3Cl from V and precipitation of the [M(mpp)$_n$]$_x$ polymer [19–24]:

$$MCl_n + m(CH_3O)C_6H_5(CH_3)P{=}O \rightarrow$$

$$M(CH_3O)C_6H_5(CH_3)P{=}O_mCl_n \xrightarrow{\Delta}$$

(IV)



V

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*See ref. 1.

Reactions of type (1) can be also carried out by using any liquid or low-melting diorganophosphinate alkylester, but would not be applicable with the corresponding arylesters, since aryl carbon–oxygen bond cleavage does not occur by interaction of metal halides with aryloxyphosphoryl compounds [26]. Up to now, complexes of mpp with the following metal ions have been prepared: M^+: M = Li, Na, K, Rb; M^{2+}: M = Mg, Ca, Sn, Mn, Fe, Co, Ni, Cu, Zn, Cd; M^{3+}: M = Al, Ga, In, Sc, Y, Dy, Ti, V, Cr, Fe; M^{4+}: M = Th, U. Most of these complexes are anhydrous; however, the Li^+, Na^+, Ca^{2+} and Ni^{2+} complexes were precipitated in the form of their dihydrates, which can be dehydrated by heating to 100–150 °C, under reduced pressure. The infrared spectra of all the metal complexes exhibit the characteristic ν_{POO} asymmetric and symmetric vibrational modes at 1170–1110 and 1050–1010 cm^{-1}, respectively [9, 19–22, 27, 28]. With a few exceptions (Mn^{2+} 5.82; Fe^{3+} 5.91; Dy^{3+} 11.23 μB), the new paramagnetic metal ion complexes exhibit subnormal ambient temperature magnetic moments, as follows (μB): Ti^{3+} 1.65; V^{3+} 2.47; Cr^{3+} 3.66; Fe^{2+} 4.52; Co^{2+} 4.29; Ni^{2+} 2.51; Cu^{2+} 1.56; U^{4+} 3.09 (the latter value is low for octacoordinated U^{4+} [21, 22]). It is well established that many polymeric paramagnetic diorgano-phosphinato, -phosphonato or -phosphato metal complexes exhibit subnormal room temperature magnetic moments [7, 9, 19–22], while a number of studies of magnetic susceptibility variation with temperature were indicative of antiferromagnetic exchange interactions, arising by the linear, chainlike bi- or poly-nuclear configurations of these complexes [7, 29].

Characterization studies of the new metal complexes, as well as attempts at the syntheses of mpp complexes with other metal and oxometal ions (*e.g.*, Si^{4+}, Ge^{4+}, Sn^{4+}, NbO^{3+}, TaO^{3+}, MoO_2^{2+}, WO^{3+}, UO_2^{2+}), are in progress and will be reported in a series of forthcoming publications. The data available for the M^{3+} and M^{4+} complexes herein reported (ν_{M-O} band assignments and electronic spectra) are suggestive of hexa- and octa-coordinated configurations, respectively [19–22]; the $[M(mpp)_3]_x$ complexes are presumably of structural type III, whilst for the $[M(mpp)_4]_x$ compounds, a chainlike structure characterized by $-M\!\prec\!(mpp)_4-M\!\prec\!(mpp)_4-$ sequences, although not unlikely, might result in too severe a steric interference between the four bridging ligands; a possible alternative would be a polymeric structure involving $-M\!\prec\!(mpp)_3-M\!\prec\!(mpp)_3-$ sequences, with one terminal bidentate, chelating mpp ligand per metal ion [30]. Regarding the M^{2+} complexes, some are apparently tetracoordinated (M = Mg, Sn, Co, Cu, Zn, Cd, as well as the dihydrated Ca^{2+} complex, which involves exclusively lattice water) of types I or II, while other are hexacoordinated (M = Mn, Fe, and both the anhydrous and dihydrated Ni^{2+} complexes). $[Ni(mpp)_2(OH_2)_2]_x$ is a linear polymer with two aqua ligands per Ni^{2+} ion, and the three $[M(mpp)_2]_x$ (M = Mn, Fe, Ni) anhydrous complexes are presumably highly cross-linked polymeric species [9]. It is worth noticing that the Mn^{2+} complex fluoresces with a pinkish hue under UV excitation, as would be expected for a fluorescent octahedral manganous compound [31]. Finally, chainlike structures with linear –M–mpp–M–mpp– sequences are also likely for the alkali metal complexes [21].

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