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Reactions of Triethyl Phosphonoformate with Metal Chlorides and Perchlorates*

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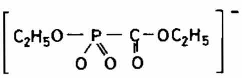
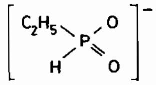
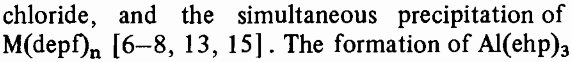
Neutral phosphinate, phosphonate or phosphate alkylesters (*i.e.*, $(RO)R'_2P{=}O$, $(RO)_2R'P{=}O$ or $(RO)_3P{=}O$, respectively; R = alkyl; R′ = alkyl or aryl) form generally adducts with metal perchlorates [2–5], but during their interaction with metal halides, polymeric metal complexes with such ligands as $XX'POO^-$, XPO_3^{2-}, $XP(OH)OO^-$ (X, X′ = RO or R′), as well as pyrophosphonato or pyrophosphato ligands are precipitated with simultaneous elimination of alkyl halide from the initially formed adduct between the metal halide and the neutral phosphoryl ester [2, 6–8]. The polymeric nature of complexes of the latter types has been established by means of several crystal structure determinations [9–11]. Analogous studies with diethyl acetyl- and diethyl benzoyl-phosphonates ($(C_2H_5O)_2\underset{O}{\underset{\|}{P}}-\underset{O}{\underset{\|}{C}}-Z$; Z = CH_3 or C_6H_5) revealed that these ligands also form easily adducts with metal perchlorates [12], while during their reactions with metal halides, polymeric metal complexes with ligands derived by elimination of either one ethyl group or both one ethyl and one acetyl or benzoyl group from the neutral ester are precipitated [13]. It should be noted here that similar reactions, involving elimination of alkyl perchlorate have been reported in a few cases; for instance, Ni^{2+} and Cu^{2+} perchlorates were found to react with triethyl thiophosphate ($(C_2H_5O)_3P{=}S$) to yield complexes of the diethylthiophosphato ($(C_2H_5O)_2POS^-$) ligand [14].

It was of interest to us to engage in similar studies with triethyl phosphonoformate (tepf; $(C_2H_5O)_2\underset{O}{\underset{\|}{P}}-\underset{O}{\underset{\|}{C}}-OC_2H_5$), in order to establish whether the reactivity of a compound of the $(RO)_2\underset{O}{\underset{\|}{P}}-\underset{O}{\underset{\|}{C}}-Z$ type changes when Z = alkoxy relative to Z = alkyl or aryl. Accordingly, work in this direction was undertaken and our initial results are reported herein. Reactions of tepf with metal chlorides (M^{n+} = Al^{3+}, Dy^{3+}, Ti^{3+}, V^{3+}, Cr^{3+}, Fe^{3+}, Th^{4+}, U^{4+}) were performed as follows: The anhydrous or hydrated metal salt is suspended in an excess of neat tepf, and the temperature of the suspension is increased at a rate of 1–2 °C/min, until precipitation of the polymeric species (following dissolution of the metal salt in tepf) occurs at 50–200 °C, depending on the metal ion [6–8]. Under these conditions, metal complexes of the $M(depf)_n$ and $Al(ehp)_3$ types are obtained (depf = diethylphosphonoformato (I) and ehp = ethylhydrogenphosphonato(II) anionic ligand; M^{n+} = Dy^{3+}, Ti^{3+}, V^{3+}, Cr^{3+}, Fe^{3+}, Th^{4+}, U^{4+}).


(I)


(II)

It is assumed that initially an adduct of the $MCl_n(tepf)_m$ type is formed and then, as the temperature of the reaction mixture is increased, the mutual interaction between the tepf and chloro ligands leads to the elimination of all the chlorine present and one ethyl (from one of the ethoxy groups attached to phosphorus) per tepf molecule, in the form of ethyl chloride, and the simultaneous precipitation of $M(depf)_n$ [6–8, 13, 15]. The formation of $Al(ehp)_3$, rather than $Al(depf)_3$, may be attributed to the presence of water in the system. In fact, $AlCl_3$ hydrate was used as starting material, as anhydrous $AlCl_3$ reacts somewhat violently with tepf even at room temperature, yielding a rubber-like polymeric species of uncertain nature. Thus, it is quite likely that $Al(depf)_3$ is formed, but the ethyl group of the $-COOC_2H_5$ fragment of depf is subsequently hydrolytically eliminated, and the P–H bond of ehp is produced by CO_2 elimination from the resulting $-COOH$ group, under the acidic conditions of our synthetic experiments [16, 17], *viz.*:



$$>\underset{O}{\underset{\|}{P}}COOC_2H_5 \xrightarrow{HOH} >\underset{O}{\underset{\|}{P}}COOH \xrightarrow{H^+} >\underset{O}{\underset{\|}{P}}-H + CO_2 \quad (1)$$

The preceding metal complexes are generally insoluble in organic media, and their ambient temperature magnetic moments (300 K) (μ_{eff}, μB: M = Dy, 10.66; M = Ti, 1.62; M = V, 2.66; M = Cr, 3.57; M = Fe, 6.18; M = U, 2.62) are in most cases (*i.e.*, Ti^{3+}, V^{3+}, Cr^{3+}, U^{4+}) subnormal, as would be expected for linear chainlike –O–P–O–bridged paramagnetic complexes of these metal ions [2,

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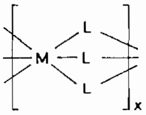
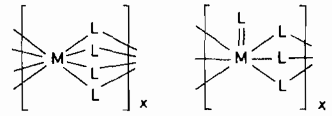
*Ref. 1.

6–10, 18]. The depf metal complexes exhibit the $\nu_{C=O}$ mode at 1730–1705 cm^{-1} ($\nu_{C=O}$ in free tepf occurs at 1700 cm^{-1}); this indicates that the C=O oxygen in depf is not involved in coordination [12, 19]. On the other hand the $\nu_{P=O}$ mode in free tepf (1251 cm^{-1}) is replaced by the characteristic ν_{POO} asymmetric and symmetric modes, which appear at 1210–1150 and 1070–1030 cm^{-1}, respectively, in the spectra of the new depf metal complexes, and are characteristic of the presence of bidentate bridging R_2POO^- ligands [6–8, 20]. Al(ehp)$_3$ on the other hand, does not of course show a $\nu_{C=O}$ band, exhibiting $\nu_{POO,as}$ and $\nu_{POO,sym}$ as doublets at 1222, 1135 and 1049, 1033 cm^{-1}, respectively, and the ν_{P-H} mode [21] at 2305 cm^{-1}. The M(depf)$_3$ (M = Dy, Ti, V, Cr, Fe) and Al(ehp)$_3$ complexes are presumably of type (III), with triple-bridges of bidentate –O–P–O– oxygen-bonded depf or ehp O,O-ligands, whilst the two M(depf)$_4$ (M = Th, U) complexes may be considered as involving either quadruple ligand bridges (IVa) or triple ligand bridges with one chelating ligand per metal ion (IVb) [8, 13, 18, 22] (L = –O–P–O–bridging depf or ehp).

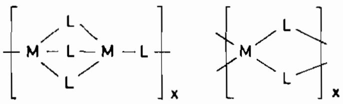


(III)

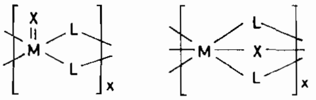


a (IV) b

The corresponding interactions between tepf and metal perchlorates were performed under conditions that would be expected to lead to adduct formation [2–5], *viz.*: the hydrated metal salt (M^{n+} = Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) was dissolved in an excess of triethyl orthoformate, and the resultant solution was stirred at *ca.* 50 °C for 2 hrs; then, tepf (at a 7:1 tepf to metal molar ratio) was added, and the mixture was stirred at 50 °C, until precipitation occurred. The precipitates obtained proved however, to be either M(depf)$_2$ (M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) or M(depf)$_2$(ClO$_4$) (M = Cr^{3+}, Fe^{3+}) complexes, rather than the anticipated M(tepf)$_m$(ClO$_4$)$_n$ adducts. The depf ligand is presumably formed by a mechanism analogous to that discussed for the reactions of metal chlorides with tepf, and involving elimination of ethyl perchlorate from the initially formed M(tepf)$_m$(ClO$_4$)$_n$ adducts [14]. The M(depf)$_2$ and M(depf)$_2$(ClO$_4$) new complexes are also insoluble in organic media. Their ambient temperature magnetic moments are, nevertheless, normal for high-spin compounds of these metal ions (μ_{eff}, μB: M^{n+} = Cr^{3+}, 3.93; Mn^{2+}, 6.14; Fe^{2+}, 5.49; Fe^{3+}, 6.16; Co^{2+}, 5.09; Ni^{2+}, 3.17; Cu^{2+}, 2.23). The normal room temperature paramagnetism of these compounds does not rule out polymeric configurations. In fact, quite often chain-like polynuclear complexes of the types herein discussed may be showing normal room temperature μ_{eff} values, and evidence of antiferromagnetic exchange interactions only at lower temperatures [10, 18, 23–26]. The IR spectra of the M(depf)$_2$(ClO$_4$) complexes (M = Cr, Fe) and three of the M(depf)$_2$ compounds (M = Fe, Cu, Zn) are very similar to those of the M(depf)$_3$ complexes (*vide supra*), *i.e.*, they involve a single $\nu_{C=O}$ band at 1720–1688 cm^{-1}, again indicative of uncomplexes C=O oxygen, and the $\nu_{POO,as}$ and $\nu_{POO,sym}$ modes at 1210–1170 and 1080–1050 cm^{-1}, respectively. The ν_3 and ν_4(ClO$_4$) fundamental vibrational modes in the spectra of the perchlorate-containing complexes are clearly split (several maxima at 1150–1010 and 650–610 cm^{-1}, respectively), while ν_1 is IR-active, appearing as a medium intensity band at *ca.* 930 cm^{-1}. These features favor the presence of coordinated perchlorate (most probably bidentate) [27, 28]. The three preceding M(depf)$_2$ complexes (M = Fe, Cu, Zn) are obviously of the familiar Va or Vb types [9], while the two M(depf)$_2$(ClO$_4$) compounds (M = Cr, Fe) may be considered as involving either chelating (VIa) or bridging (VIb) bidentate coordinated $=O_2ClO_2$ ligands [22, 29] (L = –O–P–O–bridging depf; X = bidentate coordinated $=O_2ClO_2$).

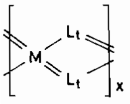


a b
(V)

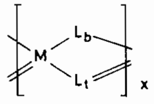


a b
(VI)

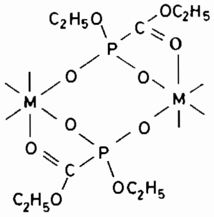
The three remaining M(depf)$_2$ complexes (M = Mn, Co, Ni) show clearcut IR evidence in favor of the presence of coordinated C=O oxygens, as follows: $\nu_{C=O}$, cm^{-1}: M = Mn, 1711, 1673, 1610; M = Co, 1650, 1610; M = Ni, 1641, 1610. The Co^{2+} and Ni^{2+} complexes obviously have both the depf ligands coordinated through their C=O oxygens, but in the Mn^{2+} compound, half of the depf ligands are coordinated through their C=O oxygens and the other half are not [12, 19]. On the other hand, the $\nu_{POO,as}$ and $\nu_{POO,sym}$ modes appear at 1210–1180 and 1080–1040 cm^{-1}, respectively, in the spectra of these three compounds, indicating the presence of bidentate coordinated –O–P–O– groupings [6–8, 20]. Hence, part or all of the depf ligands in these complexes seem to function as tridentate, coordinating through the C=O and the two POO oxygens [12, 25, 30]. Structural types analogous to Vb, with all depf ligands acting as tridentate (L_t) for M = Co, Ni (VII) and one half of the ligands functioning as bidentate (L_b) and the other half as tridentate for M = Mn (VIII) are considered as reasonable for these three complexes. Similar polymeric structures of complexes involving bridging tridentate diorganophosphinato ligands with substituents bearing groups with coordinating ability have been proposed previously [25]. The function of depf as tridentate bridging would, of course, involve chelation through the C=O and one POO oxygen to one of the metal ions and coordination of the other POO oxygen to an adjacent metal ion, as shown in (IX) [25].



(VII)



(VIII)



(IX)

Detailed characterization studies of the new metal complexes (IR, electronic spectra, magnetic measurements at 300–80 K) are in progress and will be reported in forthcoming publications. It should be mentioned here that the far-IR and electronic spectra available so far are in agreement with the coordination numbers (C.N.) corresponding to the proposed structural types (III)–(VIII), *i.e.*: C.N. = 8 for $M(depf)_4$ (M = Th, U); C.N. = 6 for $M(depf)_3$ (M = Dy, Ti, V, Cr, Fe), $Al(ehp)_3$, $M(depf)_2(ClO_4)$ (M = Cr, Fe) and $M(depf)_2$ (M = Co, Ni); C.N. = 5 for $Mn(depf)_2$; and C.N. = 4 for $M(depf)_2$ (M = Fe, Cu, Zn).

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