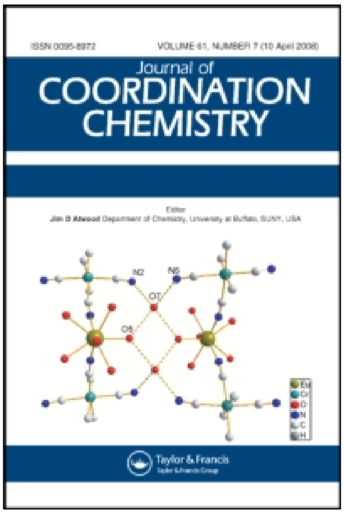

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Mikulski, Chester M. , Sanford, Patricia , Harris, Nancy , Rabin, Richard and Karayannis, Nicholas M.(1983) 'POLYMERIC COMPLEXES FORMED BY REACTION OF TRIETHYL PHOSPHONOFORMATE WITH METAL CHLORIDES', Journal of Coordination Chemistry, 12: 3, 187 — 196

To link to this Article: DOI: 10.1080/00958978308073847

URL: http://dx.doi.org/10.1080/00958978308073847

J. Coord. Chem., 1983, Vol. 12, pp. 187–196
0095-8972/83/1203-0187 $18.50/0

POLYMERIC COMPLEXES FORMED BY REACTION OF TRIETHYL PHOSPHONOFORMATE WITH METAL CHLORIDES†

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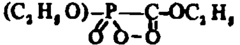
(Received May 6, 1982)

Triethyl phosphonoformate (tepf) reacts with metal chlorides at elevated temperatures to yield ethyl chloride and the corresponding $M(depf)_n$ complexes (depf = diethyl phosphonoformato ligand; M^{n+} = Dy^{3+}, Ti^{3+}, V^{3+}, Cr^{3+}, Fe^{3+}, Th^{4+}, U^{4+}). The depf ligand is in the  $(C_2H_5O)-P-C-OC_2H_5$ tautomeric form, arising by elimination of one of the $-P(OC_2H_5)_2$ ethyl groups. The new metal complexes are linear chainlike polymeric species, involving bidentate bridging depf ligands coordinating through the two POO oxygens to adjacent metal ions; the COO oxygens do not participate in coordination. The ambient temperature magnetic moments of several of the paramagnetic $M(depf)_n$ complexes (M = Ti^{3+}, V^{3+}, Cr^{3+}, U^{4+}) are subnormal, as would be expected for linear chainlike polymeric metal complexes. $AlCl_3 \cdot 6H_2O$ reacts with tepf to yield a different complex, namely $Al(ehp)_3$ (ehp = ethyl hydrogenphosphonate, $(C_2H_5O)HPOO^-$). Initial formation of $Al(depf)_3$, followed by hydrolytic elimination of the $-COOC_2H_5$ ethyl group, with the P-H bond being eventually formed by CO_2 elimination from the resulting -PCOOH grouping, is assumed.

INTRODUCTION

Neutral phosphinate, phosphonate or phospate alkylesters ($(RO)R'_2P = O$, $(RO)_2R'P = O$ and $(RO)_3P = O$, respectively; R = alkyl, R' = alkyl, aryl, etc.) readily undergo reactions of type (*1*) with metal chlorides, at temperatures ranging between 20-220, depending on the metal ion present, yielding polymeric $[M(OOPR''R''')_n]_x$ complexes (R'', R''' = RO or R' in the preceding formulae), with simultaneous elimination of alkyl chloride.[2-5]

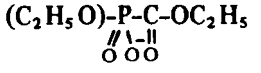
$$n(RO)R''R'''P = O + MCl_n \xrightarrow{\Delta} M[OOPR''R''']_n + nRCl \qquad (1)$$

The polymeric nature of the metal complexes produced during reactions of type (*1*) has been ascertained by several crystal structure determinations.[6-10] Diethylacetyl- and diethylbenzoyl-phosphonates (deap, debp, respectively;  $(C_2H_5O)_2\text{-}\underset{\underset{O}{\|}}{P}\text{-}\underset{\underset{O}{\|}}{C}\text{-}X$; X = CH_3 or C_6H_5) have been also found to undergo reactions of type (*1*) with many metal chlorides. In some cases, ethylacetyl- or ethylbenzoyl-phosphonato (eap, ebp, respectively) polymeric metal complexes are formed, but in many cases further substitution reactions of the organophosphoryl compound take place, leading to the formation of ethyl hydrogenphosphonate ($(C_2H_5O)HPOO^-$; ehp). As a result of the latter reaction, several $M(ehp)_n$ or mixed ligand $ML_x(ehp)_y$ (L = eap or ebp) complexes were isolated.[11] More recently we investigated the reactions of triethyl phosphonoformate ( $(C_2H_5O)_2\text{-}\underset{\underset{O}{\|}}{P}\text{-}\underset{\underset{O}{\|}}{C}\text{-}OC_2H_5$; tepf)

---

† Ref. 1.

with metal chlorides and perchlorates, and reported some of our results in a preliminary communication.[12] Reactions of type (*1*), leading to the formation of metal complexes of the diethylphosphonoformato ligand (depf; I) were found to take place not only with metal chlorides (with the exception of $AlCl_3$, which yielded $Al(ehp)_3$), but also with metal perchlorates.[12] Now our characterization studies of the reaction products between tepf and metal chlorides ($M = Al^{3+}, Dy^{3+}, Ti^{3+}, V^{3+}, Cr^{3+}, Fe^{3+}, Th^{4+}, U^{4+}$) have been completed and are reported in the present paper. The corresponding work on complexes produced by reaction of tepf with metal perchlorates will be described elsewhere.[13]


$(C_2H_5O)\text{-}\underset{O\quad O}{P}\text{-}\underset{O}{C}\text{-}OC_2H_5$

(I)

EXPERIMENTAL

Preparation of Metal Complexes: Reagent grade tepf and anhydrous ($M = Ti^{3+}, V^{3+}, Fe^{3+}$) or hydrated ($M = Al^{3+}, Dy^{3+}, Cr^{3+}, Th^{4+}, U^{4+}$) metal chlorides were used. The metal salt is suspended in a large excess of neat tepf, and the temperature of the suspension is increased at a rate of 1-2° min^{-1}, until precipitation occurs (following complete dissolution of the metal chloride in tepf) at 50-200°, depending on the metal ion present.[3-5] In most cases it does not make any difference if the reaction is carried out in the atmosphere or under nitrogen. However, with $TiCl_3$, the reaction has to be performed under dry N_2 (in a dry-box), otherwise, oxidation products (TiO^{2+} complexes) are obtained. The precipitates are separated by filtration, washed with several portions of ethanol, and stored *in vacuo* over P_4O_{10}. The new complexes are generally insoluble in water and organic media, and, with the exception of $Ti(depf)_3$, stable in the atmosphere. In most cases, $M(depf)_n$ complexes were isolated ($M^{n+} = Dy^{3+}, Ti^{3+}, V^{3+}, Cr^{3+}, Fe^{3+}, Th^{4+}, U^{4+}$). Nevertheless, in the case of $AlCl_3$ reaction with tepf, $Al(ehp)_3$ was obtained instead. The preparation of $Al(depf)_3$ was attempted by using anhydrous $AlCl_3$ and operating in a dry N_2 atmosphere, but the reaction was somewhat violent and resulted in the production of a rubber-like precipitate of uncertain nature. Analytical data for the new metal complexes are given in Table I.

Spectral and Magnetic Measurements: Infrared spectra (Table II) were obtained on Nujol mulls between IRTRAN 2 (ZnS) (4000-700 cm^{-1}) and high-density polyethylene

TABLE I
Analytical Data for $Al(ehp)_3$ and $M(depf)_n$ Complexes.[a]

Complex	Color	C% Calc.	C% Found	H% Calc.	H% Found	P% Calc.	P% Found	Metal% Calc.	Metal% Found
$Al(ehp)_3$	Off-white	20.35	19.94	5.12	5.16	26.24	26.49	7.62	7.36
$Dy(depf)_3$	White	25.53	25.88	4.28	4.27	13.16	12.81	23.02	23.44
$Ti(depf)_3$	Lavender	30.47	30.19	5.11	5.02	15.72	15.66	8.10	7.79
$V(depf)_3$	Light green	30.37	30.63	5.10	4.85	15.66	15.87	8.59	8.92
$Cr(depf)_3$	Green	30.26	30.54	5.08	5.26	15.61	15.38	8.73	9.01
$Fe(depf)_3$	Off-white[b]	30.07	30,14	5.05	4.93	15.51	15.60	9.38	9.67
$Th(depf)_4$	White	25.12	24.65	4.22	4.48	12.95	12.72	24.25	23.96
$U(depf)_4$	Pale green	24.96	25.17	4.19	4.35	12.87	13.23	24.73	24.47

[a] Cl analyses for the complexes: 0.05–0.17% Cl. [b] Pinkish tint.

TABLE II
Pertinent IR Data (cm^{-1}) for Al(ehp)$_3$ and M(depf)$_n$ Complexes.[a]

M = Al^{3+}	M = Dy^{3+}	M = Ti^{3+}	M = V^{3+}	M = Cr^{3+}	M = Fe^{3+}	M = Th^{4+}	M = U^{4+}	Band Assignment
2305w								ν_{P-H}
	1708vs	1707s	1711s	1719s	1700s	1702s	1704s	$\nu_{C=O}$
	1188vs	1199s	1200s	1197s, sh	1193vs, b	1180s	1182s	ν_{C-O}
1222vs, 1135s	1215s, b 1172s	1224s, 1163s	1229s, 1169s	1218vs, 1164s	1210vs, 1166vs	1225s, 1160s, sh	1223s, 1157s, sh	ν_{POO}, as
1160m, sh	b	1157m, sh	1152m, sh	b	b	1143m, sh	b	$\nu_{C_2H_5-O-(P)} + \nu_{C_2H_5-O-(C)}$
1052s, b 1033s	1090s, b, 1069vs	1095ms, 1080s	1102ms, 1080s	1100ms, 1063s	1078s, b, 1053vs	1087s, b, 1070vs	1085s, b, 1061vs	ν_{POO}, sym
1004ms, sh	1030vs, 998m, b	1040s, 1008s,	1039s, 1010s	1027vs, 1004m, sh	1035vs, 995s	1028s, 996s	1027s, 1009s	$\nu_{P-O-(C_2H_5)}$ + $\nu_{C_2H_5-O-(C)}$
950ms, vb	949m	948mw	950m	947m	946mw	952m	949m	C_2H_5 rocking
541s, b, 470s, 383s, b	437m, 348m, 295w, b	464s, b, 341ms, 307w	462s, b, 338ms, b, 302w	467s, 335m, sh, 299ms	444m, 440mw, b, 287w	442s, 407m, sh	440s, 407s, sh	ν_{M-O}(POO)[c]

[a] Ir bands of neat tepf, cm^{-1} (see also ref. 15); 1707vs ($\nu_{C=O}$), 1255vs ($\nu_{P=O}$), 1198 (ν_{C-O}), 1172s, sh ($\nu_{C_2H_5-O-(P)}$), 1137mw ($\nu_{C_2H_5-O-(C)}$), 1012vs, 998vs, b ($\nu_{P-O-(C_2H_5)} + \nu_{C_2H_5-O-(C)}$), 955 ms ($C_2H_5$ rocking), 640w, 579s, 547s, 505m, b, 445m, b, 420mw, sh, 388w, 310mw, b, 240mw.

[b] Masked bands.

[c] Strong depf absorption at 580–500 cm^{-1} prevents detection of metal-sensitive bands in this region.[3-5]

(800-200 cm^{-1}) windows, in conjunction with a Perkin-Elmer 621 spectrophotometer. Solid-state (Nujol mull) electronic spectra and magnetic susceptibility measurements at 298 K (Table III) were obtained by methods described elsewhere.[14]

DISCUSSION

Infrared Evidence: Pertinent absorption bands of the ir spectrum of neat tepf are shown in Table II (footnote a). The $\nu_{C=O}$, $\nu_{P=O}$ and $\nu_{P-O-(C_2H_5)}$ modes were previously assigned by Ogata and Tomioka.[15] Our band assignments were based on this previous work,[15] as well as ir studies of various neutral phosphonate[16] and carboxylic acid[17, 18] esters. Regarding $Al(ehp)_3$, it's spectrum is similar to those previously reported for other complexes with this ligand (namely, $V(ehp)_3$, $Th(ehp)_4$ and $U(ehp)_4$),[11] exhibiting the characteristic ν_{P-H} (2305 cm^{-1})[19] and ν_{POO} asymmetric and symmetric modes.[11] On the other hand, the spectrum of free depf is not available in the literature. The removal of one ethoxy ethyl group from tepf during the reactions herein described, could lead to the formation of either of the following tautomeric anionic ligands: depf (I) or the anion of diethylphosphonoformic acid (depfa; $(C_2H_5O)_2-\underset{\underset{O}{\|}}{P}-\underset{\underset{O}{\|}}{C}-O^-$). The ir spectra of the new complexes favor the presence of depf rather than depfa. 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 at 1470-1310 cm^{-1}.[22-24] The possibility of coordination of depf through the $-COOC_2H_5$ oxygens may be ruled out, since the $\nu_{C=O}$ and ν_{C-O} bands occur at 1719-1700 and 1200-1182 cm^{-1}, respectively, in the spectra of the new depf complexes.[20, 21, 25, 26] With respect to the function of both POO oxygens as ligand sites, the spectra of the depf complexes exhibit the characteristic ν_{POO}, as and ν_{POO}, sym vibrational modes at 1229-1157 and 1102-1053 cm^{-1}, respectively.[3-5,16,27-29] It should be mentioned here that the presence 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 coordination of some of the R_2POO^- ligands (R = alkyl, aryl) through only one of the POO oxygens.[27, 28] Nevertheless, with ehp or 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, where Y = functional group: $-COOC_2H_5$ +2.00; C_6H_5 +0.60; C_2H_5 -0.10),[30] the occurrence of ν_{POO}, as at wavenumbers as high as about 1230 cm^{-1} in the spectra of complexes with exclusively bidentate coordinated POO groups would not be unexpected.[16] Hence, it may be concluded that both POO oxygens are coordinated in all of the new metal complexes.

Tentative metal-ligand band assignments were based on previous studies of metal complexes with diorganophosphonato ligands.[4,5,11] These assignments are consistent with coordination numbers six for the M^{3+} and eight for the M^{4+} complexes.[4, 5, 11] Finally, it should be noted that the ir spectra of the new complexes are generally devoid of any bands attributable to the presence of coordinated or lattice water.

Electronic Spectra and Magnetic Susceptibilities: Table III gives the UV spectrum of free tepf, which shows the main $\pi \rightarrow \pi^*$ transition at 242 nm and the $n \rightarrow \pi^*$ transition band at 335 nm.[31,32] The corresponding spectra of depf or ehp are not available. It is, therefore, not possible to determine the types of shifts occurring upon complexation of these ligands. Comparison of the UV spectrum of tepf to those of the depf complexes indicates that the $\pi \rightarrow \pi^*$ transition bands are split and shifted in either direction, whilst the $n \rightarrow \pi^*$ transition band appears at 337-351 nm. The *d-d* transition bands of the 3*d* metal complexes are generally split and thus indicative of low-symmetry hexacoordinated configura-

TABLE III
Solid-state (Nujol mull) Electronic Spectra and Magnetic Properties (298 K) of Al(ehp)$_3$ and M(depf)$_n$ Complexes

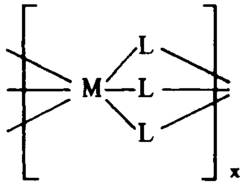
Complex	λ_{max}, nm[a, b]	$10^6\chi_M^{cor}$, cgsu	μ_{eff}, B
Al(ehp)$_3$	203vvs, 218vs, sh, 226vs, sh, 237vs, sh, 246s, sh, 259s, sh 264s, sh, 272ms, vb, 304m, sh, 325mw, vb	Diamagnetic	
Dy(depf)$_3$	202vvs, 214vvs, 219vvs, 232vvs, sh, 247vvs, b, 295s, vb, 311s, sh, 347s, b	47, 259	10.66
Ti(depf)$_3$	200vvs, 215vvs, 226vvs, b, 241vvs, b, 258vs, sh, 290s, b, 345s, b, 545ms, 682ms, sh	1164	1.68
	(Dq = 1834 cm^{-1})		
V(depf)$_3$	196vvs, 213vvs, 221vvs, b, 236vvs, sh, 247vs, sh, 253vs,sh 260vs, sh, 288s, b, 310s, b, 338ms, sh, 448m, b, 456m, sh 645m, b, 681m, b, 715m, b	3066	2.71
	(Dq = 1629 cm^{-1}; B = 584 cm^{-1})		
Cr(depf)$_3$	199vs, 209vvs, 217vs, sh, 224vs, sh, 236vs, sh, 240s, 248s, 251s, sh, 293s, vb, 342m, vb, 450m, vb, 620m, sh, 652m, vb, 684m, b	3724	2.99
	(Dq = 1534 cm^{-1})		
Fe(depf)$_3$	201vvs, 214vvs, sh, 219vvs, sh, 240vs, sh, 295vs, b, 337vs, sh	15,786	6.16
Th(depf)$_4$	197vvs, 217vvs, 244vvs, b, 259s, vb, 350m, b	Diamagnetic	
U(depf)$_4$	195vvs, 212vvs, 237vvs, 245vvs, sh, 292s, vb, 351m, b, 373m, sh, 424m, b, 440m, b, 452m, b, 497m, sh, 540m,b, 550m, sh, 597mw, b, 633m, b, 673m, 747m, sh, 785m 860mw, b, 915mw, sh, 1075m, vvb, 1285w, sh, 1400w, vvb	2850	2.62

[a] UV spectrum of free tepf (neat), nm: 200vs, 206vs, sh, 219vs, b, 242vs, b, 251s, sh, 263s, b, 335m, vb. [b] Approximate Dq and B (Racah parameter) calculations were made for pure O_h symmetry.

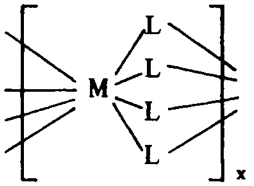
tions,[33] *viz.*, nm: Ti(depf)$_3$ $^2T_{2g} \rightarrow {}^2E_g$ 545 (main band), 682 (shoulder); V(depf)$_3$ $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ 448, 456; $\rightarrow {}^3T_{2g}(F)$ 645, 681, 715; Cr(depf)$_3$ $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 450; $\rightarrow {}^4T_{2g}(F)$ 620, 652, 684. The approximate Dq values calculated are in the same range as those previously reported for various diorganophosphonato complexes of the same metal ions (i.e., TiL$_3$ 1773-1866 cm^{-1}; VL$_3$ 1523-1613 cm^{-1}; CrL$_3$ 1508-1538 cm^{-1}).[4,5,11] As far as the visible and near-ir spectrum of U(depf)$_4$ is concerned, it is very similar to the spectra of other octacoordinated U^{4+} complexes with R_2POO^- ligands.[4,5,11,34]

The ambient temperature magnetic moments of the Ti^{3+} and V^{3+} depf complexes are slightly low, while that of the Cr^{3+} analog (2.99 μB) is clearly subnormal.[35] Likewise, the moment of U(depf)$_4$ is subnormal for octacoordinated U^{4+}.[36,37] This is in agreement with the trends previously observed for linear, polynuclear complexes of the preceding metal ions with R_2POO^- ligands, and is apparently due to antiferromagnetic exchange between adjacent metal ions in the chainlike, ligand-bridged polymeric structures of these compounds.[3-11,38-41] On the other hand, the magnetic moments of the Dy^{3+} and Fe^{3+} new complexes are normal. This is not surprising,[3-5,11] since the 4f electrons of the lanthanide ions are effectively shielded[42] and cannot participate in magnetic exchange, whilst for FeL_3 polynuclear complexes with R_2POO^- and Cl_2POO^- ligands, widely differing μ_{eff} values, ranging from as low as 3.90 to as high as 6.27 μB, have been reported.[3-5,11,34,43] The μ_{eff} variation with ligand change in a whole series of $Fe(OOPR_2)_3$ complexes could not be correlated with inductive or steric effects of the substituents on phosphorus, while the corresponding correlations for other $M(OOPR_2)_3$ (M = Ti, V, Cr) or $U(OOPR_2)_4$ complexes were quite successful.[3-5,11,34]

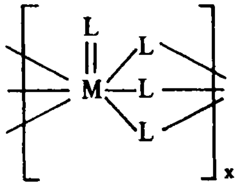
Likely Structural Types: The most likely structural type of the $Al(ehp)_3$ and $M(depf)_3$ complexes is the linear, chainlike triple-bridged polymeric configuration (II) (L = -O-P-O bridging ligand), which is common in M^{3+} complexes with R_2POO^- ligands.[8,38,39] The subnormal ambient temperature magnetic moments of most of the new paramagnetic metal ion complexes justify such an assignment. Regarding the $M(depf)_4$ complexes (M = Th, U), an analogous quadruple-bridged linear polymeric structure (III) is most likely.[3,11,34] An alternative triple-bridged structure with one chelating depf ligand per metal ion(IV), as well as highly cross-linked double-bridged structures, have been proposed for M^{4+} complexes with R_2POO^- ligands, especially in view of the possible steric interference between the four bridging ligands in structure (III).[3-5,34,41] However, several quadruple-bridged structures have been established for metal complexes with ligands of analogous bulkiness to that of depf (e.g., Cu^{2+} complexes involving four bridging adenine ligands;[44]) hence, structure (III) may be considered as quite likely for all the ML_4 complexes with R_2POO^- ligands, including the $M(depf)_4$ complexes.



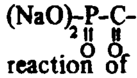
(II)



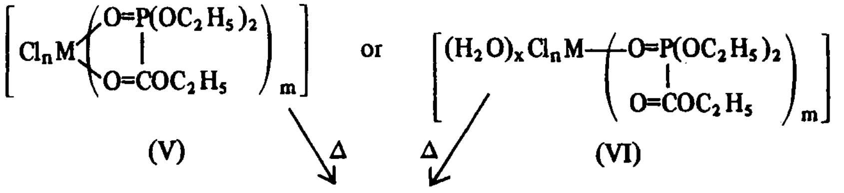
(III)



(IV)

Reactions Leading to the Formation of the New Metal Complexes: 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.[45,47] On the other hand, the trisodium salt,  $(NaO)_2\underset{O}{\underset{\|}{P}}-\underset{O}{\underset{\|}{C}}-ONa$, is reportedly formed with concomitant elimination of ethanol, during reaction of tepf with 0.1–0.2*M* aqueous NaOH.[45,47] Some reactions of compounds analogous to tepf with inorganic reagents, such as NH_3[48] and $HgCl_2$[49] lead to cleavage of the molecule into $(RO)_2P{=}O-$ and $-COOR$ groups. In most cases under study, the reaction of metal chlorides with tepf at elevated temperatures lead to elimination of one ethyl group per tepf molecule, whilst with $AlCl_3$ an additional substitution of the $-COOC_2H_5$ group also occurs. In the latter case, initial formation of $Al(depf)_3$ may be assumed. $Al(ehp)_3$ is then presumably formed by hydrolytic elimination (water source is $AlCl_3 \cdot 6H_2O$) of the ethyl group of the $-COOC_2H_5$ fragment of depf, followed by elimination of CO_2 from the resulting -PCOOH grouping, under the acidic conditions of the synthetic procedure.[47,50] In the rest of the cases studied, the depf ligands are formed by elimination of one of the $-P(OC_2H_5)_2$ ethyls rather than the $-COOC_2H_5$ ethyl from tepf, as clearly shown by the ir evidence (*vide supra*). This was anticipated, since reactions of type (*1*), leading to elimination of alkyl chloride, are quite common for neutral organophosphoryl alkylesters, and occur either by heating solutions of metal chlorides in these esters or by thermal decomposition of adducts of metal chlorides with such esters.[3-5,11,34,51-54] Whereas in the case of metal halide adducts with carboxylic acid alkylesters, 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 ion) have been reported.[55,56]

The metal chloride-tepf adducts initially formed may be either chelates of type (V), involving coordination of both the P=O and C=O oxygens (as is the case with several metal perchlorate complexes with deap and debp,[26] as well as (β-ketophosphonato)Th(IV) complexes[57]) or complexes involving unidentate P=O oxygen-bonded tepf and (wherever applicable) water ligands (VI). The latter possibility is more likely, since tepf is a weaker C=O ligand than either deap or debp,[58] while the final products (depf metal complexes) do not involve coordination of depf through the C=O oxygen. Expression (2) shows the two possible reaction pathways that lead to formation of the $M(depf)_n$ complexes.



$$M(depf)_n + nC_2H_5Cl + (m\text{-}n)tepf + (xH_2O) \qquad (2)$$

If adducts of type (VI) are indeed formed rather than chelates of type (V), an intermediate involving coordination of one of the $-P(OC_2H_5)_2$ oxygens of each tepf ligand (bidentate tepf, probably bridging, coordinating through the P=O and one P-O oxygen) would be formed, and the elimination of ethyl chloride would be further facilitated.[3-5,52] Finally, part of the ehtyl chloride eliminated disproportionates to yield HCl and ethylene, in the presence of the decomposing metal chloride-tepf adduct.[3-5,59,60]

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