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Interactions of Neutral Phosphonate Esters with Metal Halides*

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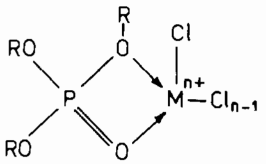
Interaction of diisopropyl methylphosphonate with trivalent metal chlorides at 50-200°C leads to the formation of tris-(isopropoxy methylphosphonato) metal complexes. Tetravalent metal chlorides yield under similar conditions bis-(methylphosphonato) complexes. During these reactions isopropyl chloride is evolved, which is partially decomposed to hydrogen chloride and propene by the catalytic action of the complex metal chloride residue. The general insolubility and the magnetic properties of the new complexes are suggestive of polynuclear configurations, involving eight-membered phosphonate bridges and, possibly, four-membered chelate rings. A distorted O_h ligand-field symmetry is assigned to the metal ions.

Introduction

The interaction of neutral phosphate esters with metal halides at elevated temperatures leads to the formation of (dialkoxyphosphato) metal complexes with simultaneous evolution of alkyl halide.[1-3] For divalent and trivalent metal ions complexes of the types ML_2 and ML_3 were reported[1-3] (L = dialkoxyphosphato group) and for Sn^{IV} a complex of the type SnL_2Cl_2 has been obtained.[1] These complexes have been tentatively characterized as monomeric metal chelates,[2,3] and the following mechanism has been proposed by Gutmann and Beer[3] for their formation:



This mechanism involves coordination of the phosphoryl oxygen to the metal ion and subsequent coordination of one of the alkoxy oxygens to the same metal ion.[3] This leads to a weakening of the O–C bond. Thus, alkyl halide is eliminated and the new complex is stabilized by the formation of a four-membered chelate ring.[3]

Similar reactions between neutral phosphonate esters and Fe^{III} halides were explored by Kokalas, who obtained compounds of the general type FeL_3 (L = methoxy methylphosphonato (MMP), ethoxy ethylphosphonato (EEP), isopropoxy methylphosphonato (IMP), and n-butoxy n-butylphosphonato (BBP) group) as final products.[4] During our studies of the metal complexes of diisopropyl methylphosphonate (DIMP), severe difficulties were encountered during attempts at the isolation of complexes of this ligand with metal halides.[5] These difficulties were due to competition between DIMP and halide ions in the first coordination sphere of the metal ion[6] and to dealkylation reactions occurring at moderately elevated temperatures.[1-4] Thus, only adducts of the type $MX_n \cdot 2DIMP$ (M = Sn^{II}, Sn^{IV}, Ti^{IV}, n = 2,4, X = Cl, Br, I) and a number of quaternary complexes from systems of the type $MgCl_2 \cdot MCl_2 \cdot DIMP \cdot H_2O$ (M = Mn, Co, Ni, Cu, Zn) could be isolated.[5] During these studies a number of (IMP)-complexes were obtained with simultaneous evolution of a mixture of isopropyl chloride, propene and hydrogen chloride. These results and the recent interest in inorganic phosphinato polymers[7,8] prompted us to undertake a study in this direction. The present paper deals with the products obtained during the interaction of DIMP and other phosphonate esters with metal halides.

Experimental Section

Chemicals. DIMP was provided by Edgewood Arsenal, Maryland. Dimethyl methylphosphonate (DMMP), diethyl ethylphosphonate (DEEP), and di-n-butyl n-butylphosphonate (DBBP) were products of Mobil Chemical Company. The IR spectra of these esters did not indicate the presence of water. No attempts at further dehydration were made, as it was found that the final products of the interaction of either anhydrous or hydrated metal chlorides with neutral phosphonate esters are the same. The metal salts and solvents utilized were the purest commercially available.

Interaction of Phosphonate Esters with Metal Halides. The general procedure involves the dissolution of the metal halide (anhydrous or hydrate) in excess

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(*) The support of U.S. Army Edgewood Arsenal under contract No. DAAA 15.C-67-0644 is gratefully acknowledged.

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Table I. Analyses, Colors and Temperatures of Initiation of Precipitation of tris(IMP)— and bis(MP)— Metal Complexes and some Eu^{III} Analogs

			Analysis							
		Temperature of	C%		H%		P%		Metal %	
Complex	Color	Precipitation, °C	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$Al(IMP)_3$	White	40-50	32.87	31.69	6.90	6.28	21.20	21.91	6.16	6.22
$Ga(IMP)_3$	White	50-60	29.96	29.53	6.29	6.79	19.32	19.16	14.49	14.22
$In(IMP)_3$	White	100	27.39	27.26	5.74	5.82	17.76	17.63	21.82	21.82
$Sc(IMP)_3$	White	50-60	31.59	31.45	6.63	6.58	20.37	19.80	9.85	9.92
$Ti(IMP)_3$	Light blue	160	31.39	31.18	6.58	6.51	20.23	19.97	10.43	10.12
$V(IMP)_3$	Yellow-green	160	31.17	31.05	6.54	6.49	20.10	20.20	11.02	10.81
$Cr(IMP)_3$	Light green	90-100	31.11	30.52	6.53	6.34	20.06	19.36	11.22	10.90
$Y(IMP)_3$	White	70	28.82	29.12	6.05	6.20	18.58	18.49	17.77	17.72
$Eu(IMP)_3$	White	70	25.59	25.71	5.37	5.59	16.50	16.45	26.98	27.06
$Eu(MMP)_3$	White	70	15.04	15.04	3.79	3.70	19.40	19.40	31.72	32.19
$Eu(EEP)_3$	White	70	25.59	24.80	5.37	5.34	16.50	16.63	26.98	26.76
$Eu(BBP)_3$	White	70	39.40	38.62	7.44	7.31	12.70	12.91	20.77	21.31
$Sn(MP)_2$	White	130	7.83	8.60	1.97	2.32	20.19	19.86	38.69	37.54
$Zr(MP)_2$	Cream-white	150	8.60	9.32	2.17	2.43			32.67	31.88
$Te(MP)_2$	Grey	150	7.61	8.30	1.92	2.27			40.43	41.50

Elemental analyses established that with the exception of $Sn(MP)_2$ (see text) the above complexes are chlorine-free.

DIMP and gradual elevation of the temperature until precipitation of the complex occurs. Hydrated salts were utilized in the cases of Al^{III}, Ga^{III}, In^{III}, Sc^{III}, Y^{III}, and Sn^{IV}. The anhydrous chlorides of trivalent metal ions react immediately upon addition of DIMP at room temperature with evolution of heat and HCl fumes. Anhydrous $AlCl_3$ reacts with DIMP at temperatures as low as –25°C. With divalent metal halides (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}) the final products gave poor analytical results. Further work in this direction is currently in progress. Trivalent metal halides react with DIMP with formation of $M(IMP)_3$ complexes (M = Al, Ga, In, Sc, Y, lanthanides, Ti, V, Cr, Fe). With the exception of $Ti(IMP)_3$, no special precautions were necessary during the preparation of the $M(IMP)_3$ complexes. $Ti(IMP)_3$ was prepared in a nitrogen atmosphere, as reaction in the presence of air leads to formation of diamagnetic Ti^{IV} products. $Ti(IMP)_3$, when very dry, can be exposed for several days to the atmosphere without any appreciable oxidation to occur. The other $M(IMP)_3$ complexes, as well as the $M(MP)_2$ complexes (MP = methylphosphonato group), mentioned below, are stable in the atmosphere, non-hygroscopic, do not melt or decompose at temperatures up to 350°C, and are insoluble in all common organic solvents (acetone, alcohols, halogenated hydrocarbons, acetonitrile, nitromethane, decahydronaphthalene, piperidine, etc.), DIMP and water. They dissolve with decomposition in mineral acids. Tetravalent metal halides react with DIMP, under the same conditions, with formation of $M(MP)_2$ complexes (M = Sn, Zr, Te) as final products. The Zr^{IV} and Te^{IV} complexes are chlorine-free, but that of Sn^{IV} was obtained contaminated with chlorine-containing impurities (Cl content varying from 1-5%, during various synthetic attempts). A tetrameric intermediate of the type $[Sn(IMP)(DIMP)Cl_3]_4$ has been isolated during the reaction of DIMP with $SnCl_4$.[9] Variable amounts of isopropyl chloride, propene and HCl are evolved during the reactions reported here. These were collected and identified as reported elsewhere.[9]

After their precipitation the $M(IMP)_3$ and $M(MP)_2$ complexes are filtered, washed with acetone and anhydrous ether and dried over $Mg(ClO_4)_2$ in an evacuated desiccator. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York and are given in Table I. The yields of the synthetic reactions are almost quantitative (95-100%), and the reproducibility of the syntheses of the complexes reported is excellent. It is noteworthy that complexes obtained at relatively low temperatures (Table I) differ in appearance from those obtained at higher temperatures. The lower temperature products are obtained in the form of crystalline powders. At higher temperatures (*ca.* 200°C) the precipitates are obtained in the form of membranes (*e.g.* $Cr(IMP)_3$) or rubber-like materials (*e.g.* $Eu(IMP)_3$). Both high and low temperature products give analyses corresponding to the formula $M(IMP)_3$. This implies that the temperature of preparation affects the degree of polymerization of the complexes. Studies on the $M(MP)_2$ complexes, $M(IMP)_3$ complexes with Al, Ga, In, Sc, Y, Eu, Ti, V, and Cr, and the Eu^{III} analogs with MMP, EEP, and BBP are reported here. Our studies on $Ln(IMP)_3$ complexes will be reported in a subsequent publication.

Table II. ν_{POO} Bands in the Infrared Spectra of tris-(alkoxy alkylphosphonato) Metal Complexes[a]

Compound	ν_{POO} bands, cm^{-1} [b]
$Al(IMP)_3$	1743 m, 1172 vs, 1088 vs
$Ga(IMP)_3$	1729 m, 1165 vs, 1073 s, sh
$In(IMP)_3$	1734 m, 1146 s, 1070 s
$Sc(IMP)_3$	1725 m, 1160 m-s, 1072 m-s
$Ti(IMP)_3$	1735 m, 1157 s, 1063 vs
$V(IMP)_3$	1734 m, 1155 s, 1060 s
$Cr(IMP)_3$	1730 m, 1135 vs, b, 1064 vs
$Y(IMP)_3$	1732 m, 1141 s, 1073 s
$Eu(IMP)_3$	1732 m, 1121 s, 1067 s
$Eu(MMP)_3$	1780 w, 1183 s, 1073 vs
$Eu(EEP)_3$	1750 vw, 1130 s, sh, 1074 vs
$Eu(BBP)_3$	1710 m, 1135 s, 1080 s

[a] The spectral data given in the Table concern the complexes obtained at the temperatures mentioned in Table I. The complexes obtained at higher temperatures (180-200°) exhibit similar spectra. [b] w, weak; m, medium; s, strong; v, very; sh, shoulder; b, broad.

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(9) C. Owens, Ph. D Thesis, Drexel Institute of Technology, Philadelphia, Pa., 1969; C. Owens, L. L. Pytlewski, N. M. Karayannis, J. Wysoczanski and M. M. Labes, Polymer Letters in press.

Spectral and Magnetic Measurements. Infrared spectra (Table II), solid state electronic spectra (Nujol mulls) and magnetic measurements were obtained as described elsewhere.[10]

Discussion

Origin of the Volatile Products of the Reactions. The evolution of isopropyl chloride was expected.[3] The presence of HCl and propene among the volatile products is attributed to dehydrochlorination of isopropyl chloride, catalyzed by the presence of the complex metal halide residue.[11,12] This is substantiated by the fact that during the decomposition of $SnCl_4 . 2$-DIMP, the amount of propene and HCl produced decreases as the reaction proceeds and in the final stages only isopropyl chloride is evolved.[9] This is, presumably, due to the fact that the halogen content of the solid residue is decreased during the progress of the reaction. The co-precipitation of polyalkenes, produced by catalytic polymerization of propene is also probable.[13] In fact, the light-colored $M(IMP)_3$ or $M(MP)_2$ precipitates (*e.g.* Al^{III}, Sn^{IV}), are initially obtained in the form of yellowish to brown solids. The impurities are removed after thorough washing with acetone.

Spectral, Magnetic and Other Data. X-ray powder diffraction patterns of the $M(IMP)_3$ complexes are generally similar and the complexes are of about the same structure. Complexes obtained at low temperatures (Table I) give patterns characterized by various X-ray bands in the $2\theta = 5$-$30°$ region and are, therefore, crystalline. The analogs obtained at high temperatures (180-200°C) exhibit only one strong band at $2\theta = 7$-$9°$, which is also present in the low temperature products. This may indicate a lower degree of crystallinity, due to formation of higher polymeric products. The $M(MP)_2$ complexes are also crystalline, but their patterns differ.

The solid state electronic spectra (Nujol mull) and magnetic moments of the 3d metal complexes are given below: $Ti(IMP)_3$: $\mu_{eff} = 1.53$ BM, λ_{max}, nm: 304 sh, 564 s, 652 sh. $V(IMP)_3$: $\mu_{eff} = 2.45$ BM, λ_{max}, nm: 311 vs, 452 s, 706 m-s. $Cr(IMP)_3$: $\mu_{eff} = 3.56$ BM, λ_{max}, nm: 308 sh, 406 s, 638 s, 661 s, 690 s, sh, 760 sh. These data clearly indicate that the metal ions are in the +3 oxidation state. The spectral bands at 304-311 nm are attributed to the ligand. The spectrum of $V(IMP)_3$ resembles those of essentially octahedral V^{III} compounds (*e.g.* $(NH_4)_3VF_6$, $VCl_3 . 3CH_3CN$[14]). If a pure O_h symmetry was assumed for this complex and the bands at 706 and 452 nm were, respectively, assigned to the ${}^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ and ${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, the following spectrochemical parameters are calculated for IMP toward V^{III}: $Dq = 1510\ cm^{-1}$, B (Racah parameter) $= 604\ cm^{-1}$. Thus, as in the case of the tris-(dimethoxyphosphato) analogs,[3] $V(IMP)_3$ exhibits a considerably lower Dq value than that observed for the hexa-aquo-V^{III} cation ($1860\ cm^{-1}$). The splittings of the d-d bands observed in the Ti^{III} (564, 652 nm) and Cr^{III} (638, 661, 690 nm) complexes clearly indicate the presence of lower symmetry components in the ligand-field,[15] leading to a distorted O_h symmetry. In view of the general similarity of the X-ray powder diffraction patterns of the $M(IMP)_3$ complexes, a distorted O_h ligand-field symmetry is assigned to the metal ions in these compounds.

The magnetic moments of the 3d metal complexes are lower than the spin-only values for d^1-d^3 metal ions. This is most probably due to molecular association. In fact, magnetic moments in the same regions to those observed for the $M(IMP)_3$ complexes have been reported for bi- and poly- nuclear V^{III}, Cr^{III} and Ti^{III} complexes.[16] It is also noteworthy that the polymeric tris-(dichlorophosphato)Fe^{III} exhibits a subnormal magnetic moment (5.02 BM).[17] Further, the FeL_3 (L = alkoxy alkylphosphonato) complexes synthesized by Kokalas also have subnormal magnetic moments.[4] The magnetic evidence is, thus, in favor of a polymeric configuration for the $M(IMP)_3$ complexes. The magnetic moments of the Eu^{III} complexes are as follows (BM): $Eu(MMP)_3$ 3.48, $Eu(EEP)_3$ 3.22, $Eu(IMP)_3$ 3.50, $Eu(BBP)_3$ 3.69. All the Eu^{III} complexes reported exhibit, as expected, an intense red-orange fluorescence in the near UV.

The IR spectrum of isopropyl methylphosphonate has been reported[18,19] The main bands (cm^{-1}) in the 2700-700 cm^{-1} region were assigned as follows:[18-21] 2650b (–OH vibration), 2290b ($\nu_{P-O-(H)} + \delta_{OH}$), 1680-1675 b (combination of POO^- vibrations), 1312 s (ν_{P-CH_3}), 1210 s[18] or 1205 s[19] (ν_{P-O}), 1180 s, 1139 s, 1099 s ($\nu_{>CH-O-(P)}$), 1000 vs, 988 sh ($\nu_{P-O-(H)} + \nu_{P-O-(C)}$), 900 s ($\nu_{P-CH_3}$), 777 s ($\nu_{P-O-(C)}$), 720 s ($\nu_{P-C}$). The IR spectra of the $M(IMP)_3$ complexes (Table II) exhibit three bands assigned to ν_{POO} modes, occurring at 1750-1710, 1172-1121 and 1088-1064 cm^{-1}.[20,22] No absorptions are observed in the 2700-2000 cm^{-1} region, where vibrational modes of the P–O–H and OH groups occur.[19] Additional features of the IR spectra of the $M(IMP)_3$ complexes are the ν_{P-CH_3} bands at 1309 and 900 cm^{-1},[20-22] a band at 990 cm^{-1}, which is assigned to pure $\nu_{P-O-(C)}$ and the $\nu_{>CH-O-(P)}$ bands at 1175-1100 cm^{-1}.[20-22] The latter bands appear as shoulders of the strong ν_{POO} absorption at 1172-1121 cm^{-1}.

The IR spectra of the $M(MP)_2$ complexes are generally characterized by a very broad absorption at

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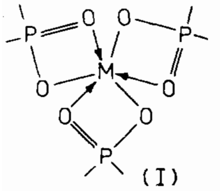
1200-1000 cm^{-1}, with its maximum located between 1120-1030 cm^{-1}. These bands are, presumably, associated with vibrational modes of the PO_3 group. No band is observed at 1750-1700 cm^{-1}, but the characteristic ν_{P-CH_3} bands at 1309 and 900 cm^{-1} are present.

Nature of the Phosphonato Complexes. Gutmann et al characterized the bis- and tris- (dimethoxyphosphato) metal complexes as metal chelates.[2,3] Pitts *et. al.* point out, however, that monomeric thiophosphinate chelates are generally soluble in organic solvents, while polymeric phosphinate complexes are insoluble in all common organic solvents.[8] The general insolubility and the magnetic properties of the complexes reported are in favor of a polymer structure, but the crystalline character of these compounds is indicative of a monomeric or oligomeric structure. No unambiguous characterization of the M(IMP)$_3$ complexes can be made at this point. Nevertheless, the difference in properties (texture, X-ray powder patterns) of the complexes obtained at lower and higher temperatures, is probably suggestive of a structure involving four-membered chelate rings and, possibly, eight-membered phosphonate bridges for the former:



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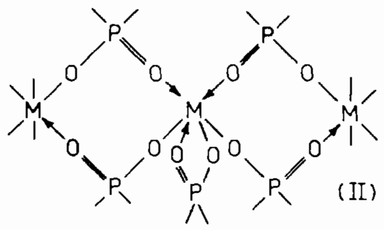
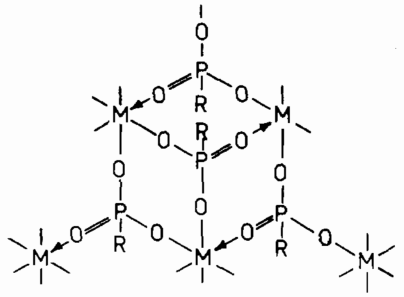


II

Structure (II) has been proposed for a number of phosphinate complexes of trivalent metal ions.[23] The complexes obtained at high temperatures may contain exclusively eight-membered phosphonate bridges.[24]

The possible structure of Sn(MP)$_2$ has already been discussed, and a cross-linked polymeric configuration has been tentatively assigned to this complex.[9] This assignment is supported by the isolation of the intermediate [Sn(DIMP)(IMP)Cl$_3$]$_4$.[9] A similar structure may be tentatively assigned to the Zr^{IV} and Te^{IV} complexes:



The novel feature of these complexes is that they do not involve linear polymeric molecules, as is the case with the inorganic phosphinate complexes.[7,8,23,24] It is interesting that Zr^{IV} does not yield Zr(IMP)$_4$, as would be expected for this metal ion,[23] but Zr(MP)$_2$. Further characterization studies of the new complexes, including far infrared spectra, are in progress.

In conclusion, trivalent metal halides react with neutral phosphonate esters to yield tris-(alkoxy alkylphosphonato) metal complexes, and tetravalent metal halides yield, under the same conditions, bis-(alkylphosphonato) complexes. The reaction proceeds via formation of complexes of the types MX$_3$. 3L and MX$_4$. 2L (L = neutral phosphonate ester) and subsequent coordination of alkoxy oxygens to the metal ions.[3] The O–C bond of the alkoxy group is weakened and this results in the evolution of alkyl halide and precipitation of the decomposition product.[3] The alkyl halide is partially dehydrohalogenated if the alkyl group is higher than methyl.[11-13] The tris-(IMP) and bis-(MP) complexes reported have most probably a polymeric structure.

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