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First Row Transition Metal Diethyl Phosphonoformates*

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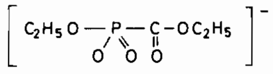
During interactions of triethyl phosphonoformate (tepf) with 3d metal perchlorates in triethyl orthoformate solution at 50 °C, the corresponding diethyl phosphonoformato (depf; $(C_2H_5O)\underset{O\;\;O}{P}-\underset{\overset{\|}{O}}{C}-OC_2H_5^{-})$ *metal complexes were precipitated, with concomitant elimination of ethyl perchlorate. Most of the new metal complexes (*$Cr(depf)_2(ClO_4)$*,* $Fe(depf)_3$*,* $M(depf)_2$ *(M = Fe, Cu, Zn)) involve bidentate bridging depf ligands, coordinating through the two POO oxygens, and appear to be hexa- (for* M^{3+}*) or tetra- (for* M^{2+}*) coordinated linear chain-like polymeric species.* $Mn(depf)_2$*, in which part of the depf ligands coordinate also through the C=O oxygen, has apparently a pentacoordinated chain-like polymeric structure, with both bi- and tridentate depf bridging ligands. Finally,* $M(depf)_2$ *(M = Co, Ni), which unlike all the preceding complexes dissolve in some organic solvents and contain exclusively tridentate depf ligands, binding through the C=O and the two POO oxygens, are considered to be either monomeric chelates or low chain-like oligomers. In the cases involving bridging tridentate depf (M =* Mn^{2+} *and, possibly,* Co^{2+} *and* Ni^{2+}*), the C=O and one of the POO oxygens would form a chelate ring with one metal ion, while the second POO oxygen of the same depf ligand would coordinate to an adjacent metal ion in the linear polymeric chain.*

Introduction

Neutral phosphinate, phosphonate or phosphate alkylesters (*i.e.*, $(RO)R'_2P=O$, $(RO)_2R'P=O$ and $(RO)_3P=O$, respectively; R = alkyl; R′ = alkyl, aryl, *etc.*) readily form adducts with metal perchlorates, in non-aqueous media [2–5]. Diethyl acetyl- and diethyl benzoyl-phosphonates ($((C_2H_5O)_2\underset{\overset{\|}{O}}{P}-\underset{\overset{\|}{O}}{C}-Z$; $Z = CH_3$ or C_6H_5) behave in a similar manner, and several of their adducts with 3d metal perchlorates have been isolated and characterized [6]. In contrast, triethyl phosphonoformate (tepf; $(C_2H_5O)_2\underset{\overset{\|}{O}}{P}-\underset{\overset{\|}{O}}{C}-OC_2H_5$) was recently found to react with 3d metal perchlorates, under relatively mild experimental conditions, forming the corresponding diethyl phosphonoformato (depf; I) metal complexes and ethyl perchlorate [1a, 7]. The present paper deals with our studies in this direction. It should be mentioned here that reactions of the type



(I)

$$n(RO)R'R''P=O + MX_n \rightarrow M[OOPR'R'']_n + nRX \qquad (1)$$

are facile when X = Cl, Br or I [2, 8, 9], but do not seem to be very common when X is a polyanion, such as ClO_4^- or NO_3^-. Actually, only a number of metal diethylthiophosphates ($M[SOP(OC_2H_5)_2]_n$) have been reportedly isolated during reactions of triethyl thiophosphate with some metal nitrates (M = Ag^+) [10] and perchlorates (M = $Al^{3+}, Ni^{2+}, Cu^{2+}$) [11, 12]. In these cases, the isolation of the triethyl thiophosphate adduct with MX_n is also possible [10, 13], whereas in the case of interaction of tepf with metal perchlorates we have been so far unable to isolate $M(ClO_4)_n(tepf)_m$ adducts.

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*Ref. 1.

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TABLE I. Analytical Data for depf Metal Complexes.

Complex	Color	C%		H%		P%		Metal%	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Cr(depf)_2(ClO_4)$[a]	Green	23.38	23.46	3.92	3.79	12.06	11.68	10.12	10.29
$Mn(depf)_2$	Lilac	28.79	29.03	4.83	4.75	14.85	15.13	13.17	12.85
$Fe(depf)_2$	Off white	28.73	28.95	4.82	5.14	14.82	14.57	13.36	13.02
$Fe(depf)_3$	Off white	30.07	30.42	5.05	4.89	15.51	15.76	9.38	9.73
$Co(depf)_2$	Deep pink	28.52	28.47	4.79	4.60	14.71	14.63	13.99	13.54
$Ni(depf)_2$	Yellow green	28.54	28.30	4.79	4.47	14.72	14.39	13.95	13.47
$Cu(depf)_2$	Pale green	28.21	28.44	4.73	4.86	14.55	14.81	14.92	15.08
$Zn(depf)_2$	White	28.09	27.88	4.71	5.11	14.49	14.32	15.29	15.56

[a] Cl analysis: Calc. 6.90%; Found 7.11%. Analyses of the rest of the new complexes showed Cl content ranging between 0–0.2%.

TABLE II. Pertinent Infrared Data (cm^{-1}) for depf Metal Complexes.[a]

$M = Cr^{3+}$	$M = Mn^{2+}$	$M = Fe^{2+}$	$M = Fe^{3+}$	$M = Co^{2+}$	$M = Ni^{2+}$	$M = Cu^{2+}$	$M = Zn^{2+}$	Band Assignment
1713ms	1711m 1673ms	1711ms	1700s	1650s	1641ms	1695vs	1723ms	$\nu_{C=O}$
1212s,sh, 1115vs, 1030vs								$\nu_3(ClO_4)$
1190s,sh	1285m,sh 1263s, 1200s	1190vs,sh	1193vs,sh	1285ms, 1261ms	1291s 1276ms	1197s,sh	1195s,sh	ν_{C-O}
1155vs	1230s, 1211s,sh	1215vs, 1175vs	1210vs, 1166vs	1206ms	1212s	1239s, 1187s	1237s, 1205s	ν_{POO}, as
b	1155w,b	b	b	1151w,b	1155w,b	1170w,b	1165w,sh	$\nu_{C_2H_5-O-(P)}$ + $\nu_{C_2H_5-O-(C)}$
1075vs	1085w,b 1062s	1990vs, 1067vs	1078s,sh 1053vs	1090m,sh 1071ms	1088m,sh 1077ms	1095m,sh, 1079ms	1100m, 1090ms	ν_{POO}, sym
b	1025s,vb	1020vs,vb	1035vs, 995s,	1030s, 980w	1035s, 987w	1040s, 990w	1040s, 1005w	$\nu_{P-O-(C_2H_5)}$ + $\nu_{C_2H_5-O-(C)}$
950m	953w	950mw	946mw	950w	953w	952w	960w	C_2H_5 rocking
932m								$\nu_1(ClO_4)$
655w, 633m, 621m								$\nu_4(ClO_4)$
480w, 460w								$\nu_2(ClO_4)$
452m, 411mw	391mw, 359mw	442m, 380m	444m, 400mw,b	355mw, 341mw	367mw, 346mw	460m, 431m	427m, 370mw	$\nu_{M-O}(POO)$[c]
355w								$\nu_{M-O}(ClO_4)$
	262mw			246mw	257mw			$\nu_{M-O}(C=O)$

[a] Neat tepf IR bands [16–19]: 1707vs ($\nu_{C=O}$), 1255vs ($\nu_{P=O}$), 1198vs (ν_{C-O}), 1172s,sh ($\nu_{C_2H_5-O-(P)}$), 1137mw ($\nu_{C_2H_5-O-(C)}$), 1012vs, 998vs,b ($\nu_{P-O-(C_2H_5)}$ + $\nu_{C_2H_5-O-(C)}$), 955ms (C_2H_5 rocking), 640w, 579s, 547s, 505m,b, 445m,b, 420mw,sh, 388w, 310mw,b, 240mw. [b] Masked bands. [c] Ligand absorption at 580–500 cm^{-1} prevents the detection of metal-sensitive bands in this region [42, 43].

TABLE III. Solid-state (Nujol mull) Electronic Spectra and Magnetic Properties (300 K) of the depf Metal Complexes.

Complex	λ_{max}, nm[a]	$10^6\ \chi_M^{cor}$, cgsu	μ_{eff}, μB
Cr(depf)$_2$(ClO$_4$)	196vvs, 210vvs,sh, 220vvs,sh, 233vvs,sh, 248vs,sh, 283vs,b, 338ms,sh, 450m,vb, 633m,sh, 664m,vb, 691m	6402	3.92
Mn(depf)$_2$	200vvs, 217vvs,sh, 257vs,sh, 276vs,b, 335s,b	15,664	6.14
Fe(depf)$_2$	202vvs, 218vs,sh, 227vs,sh, 245vs,b, 292s,b, 351s,sh, 935m,vvb	12,542	5.49
Fe(depf)$_3$	201vvs, 214vvs,sh, 219vvs,sh, 240vs,sh, 295vs,b, 337vs,sh	15,786	6.16
Co(depf)$_2$	198vvs, 210vvs,b, 228vs,sh, 235vs,sh, 298s,b, 332ms,b, 510ms,b, 1235w,b	10,770	5.09
Ni(depf)$_2$	198vvs, 217vvs,vb, 241vs,sh, 253vs,sh, 274vs,b, 300s,b, 346ms,b, 411ms,b, 655m, 712m, 1243w	4173	3.17
Cu(depf)$_2$	204vvs, 216vvs,sh, 224vvs,sh, 239vs,sh, 290s,b, 332ms,b, 630ms,vb	2065	2.23
Zn(depf)$_2$	197vvs, 218vvs, 242vvs,b, 290s,b, 341m,b	Diamagnetic	

[a] UV spectrum of free tepf (nm): 200vs, 206vs,sh, 219vs,b, 242vs,b, 251s,sh, 263s,b, 295ms,b, 335m,vb.

Experimental

Preparation of Metal Complexes

Reagent grade tepf, hydrated metal perchlorates (M = Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and organic solvents were generally used. The reactions were performed under relatively mild preparative conditions, that would be normally expected to yield tepf adducts with the metal perchlorates [2–6], *viz.*: the hydrated metal salt was dissolved in an excess of triethyl orthoformate (teof), a dehydrating agent [14], and the resultant solution was stirred at 50 °C for 2 hr; then, tepf (at a 7:1 tepf to metal molar ratio) was added, and the mixture was stirred at 50 °C, until precipitation occurred. Under these conditions, all the metal(II) and the Fe^{3+} salts reacted to yield M(depf)$_2$ and Fe(depf)$_3$, respectively, while Cr^{3+} perchlorate formed the Cr(depf)$_2$(ClO$_4$) species. It should be noted here that, when the stirring after the addition of tepf was effected at ambient temperature, the same depf complexes were obtained, although at significantly lower yields (20–30% *vs.* 80% at 50 °C). At lower temperatures (0–10 °C) no precipitates were obtained, even when the mixtures were allowed to stand at these temperatures for several days. Attempts to induce precipitation of adducts of tepf with the metal perchlorates, by adding a large excess of diethyl ether, ligroin or other appropriate agents, were not successful. Analyses (Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.) of the new depf metal complexes are given in Table I. Most of these compounds are insoluble in water and all common organic solvents; however, the Co^{2+} and Ni^{2+} complexes dissolve in some organic solvents, including nitromethane.

Spectral, Magnetic and Conductance Measurements

Infrared spectra (Table II) were obtained on Nujol and hexachlorobutadiene mulls between IRTRAN 2 (ZnS) windows (4000–700 cm^{-1}) and on Nujol mulls between high-density polyethylene windows (800–200 cm^{-1}) in conjunction with a Perkin-Elmer 621 spectrophotometer. Solid-state (Nujol mull) electronic spectra, magnetic susceptibility (300 K) (Table III) and conductance measurements were obtained by methods described elsewhere [15]. Molar conductivities of 10^{-3} *M* nitromethane solutions of the soluble new complexes at 25 °C were 32 (M = Co) and 28 (M = Ni) Ω^{-1} cm^2 mol^{-1}.

Discussion

Types of Complexes Isolated

As may be seen from Table I, all of the M^{2+} complexes isolated are of the M(depf)$_2$ type. Reaction of tepf with Fe(ClO$_4$)$_3$ also led to complete substitution of ClO$_4$ with depf ligands, leading to the formation of Fe(depf)$_3$, but with Cr(ClO$_4$)$_3$, substitution was only partial and Cr(depf)$_2$(ClO$_4$) was precipitated. The new complexes were generally precipitated in the form of powders of low crystallinity. As already mentioned, most of these compounds are insoluble in organic media, so that it was impossible to grow single crystals for X-ray structural studies. But even in the cases of the Co^{2+} and Ni^{2+} complexes, which dissolve in some organic solvents, attempts at recrystallization failed to produce crystals satisfactory for structural studies.

The depf ligand appears to function in some cases as bidentate, coordinating through the two POO oxygens, and in other cases as tridentate, bind-

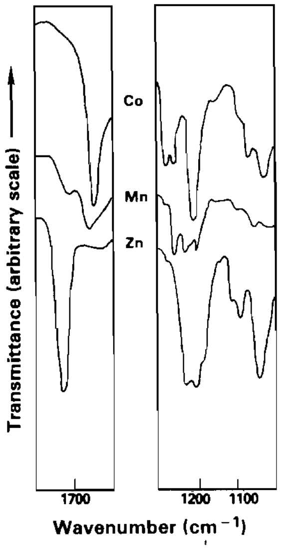


Fig. 1. Infrared spectra (1800–1600 and 1300–1000 cm^{-1}) of Co(depf)$_2$ (with exclusively C=O oxygen-bonded depf), Mn(depf)$_2$ (in which half of the depf ligands coordinate through their C=O oxygen and the other half do not) and Zn(depf)$_2$ (in which none of the depf ligands coordinates through the C=O oxygen).

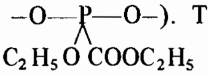
ding through the C=O and the two POO oxygens, as indicated by the pertinent IR evidence (Table II, Fig. 1), which is discussed here: Footnote a of Table II shows absorptions of interest in the IR spectrum of free tepf. The $\nu_{C=O}$, $\nu_{P=O}$ and $\nu_{P-O-(C_2H_5)}$ modes had been previously assigned at 1710, 1270 and 1015 cm^{-1}, respectively, by Ogata and Tomioka [16]; our assignments were based on this previous work [16], as well as IR studies of neutral phosphonate [17] and carboxylic acid [18, 19] esters. The IR spectrum of the ligand of interest, *i.e.*, depf, has not been reported so far; the removal of one ethoxy ethyl group from tepf during the reactions herein described, could conceivably lead to the formation of either of the following anionic isomeric ligands: depf (I; $(C_2H_5O)(O^-)\text{-}\underset{\underset{O}{\|}}{P}\text{-}\underset{\underset{O}{\|}}{C}\text{-}OC_2H_5$) and the anion of diethylphosphonoformic acid (depfa; $(C_2H_5O)_2\underset{\underset{O}{\|}}{P}\text{-}\underset{\underset{O}{\|}}{C}\text{-}O^-$). The IR spectra of the new metal complexes herein reported clearly favor the presence of the former anionic ligand. In fact, the ν_{C-O} mode in metal complexes with carboxylic acid esters reportedly occurs below 1300 cm^{-1} [20, 21], while in $(RCOO)_nM$ species the ν_{CO_2} sym band appears in the 1470–1310 cm^{-1} region [22–24]. As may be seen in Table II, the ν_{C-O} mode of the new complexes occurs in all cases below 1300 cm^{-1}. Regarding possible coordination of depf through the $-COOC_2H_5$ oxygens, in most cases (*i.e.*, M = Cr^{3+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}) the $\nu_{C=O}$ and ν_{C-O} bands are located at 1723–1695 and 1197–1190 cm^{-1}, respectively. These features indicate that no coordination of depf through any of the COO oxygens occurs in these complexes [6, 20, 21, 25]. In contrast, the Mn^{2+} complex shows bands attributable to the presence of both non-coordinated ($\nu_{C=O}$ at 1711; ν_{C-O} at 1200 cm^{-1}) and coordinated ($\nu_{C=O}$ at 1673; ν_{C-O} at 1285, 1263 cm^{-1}) COO oxygens; coordination would be through the C=O oxygen of the carboxyl group [20, 21]. Finally, in the spectra of the Co^{2+} and Ni^{2+} complexes, both $\nu_{C=O}$ and ν_{C-O} are significantly shifted (to lower and higher wavenumbers, respectively), thus manifesting that, in these compounds, all of the $-COOC_2H_5$ groups present are coordinated through their C=O oxygen [20, 21, 26]. As far as the function of the POO oxygens as ligand sites is concerned, the spectra of the complexes exhibit the characteristic ν_{POO^-}, as and ν_{POO^-} sym vibrational modes at 1250–1155 and 1100–1053 cm^{-1}, respectively [8, 9, 17, 27–29]. In most cases, both these bands are split into two components. It should be noted that the occurrence of ν_{POO^-} as bands at wavenumbers higher than 1210–1220 cm^{-1}, in the spectra of diorganophosphinato metal complexes has been interpreted in terms of R_2POO^- ligands (R = alkyl, aryl) coordinating through only one of the POO oxygens [27, 28]. Nevertheless, with diorganophosphonato ligands ($(RO)R'POO^-$), involving R′ groups with dramatically different inductive effects relative to alkyl or aryl substituents (*e.g.*, σ^* constants for substituent R′ in R′Y compounds (Y = functional group): $-COOCH_3$ +2.00; C_6H_5 +0.60; C_2H_5 −0.10) [30], the occurrence of ν_{POO^-} as bands at wavenumbers as high as 1250–1230 cm^{-1} (Mn^{2+}, Cu^{2+} and Zn^{2+} complexes) in the spectra of complexes with exclusively bidentate coordinated POO groups would not be unexpected [17]. Actually, on the basis of the overall evidence it appears that in all the metal complexes herein reported, the POO grouping of depf acts as a bidentate ligand (*vide infra*). It should be noted here that the spectra of the complexes are generally devoid of bands attributable to the presence of water or ethanol (the latter arising by hydrolysis of teof [14]).

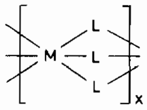
Regarding the ultraviolet spectral data, Table III gives the UV spectrum of free tepf, which shows the main $\pi \rightarrow \pi^*$ transition at 219 and 242 nm, and the $n \rightarrow \pi^*$ transition band at 335 nm [31, 32]. The corresponding spectrum of depf is not available in the literature. It is, thus, not possible to determine what types of shifts of the UV bands of this ligand occur upon 3d metal complex formation. Comparison of the UV spectra of the new complexes to that of tepf indicates that the $\pi \rightarrow \pi^*$ transition bands are shifted in either direction, and appear occasionally as split in the spectra of the complexes; the n → π^* transition band is present in all the metal complex spectra (332–351 nm region). Charge-transfer absorption, originating in the UV and trailing off into part of the visible region (up to about 400 nm) masks the d–d transition bands of the Mn^{2+} and Fe^{3+} complexes. For the rest of the paramagnetic metal complexes, most of the main d–d transition bands are identifiable.

The ambient temperature magnetic moments of the new complexes are generally normal for high-spin $3d^3$ and $3d^5$–$3d^8$ systems or the $3d^9$ configuration [33]. In view of the apparent polymeric nature of the new complexes, it should be pointed out here that, quite often, linear chain-like polynuclear 3d metal complexes, involving bridging $-O-P(R_2)-O-$ ligands, exhibit normal room temperature magnetic moments, but show evidence of antiferromagnetic exchange interactions at lower temperatures [34–39]. Supplementary magnetic studies at 300–80 K are planned for the future for the new complexes.

Complexes with Bidentate depf Ligands

Complexes with depf ligands exclusively binding through the two POO oxygens are $Cr(depf)_2(ClO_4)$, $Fe(depf)_3$ and three of the $M(depf)_2$ (M = Fe, Cu, Zn) compounds. The Cr^{3+} complex exhibits triply split ν_3 and $\nu_4(ClO_4)$ bands, IR-active ν_1 and ν_2-(ClO_4) absorptions [40], as well as $\nu_{Cr-O}(ClO_4)$ [41]. These features are consistent with the presence of bidentate $(=O_2ClO_2)$ coordinated perchlorate [40, 41]. The tentative $\nu_{M-O}(POO)$ band assignments [8, 42, 43] (Table II) favor coordination number six for the Cr^{3+} and Fe^{3+} complexes and coordination number four for the Fe^{2+}, Cu^{2+} and Zn^{2+} compounds [8, 41–43]. The anticipated trends of wavenumber increase of the $\nu_{M-O}(POO)$ doublets along the series $Fe^{3+} < Cr^{3+}$ and $Zn^{2+} < Fe^{2+} < Cu^{2+}$ are observed [44]. The d–d transition spectrum of the Cr^{3+} complex is compatible with a low symmetry hexacoordinated configuration ($^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 450; $\rightarrow {}^4T_{2g}(F)$ 633, 664, 691 nm; Dq = 1509 cm^{-1}) [45]. The approximate Dq of 1509 cm^{-1} is in the same region as the corresponding values for tris(ethyl acetylphosphonato)- and tris(ethyl benzoylphosphonato)-Cr(III) (1513–1514 cm^{-1}) [46]. The d–d transition spectra of the Fe^{2+} and Cu^{2+} complexes are, on the other hand, consistent with tetracoordinated configurations, *i.e.* distorted or flattened tetrahedral for Fe^{2+} [47], and square-planar for Cu^{2+} [45].

The linear polymeric nature of metal complexes with bidentate bridging $-O-P(R)_2-O-$ ligands has been established by means of several crystal structure determinations [34, 35, 48, 49]. ML_3 complexes of this type are triple-bridged polymers (II) [35, 49], while ML_2 complexes involve either alternating single and triple L bridges (III) or exclusively double bridges (IV) [34, 48]. Thus, in view of these previous structural studies, the overall evidence available, and the insolubility of the preceding complexes in organic media, it is reasonable to consider the Fe^{3+} complex as being of structural type (II), and the three M^{2+} complexes with exclusively bidentate POO oxygen-bonded depf ligands (M = Fe, Cu, Zn) as having either of the type (III) or (IV) structures (L =  $-O-\underset{C_2H_5O\ \ COOC_2H_5}{P}-O-$). The Fe^{2+} and Zn^{2+} complexes are distorted tetrahedral, and the Cu^{2+} compound is square planar. The Cr^{3+} complex, which is of the mixed (depf-perchlorato) ligand type, and seems to contain bidentate coordinated $=O_2ClO_2$ groups (designated as X), may involve either chelating (V) or bridging (VI) perchlorate, in addition to two bridging depf ligands per Cr^{3+} ion [49, 50].



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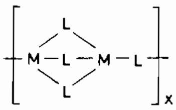

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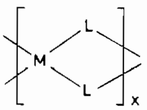

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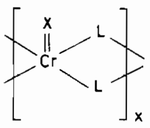

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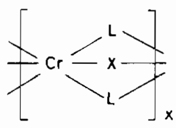
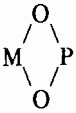
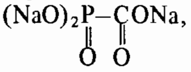


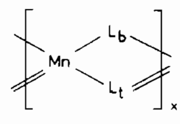
(VI)

Complexes with Tridentate depf Ligands

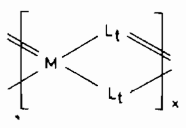
The three remaining new complexes (M = Mn^{2+}, Co^{2+}, Ni^{2+}) clearly involve coordinated C=O oxygens, in addition to the coordinated two POO oxygens (*vide supra*). Both $\nu_{M-O}(POO)$ and ν_{M-O}-(C=O) IR bands were identified in their spectra [8, 20, 42, 43]. The trend of wavenumber increase of the $\nu_{M-O}(C=O)$ bands along the series $Co^{2+} < Ni^{2+} < Mn^{2+}$, and the $\nu_{M-O}(POO)$ doublets along the $Co^{2+} < Ni^{2+} < Mn^{2+} < Zn^{2+} < Fe^{2+} < Cu^{2+}$ series, indicates that the three complexes under discussion have coordination numbers higher than four, and that the coordination number of the Mn^{2+} complex is lower than those of the Co^{2+} and Ni^{2+} complexes [44]. The d–d transition spectra of the Co^{2+} and Ni^{2+} complexes are compatible with low symmetry hexacoordinated configurations, *viz.* (nm): M = Co^{2+}: $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, $^4A_{2g}(F)$ 510 (broad, unresolved); $\rightarrow {}^4T_{2g}(F)$ 1235. M = Ni^{2+}: $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 411; $\rightarrow {}^3T_{1g}(F)$ 655, 712; $\rightarrow {}^3T_{2g}(F)$ 1243 (approximate Dq = 805 cm^{-1}, which is within the range of values (800–850 nm) reported for Ni^{2+} perchlorate complexes with diethyl acetyl- and diethyl benzoyl-phosphonates [6]). Since the new Co^{2+} and Ni^{2+} complexes involve coordination number six, it follows that $Mn(depf)_2$ is pentacoordinated. This compound is insoluble in organic media and its IR spectrum suggests that half of the depf ligands coordinate through the C=O oxygen, while the other half do not. Hence, a linear double-bridged polymeric structure (VII), in which one of the ligands is bidentate, POO oxygen-bonded (L_b), and the other is tridentate (L_t), coordinating through the C=O and the two POO oxygens [6, 37, 51], would be most likely. The Co^{2+} and Ni^{2+} complexes are the only new compounds that are soluble in organic media. Their molar conductivities in nitromethane are intermediate between those corresponding to "non"- and 1:1-electrolytes [52]. This suggests that some dissociation of these $[M(depf)_2]$ species occurs in solution. Since both depf ligands in these hexacoordinated compounds are tridentate, the complexes would be either $[M(L_t)_2]$ monomers or linear low oligomers of type (VIII). Bridging of type (IX), involving chelation of depf through the C=O and one POO oxygen to one metal ion and coordination of the second POO oxygen to an adjacent metal ion, may be more favorable [6, 37, 51] than the function of depf as a tridentate chelating agent (X), since R_2POO^- ligands do not have but little tendency to act as bidentate chelating agents [27, 34, 35, 48, 49]; for instance, $[Mn(OOPR_2)_2]_x$ complexes (R = alkyl, alkoxy) are generally bi- or poly-nuclear with bridging ligands, but the corresponding $[Mn(OOPR_2)_2L_2]$ species (L = pyridine, N,N-dimethylformamide, *etc.*) are monomeric with chelating R_2POO^- groups [53]. It is, nevertheless, possible that the presence of the third (C=O oxygen) depf binding site contributes to the stabilization of the  chelate ring in the new Co^{2+} and Ni^{2+} complexes.

Reactions Leading to depf Metal Complex Formation

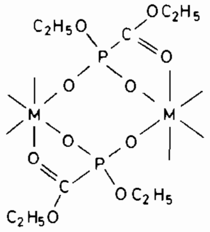
Depending on the experimental conditions, hydrolysis of tepf in neutral, acid or alkaline media may lead to removal of one or all three of the ethyl groups [54, 55]. On the other hand, the trisodium salt,  $(NaO)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{O}{\|}}{C}ONa$, is reportedly formed with concomitant elimination of ethanol, during reaction of tepf with 0.1–0.2 *N* aqueous NaOH [54, 56]. Some reactions of compounds analogous to tepf with inorganic reagents, such as NH_3 [57] or $HgCl_2$ [58], have led to cleavage of the molecule into $(RO)_2P–O–$ and $–COOR$ groups. In the cases under study, the reactions of metal perchlorates with tepf lead to the elimination of one ethyl group per tepf molecule. The IR evidence (*vide supra*) is clearly in favor of removal of one of the $–P(OC_2H_5)_2$ ethyls rather than the $–COOC_2H_5$ ethyl group. This was anticipated, since reactions of type (1), leading to elimination of RX (R = alkyl; X = halide, NO_3, ClO_4) can reportedly occur in solutions containing metal salts and neutral phosphoryl or thiophosphoryl alkylesters [2, 8–12], as well as during the thermal decomposition of metal halide adducts with ligands of this type [59, 60]. Whereas, in the case of the metal halide adducts with carboxyclic acid esters, only a few cases of thermal decomposition of the solid adducts to RX and $R'COOMX_3$ (M = Ti^{4+}, Zr^{4+}, Hf^{4+}; X = halide) have been reported [61, 62].



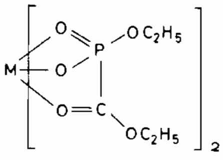
(VII)



(VIII)

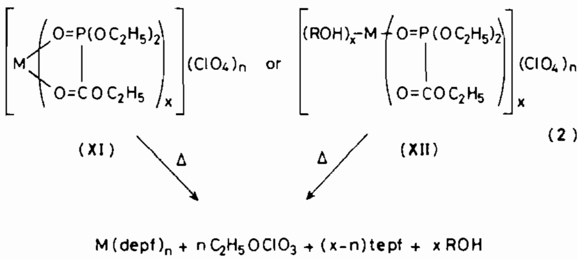


(IX)



(X)

Initially, adducts of tepf with the metal perchlorates are presumably formed by our synthetic process [2–6]. Since diethyl acetyl- and diethyl benzoyl-phosphonates were found to act as chelating agents toward the same metal perchlorates [6], it is possible that the tepf adducts with metal perchlorates are also chelates (XI), although the strength of tepf as a ligand is relatively weaker [63] and competition with water or the ethanol produced by hydrolysis of teof for the first coordination sphere of the metal ion would not be unlikely (XII) [6]. Thus, formation of the new depf complexes and ethyl perchlorate occurs by thermal decomposition of either the chelate (XI) or the mixed-ligand complex (XII), *viz.* (R = H or C_2H_5) [2, 8–12, 64]:



Each of the ionic ClO_4^- groups combines with one of the $-P(OC_2H_5)_2$ ethyls of the coordinated tepf ligands. It should be noted, in this connection, that the rather uncommon alkyl perchlorates have been previously observed as products of reactions between $AgClO_4$ and alkyl halides [65, 66] or alcohols and anhydrous $HClO_4$ [67]. No attempts at the isolation of ethyl perchlorate were made, in view of its extremely explosive nature [66, 68].

The reasons why the initially formed tepf adducts are not precipitated and recovered intact are not quite clear. The most likely possibility is that mixed-ligand (tepf-ROH) adducts of type XII, soluble in the mother liquor, are formed; since the precipitation of these adducts could not be induced by conventional methods, they remained in solution and had the opportunity to undergo a reaction of type (2), yielding the $M(depf)_n$ complexes. It is noteworthy, in this connection, that, in addition to $[M(deap)_3](ClO_4)_2$ chelates (M = Mn, Co; deap = diethyl acetylphosphonate), a number of adducts of the type $[M(deap)_3(OH_2)_3](ClO_4)_n$ (M = Fe^{2+}, Fe^{3+}, Ni^{2+}, Zn^{2+}) were obtained in the form of viscous oily precipitates, only after the addition of a very large excess of diethyl ether, during our synthetic studies of deap complexes with metal perchlorates [6b]. In view of the deethylation ractions observed in the present study, we are planning to explore the possibility of the occurrence of analogous reactions with other phosphonate or phosphate alkylesters (*e.g.*, deap [6b], diisopropyl methylphosphonate [4], trimethyl phosphate [5]). Emphasis in these future studies will be given to attempts to prevent precipitation of the adduct, so that reactions of type (2) will be favored as the temperature of the solution increases.

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