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Addition and Reaction Products of Triethyl Thiophosphate and Metal Perchlorates at just over Ambient and Elevated Temperatures*

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Abstract

Triethyl thiophosphate (tetp) invariably forms adducts with various metal perchlorates (M = Mg^{2+}, Al^{3+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}) at 35–40 °C in ethanol–triethyl orthoformate (teof). Only certain of these adducts, which involve S-bonded tetp in the thione form for soft or borderline metal ions and O-bonded tetp in the thiol tautomeric form for hard metal ions, could be isolated in solid form, owing to their tendency to decompose yielding diethylthiophosphato (detp) metal complexes and ethyl perchlorate, at temperatures ranging between ambient and 80–90 °C, depending on the metal ion. Several well-defined detp and detp–perchlorato metal complexes were obtained by heating solutions of mixtures of tetp and metal perchlorates in ethanol–teof at 80–90 °C, and characterized. In most cases, linear polymeric or dimeric complexes involving double or triple bridges of O,S-bonded bidentate detp between adjacent metal ions were isolated. However, in a number of occasions, heavily hydrated monomeric species, containing terminal S-bonded detp were obtained.

Introduction

Earlier work in these laboratories has dealt with the reactions of triethyl and tri-n-butyl thiophosphates (tetp and tbtp, respectively) with numerous metal halides at elevated temperatures [2–5]. These reactions led invariably to the formation of metal complexes with anionic ligands derived by elimination of one or more alkyl groups from the neutral thiophosphate ester. More specifically, reactions of $FeCl_2$, $VOCl_2$, MCl_3 (M = Ti, V, Cr, Fe, Y, Ln) and MCl_4 (M = Th, U) with the neutral esters at 140–230 °C resulted in the elimination of alkyl chloride and the precipitation of metal complexes with the corresponding dialkyl thiophosphato monoanionic ligand, *i.e.*, $M(detp)_n$ and $M(dbtp)_n$ (n = 2, 3 or 4), including a number of hydrated species such as $Fe(detp)_2 \cdot 2H_2O$, $Y(detp)_3 \cdot xH_2O$ and $Ln(dbtp)_3 \cdot xH_2O$ (Ln = lanthanide) [2–4]. On the other hand, reactions of tetp with alkali metal (Li, K, Na, Rb, Cs) iodides and MCl_2 (M = Mn, Co, Zn) at 180–270 °C led to the formation of ethyl pyrothiophosphato metal complexes, while tbtp reactions with the preceding metal halides, $AlCl_3$ and $NiCl_2$ resulted in the precipitation of either n-butyl pyrothiophosphato (M = alkali metal, Al^{3+}) or inorganic (alkyl-free) pyrothiophosphato (M = Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}) metal complexes [5]. The pyrothiophosphato ligands were presumably produced by partial disproportionation of the alkyl halide formed initially along with the ML_n (L = detp, dbtp) complexes to alkene and HX (X = Cl, I), subsequent attack of the $(RO)_2POS^-$ ligand by HX with formation of RX and $(HO)(RO)POS^-$ or $(HO)_2POS^-$, and condensation of two molecules of either of the latter two products to alkyl or inorganic pyrothiophosphate, respectively, with H_2S elimination [5]. The water-free ML_n (L = detp, dbtp) complexes were characterized as polymeric with multiple bridges of bidentate O,S-bonded $-OP(OR)_2S-$ ligands between adjacent metal ions, on the basis of several crystal structures of analogous diorgano-phosphinato [6–8] and -thiophosphinato [9, 10] metal complexes available at that time [2–4]. Since then, several additional crystal structure determinations of diorganophosphinato metal complexes [11–16] established that these compounds are generally linear chainlike polymeric species with multiple bridges of $-OP(R)_2O-$ [6–8, 11–16] (or $-OP(R)_2S-$ for the diorganothiophosphinates [9, 10]) ligands between neighboring metal ions. In the case of hydrated detp or dbtp metal

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complexes, polymeric structures involving both bridging O,S-bonded and terminal O-bonded dialkyl thiophosphato ligands were proposed, on the basis of IR data favoring the presence of both coordinated and non-coordinated S ligand sites [3, 4]; it should be noted that some metal diorganophosphinates, in which some of the ligands are terminal unidentate, were also characterized as such by means of IR studies [17]. Finally, the alkyl or inorganic pyrothiophosphato metal complexes were characterized as bi- or poly-nuclear [5] by analogy to alkyl pyrophosphonato [18] and pyrophosphato [19] metal complexes previously studied.

In a subsequent research project, we attempted the preparation of tetp adducts with metal perchlorates [20]. Unlike analogous work with trialkyl phosphates [21], dialkyl alkylphosphonates [22] and methyl methylphenylphosphinate [23], all of which yielded well-defined adducts with various metal perchlorates from triethyl orthoformate (teof) [21–24], we encountered severe difficulties in isolating tetp adducts [20]. In fact, interaction of tetp with $M(ClO_4)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn) at an 8:1 molar ratio in teof at 50 °C led to the precipitation of soft solid products for M = Mn, Fe, Co, Zn, that appeared to be mixtures of authentic tetp adducts and detp complexes (analytical results), while with M = Ni, Cu solid detp complexes of the $Ni(detp)ClO_4 \cdot 3H_2O$ and $Cu_2(detp)(ClO_4)_3 \cdot 4H_2O$ were isolated [20]. Thus, in contrast to phosphoryl esters [21–24], tetp shows a pronounced tendency to react with the metal perchlorate with detp metal complex formation and concomitant elimination of ethyl perchlorate [20]. This type of reaction is analogous to that reported during the thermal decomposition of $Ag(tetp)NO_3$ to Ag(detp) and $C_2H_5ONO_2$ [25, 26]. Among phosphoryl esters, only triethyl phosphonoformate (tepf; $(C_2H_5O)_2P(=O)COOC_2H_5$) has been found to undergo reactions with metal perchlorates, leading to formation of diethyl phosphonoformato metal complexes [27]. We were later able to isolate well-defined tetp adducts with some metal perchlorates (M = Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ag^{+}), by operating at 35–40 °C in teof solution [28]. Furthermore, we took advantage of the tendency of tetp to react with metal perchlorates and prepared $Al(detp)_3$, which we had been unable to produce from the $AlCl_3$–tetp reaction [5], by reacting $Al(ClO_4)_3$ with excess neat tetp at 85–90 °C [29].

It was felt that further investigation of the tetp interactions with metal perchlorates was in order, especially in view of the fact that we had been unable to isolate several $M(detp)_2$ (M = Mn, Co, Ni, Cu, Zn, Cd) complexes by reacting MCl_2 with tetp [4, 5]. It was decided to study the interaction of tetp with various M^{2+} (Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd) as well as three M^{3+} (Al, Cr, Fe) perchlorates in ethanol–teof at two different temperature regions, *i.e.,* slightly over ambient (35–40 °C; hereinafter referred to as Condition I) and at 80–90 °C (Condition II). These studies, which are the subject of the present paper, resulted in the isolation of some previously reported [2, 4, 28, 29] as well as many new complexes, which were characterized. Also, supplementary characterization data were collected for $M(detp)_3$ (M = Al, Cr, Fe) [4, 29], $Fe(detp)_2 \cdot 2H_2O$, $Ni(detp)ClO_4 \cdot 3H_2O$ and $Cu_2(detp)(ClO_4)_3 \cdot 4H_2O$ [20].

Experimental

The general procedure employed involved dissolution of 1 mmol hydrated metal perchlorate in 50 ml of a 7:3 (v/v) mixture of ethanol–teof, warming the resultant solution at 50 °C for 2 h under stirring, allowing to cool to room temperature and adding 6 mmol tetp.

Condition I

The tetp–$M(ClO_4)_n$ solution was warmed to 35–40 °C and allowed to remain at this temperature, under vigorous stirring, until precipitation occurred. Under this condition, the same tetp adducts that were previously prepared from teof [28] were precipitated, *i.e.*: $M(tetp)_4(ClO_4)_3$ (M = Al, Fe), $Cr(tetp)_2(ClO_4)_3 \cdot 2H_2O$, and $M(tetp)_4(ClO_4)_2$ (M = Co, Zn, Cd). These precipitates were separated by filtration, washed with n-heptane and stored *in vacuo* over P_4O_{10}. They are stable under N_2 atmosphere, but start immediately decomposing upon exposure to atmospheric moisture. Analyses, IR and d–d transition spectra, magnetic moments at 294 K and molar conductivities in 10^{-3} M nitromethane solutions at 25 °C are either identical or very similar to those previously reported [28]. Thus, magnetic moments and molar conductivities compare well with the earlier data, which are shown in parentheses, *viz.*: μ_{eff}, μB: $M^{n+} = Cr^{3+}$ 3.83(3.85); Fe^{3+} 6.09(6.12); Co^{2+} 4.53(4.53); Λ_M, Ω^{-1} cm^2 mol^{-1}:$M^{n+} = Al^{3+}$ 79(74); Cr^{3+} 76(80); Fe^{3+} 73(77); Co^{2+} 89(82); Zn^{2+} 72(74); Cd^{2+} 173(164); whereas the d–d transition maxima (nm) of the Cr^{3+} (415vs,vb, 595s,vb, 660m,b) and Co^{2+} (485s,b, 542s,b, 802m, 1200vw,b, 1850vw) complexes are identical to those recorded in our earlier work [28]. Table I gives more detailed IR spectral data than those published previously [28] for these adducts. As regards interaction of tetp at 35–40 °C with the remaining metal(II) perchlorates studied (Mg, Mn, Fe, Ni, Cu), deliquescent soft solids, consisting of mixtures of tetp adducts and detp complexes (analytical data indicating C:P and Cl:M ratios consistently well below the theoretical values for tetp (C:P 2.327) and the $M(ClO_4)_2$ salt, respectively, were obtained). These products were not studied any further.

TABLE I. Relevant IR Data for the $M(ClO_4)_n$ Adducts with tetp (cm^{-1}).[a]

M^{n+}	$\nu_{P=O}$	$\nu_{C-O-(P)}$	$\nu_{P-O-(C)}$	$\nu_{P=S}$	$\nu_{P-O-(C)}$	$\nu_{P=S}$	$\nu_{P-S-(C)}$[b]	ClO_4 Bands			
								ν_3	ν_1	ν_4	ν_2
Al^{3+}	1212s	1111vs,sh	1030vs,sh		824vw, 794m		567w,sh	1120vs, 1090vs, 1042vs	920m,sh	652s, 638s, 621s	475m,b
Cr^{3+}	1190s	1105vs,sh	1028vs,sh		821vw, 797m		570w,sh	1147vs, 1093vs, 1039vs	922m,sh	650s, 635s, 620s	475m,b
Fe^{3+}	1178s	1110vs,sh	1025vs,sh		819vw, 789m		562w,sh	1142vs, 1079vs, 1044vs	923m,sh	655s, 637s, sh, 624s	470m,b
Co^{2+}		c	1032vs,sh	840m,b, 781mw,sh	c	598m		1141vs, 1105vvs, sh, 1050s,sh	920m	650m,sh, 629s, 619s	465m,b
Zn^{2+}		1105vs,sh	1035vs,sh	784ms	c	593m		1140vs, 1095vs, 1048s	924m,	647m,sh 631s, 622s	480m,b
Cd^{2+}		1113vs,sh	1032s,sh	772m,b	c	603ms		1075vvs,b	918vvw	618ms	

[a] Free tetp shows $\nu_{P=S}$ bands at 828 (s) and at 631, 610 (ms) cm^{-1}; band assignments were based on refs. 28 and 31–35. [b] $\nu_{P-S-(C)}$ bands at 650–600 cm^{-1} were masked by $\nu_4(ClO_4)$. [c] Masked absorptions.

TABLE II. Analyses of detp Metal Complexes Prepared by Employing Synthetic Condition II[a]

Complex	Color	C%		H%		P%		S%		Metal%	
		Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
$Al(detp)_3$	White	26.97	27.41	5.66	5.61	17.39	17.65	18.00	17.82	5.05	5.24
$Cr(detp)_3$	Light green–blue	25.76	25.38	5.39	5.46	16.60	16.93	17.19	16.98	9.29	9.44
$Fe(detp)_3$	Light green	25.59	25.76	5.36	5.17	16.49	16.61	17.08	17.24	9.92	10.15
$Cu(detp)_2$	Brown	23.91	24.18	5.02	4.84	15.41	15.26	15.96	16.33	15.81	15.47
$Cu(detp)_2 \cdot 2H_2O$	Gray	21.94	22.20	5.52	5.73	14.15	13.89	14.64	14.90	14.51	14.70
$Zn(detp)_2 \cdot 4H_2O$	White	20.20	20.47	5.93	6.11	13.02	12.77	13.48	13.73	13.74	14.02
$Cd(detp)_2 \cdot 4H_2O$	White	18.38	18.05	5.40	5.55	11.85	12.13	12.27	12.34	21.50	21.92
$Fe(detp)ClO_4 \cdot 2H_2O$	Light brown	13.33	13.61	3.91	4.22	8.59	8.67	8.89	9.14	15.49	15.82
$Co(detp)ClO_4 \cdot 4H_2O$	Lavender	12.02	11.65	4.54	4.70	7.75	7.95	8.02	7.76	14.75	14.48
$Ni(detp)ClO_4 \cdot 4H_2O$	Green	12.03	12.38	4.54	4.67	7.76	7.42	8.03	8.12	14.70	14.51

[a] Cl analyses for the $M(detp)ClO_4 \cdot xH_2O$ complexes, found (cald.) %: M = Fe 9.70 (9.83); Co 9.11 (8.87); Ni 8.63 (8.88). The rest of the complexes in the Table are Cl-free (Cl analysis ranging between 0.0–0.2%).

Condition II

The flask containing the tetp–$M(ClO_4)_n$ solution in ethanol–teof was left to stir at 80–90 °C. Under this condition, the M^{3+} (Al, Cr, Fe) and some M^{2+} (Co, Ni, Zn, Cd) perchlorates produced precipitates after 20–40 min (yields of 35–50%). With M = Mg^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, precipitates formed in low yields (2–15%) after about 2 h of heating. The solid complexes obtained are of the following types (Table II): $M(detp)_3$ (M = Al, Cr, Fe), $M(detp)ClO_4 \cdot 4H_2O$ (M = Co, Ni), $M(detp)_2 \cdot 4H_2O$ (M = Zn, Cd), $Fe(detp)ClO_4 \cdot 2H_2O$ and $Cu(detp)_2 \cdot 2H_2O$. Mg^{2+} and Mn^{2+} perchlorates produced viscous oily precipitates, which are Cl-free and appear to involve both detp and ligands derived by elimination of more than one alkyl group per tetp molecule (C:P ratios between 1.55 and 0.776, which are the theoretical values for detp and $(C_2H_5O)PO_2S^{2-}$); these products were not studied any further. An additional experiment was interaction of tetp and $Cu(ClO_4)_2$ in the same manner as above (condition II), but in excess teof, *i.e.*, in 70 ml of a 1:1 (*v*/*v*) mixture of ethanol–teof; the complex obtained in low yield (3%) after 2 h of heating was anhydrous $Cu(detp)_2$.

Infrared spectra of the complexes (4000–400 cm^{-1}) were recorded on KBr pellets, in conjunction with a Nicolet 7199 FT-IR spectrophotometer. Table III gives relevant IR data for the detp complexes obtained under Condition II, as well as some previously reported detp complexes. Solid-state (Nujol mull) electronic spectra and magnetic susceptibility measurements (Table IV) of the paramagnetic detp complexes were obtained by methods described elsewhere [28]. Molar conductivities of the detp complexes that are sufficiently soluble in organic media were obtained on 10^{-3} M nitromethane solutions at 25 °C, by using a Wayne–Kerr Universal Conductivity Bridge and a cell calibrated with 10^{-3} M tetra-n-butylammonium perchlorate in nitromethane ($\Lambda_M = 92\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 25 °C). The

TABLE III. Relevant IR Spectral Data for detp (L) Metal Complexes (cm^{-1})[a]

Complex	ν_{P-O}	$\nu_{C-O-(P)}$	$\nu_{P-O-(C)}$	$\rho_{C_2H_5}$	ν_{P-S}	$\nu_{P-O-(C)}$	ρ_{CH_2}	ν_{P-S}	ClO_4 modes				ν_{OH}/δ_{HOH}
									ν_3	ν_1	ν_4	ν_2	
AlL_3	1210vs	1111vs	1030vs	951ms	817w,sh	788ms	712w	596ms					
CrL_3[b]	1157vs	1120m, 1110m	1040vs	950ms	815w,sh	790ms	715w	560s					
FeL_3[b]	1165vs	1125m, 1112m	1035vs	952ms	812w,sh	793ms	712w	553s					
$FeL_2 \cdot 2H_2O$[c]	1167s	1115ms	1033vs	955ms	822w,sh	785ms	713w	620s, 598vs					3360s,b, 1632m
$FeLClO_4 \cdot 2H_2O$	1168vs	d	1040vs	960ms	822w	792m	714w	601s	1110vs, 1080vs	920m, sh	641m, 620m,sh	480w,b	3430s,b, 1630m
$CoLClO_4 \cdot 4H_2O$	1264vs, 1220vs	1104vs	1010s	956s	820w,sh	788m	708w	600m, 559m	1120vs, 1078vs	930m, sh	638w, 621m	475w,b	3420s,b, 1640m
$NiLClO_4 \cdot 4H_2O$	1270vs, 1224vs	d	1020s	955s	818m,sh	797m	716mw	555s,b	1130vs, 1060vs	932ms	636m, 622ms	475w,b	3400vs,b 1642m
$NiLClO_4 \cdot 3H_2O$[c]	1167vs	d	1027s,sh	953s	815m,sh	792m	712mw	592vs	1137vs, 1043vs	923m	644s, 626s	471m,b	3380vs,b, 1625m
CuL_2	1211s, 1166vs	1133m, 1120m	1008ms, 977m	960m,sh	820w,b	777w,b	710vw	612m, 598m					
$CuL_2 \cdot 2H_2O$	1198vs, 1159vs	1120m, 1110m	1041m, 992s	959m	818w,sh	780w, 750w	704w	600m 581m					3460vs,b, 1628m
$Cu_2L(ClO_4)_3 \cdot 4H_2O$[c]	1163vs	d	d	960s	717m,sh	790ms	715mw	597s	1176vs, 1137vs, 1090vs,vb, 1041vs	935ms	655s, 634s, 621s, 604s,sh	458m	3350vs,b, 1630m
$ZnL_2 \cdot 4H_2O$	1265vvs	1115vs	1040vs	960m	818w,sh	780w,b	715vw	609m, 580m					3435s,b, 1630m
$CdL_2 \cdot 4H_2O$	1260vvs	1110vs	1038vs	955m	820w,sh	790mw	711w,b	610m, 579m					3440s,b, 1623m

[a] Band assignments based on refs. 2–4, 17, 20, 29, 31–35 and 38–41. An unassigned strong band at 675–660 cm^{-1} was observed in the spectra of CuL_2 and $CuL_2 \cdot 2H_2O$, but not in those of the remaining complexes. [b] These complexes have been also prepared by reaction of MCl_3 with tetp [4]. [c] Complexes prepared in earlier works [4, 20]. [d] Masked absorptions.

TABLE IV. Solid-state (Nujol mull) Electronic Spectra and Magnetic Properties at 294 K of the Paramagnetic detp (L) Metal Complexes

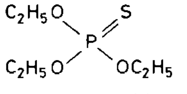
Complex	λ_{max} (nm)	$10^6\chi_A^{cor}$ (cgsu)	μ_{eff} (μB)
CrL_3 [a]	<300vs, 402vs, 422s,sh, 560s, 620s,sh	6420	3.90
FeL_3 [a]	302vs, 550s,sh	14802	5.92
$FeL_2 \cdot 2H_2O$ [b]	<300vvs, 343vs,sh, 485vs,sh, 620s,sh, 645s,sh, 840s,b, 1350s,b	12571	5.46
$FeLClO_4 \cdot 2H_2O$	<300vvs, 350vs,sh, 490vs,sh, 650ms,b, 845m,b 1125w,b, 1360w,b	11541	5.23
$CoLClO_4 \cdot 4H_2O$	<300vs, 462s, 517s,b, 1200w,b	9816	4.82
$NiLClO_4 \cdot 4H_2O$	<300vs, 424s, 612m, 700m, 1135w,b	4088	3.11
$NiLClO_4 \cdot 3H_2O$ [b]	<300vs, 385s,b, 410s,sh, 597m, 683m, 1150w,b	4255	3.18
CuL_2	<300vs, 370s,sh, 685m,sh,747ms,sh, 820s,b, 997mw,sh	974	1.52
$CuL_2 \cdot 2H_2O$	<300vs, 365vs,sh, 660ms,sh, 702s,vb, 898m,sh	1115	1.63
$Cu_2L(ClO_4)_3 \cdot 4H_2O$ [b]	<300vs, 588vs,b, 657vs,sh, 816m,sh, 995mw,sh	1427	1.84

[a] These complexes have been also prepared by reacting tetp with MCl_3 [4]. [b] Complexes prepared previously [4, 20].

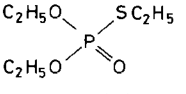
following Λ_M values were obtained, Ω^{-1} cm^2 mol^{-1}: $Fe(detp)ClO_4 \cdot 2H_2O$, 27; $Co(detp)ClO_4 \cdot 4H_2O$, 32; $Ni(detp)ClO_4 \cdot 4H_2O$, 26; $Ni(detp)ClO_4 \cdot 3H_2O$, 43 [20]; $Zn(detp)_2 \cdot 4H_2O$, 4; $Cd(detp)_2 \cdot 4H_2O$, 7. The remaining detp complexes, *i.e.*, $M(detp)_3$ (M = Al, Cr, Fe), $Fe(detp)_2 \cdot 2H_2O$, $Cu(detp)_2$, $Cu(detp)_2 \cdot 2H_2O$ and $Cu_2(detp)(ClO_4)_3 \cdot 4H_2O$ are either completely insoluble [4, 29] or very sparingly soluble [20] in organic media.

Discussion

Regarding the tetp adducts of Table I, they were previously characterized as involving S-bonded tetp in the thione form (teptn; I) for the borderline metal ions [30] (Co^{2+}, Zn^{2+}) and the soft Cd^{2+}, and O-bonded tetp in the thiol form (teptl; II) for the hard metal ions [30] (Al^{3+}, Cr^{3+}, Fe^{3+}) [28]. The adducts were formulated as $[M(teptl)_4(OClO_3)_2]ClO_4$ (M = Al, Fe), $[Cr(teptl)_2(OClO_3)_2(OH_2)_2]ClO_4$, $[M(teptn)_4(OClO_3)]ClO_4$ (M = Co, Zn) and $[Cd(teptn)_4](ClO_4)_2$ [28]. The data of Table I substantiate these formulations: Free tetp which is in the thione form and the S-bonded teptn complexes exhibit two $\nu_{P=S}$ [31, 32] bands and no $\nu_{P=O}$ absorption, whilst the O-bonded teptl adducts show the $\nu_{P=O}$ [33] but no $\nu_{P=S}$ bands. The Cd^{2+} complex exhibits single ν_3 and $\nu_4(ClO_4)$ bands due to exclusively ionic ClO_4^-, while the rest of the adducts show each of these bands split into three components and IR-active ν_1 and $\nu_2(ClO_4)$ modes, as is typical for compounds with both ionic ClO_4^- and unidentate coordinated $-OClO_3$ [34, 35]. The electronic spectrum [36] and magnetic moment [37] of the Co^{2+} adduct are compatible with coordination number five [28].



teptn (I)



teptl (II)

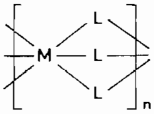
Quite interesting differences are observed in the IR spectra of the various detp complexes of Table III; band assignments in this Table were based on previous studies of diorganothiophosphates and their metal complexes [2–4, 17, 20, 29, 31–33, 38–40], as well as perchlorato [34, 35] and aqua [41] metal complexes. With five exceptions, these complexes exhibit ν_{P-O} bands at 1211 cm^{-1} or below and their lower frequency ν_{P-S} absorptions at 612 cm^{-1} or below. These features are consistent with the exclusive presence of bidentate O,S-bonded detp ligands [2–4, 17, 20, 29]. The exceptions are: $Fe(detp)_2 \cdot 2H_2O$, which shows two ν_{P-S} bands at 620 and 598 cm^{-1} (ν_{P-O} 1167 cm^{-1}) and was earlier characterized as involving both bidentate bridging O,S-bonded and unidentate terminal O-bonded detp [3, 4]; and $M(detp)ClO_4 \cdot 4H_2O$ (M = Co, Ni) and $M(detp)_2 \cdot 4H_2O$ (M = Zn, Cd), which exhibit the ν_{P-S} bands at 610–555 cm^{-1} (*i.e.*, indicative of S-bonded detp), and their ν_{P-O} absorptions at 1270–1220 cm^{-1}; the latter is definitely in favor of exclusively non-coordinated POS oxygen sites [17]. The apparent monomeric character of the latter four complexes, which obviously involve terminal unidentate S-bonded detp, is also suggested by their solubility in organic solvents. Regarding mixed detp-perchlorato metal complexes, those of the general $M(detp)ClO_4 \cdot xH_2O$ type (M = Fe, $x = 2$; M = Co, Ni, $x = 4$; M = Ni, $x = 3$) exhibit doubly split ν_3 and $\nu_4(ClO_4)$ and IR-active ν_1 and $\nu_2(ClO_4)$ bands, and apparently involve exclusively coordinated

$-OClO_3$ ligands [20, 34, 35]. Whereas $Cu_2(detp)(ClO_4)_3 \cdot 4H_2O$ shows also IR-active ν_1 and ν_2 and quadruply split ν_3 and ν_4 (ClO_4) absorptions; these features were interpreted in terms of the presence of both ionic ClO_4^- and bidentate $=O_2ClO_2$ ligands [20, 34, 35]. Finally, all the hydrated detp complexes show the characteristic ν_{OH} and δ_{H-O-H} bands of coordinated water at 3460–3350 and 1642–1625 cm^{-1}, respectively [41].

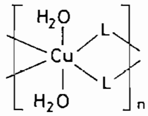
The d–d transition spectra of the new complexes reported (Table IV) favor coordination number six for $Co(detp)ClO_4 \cdot 4H_2O$ ($^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ 462; $\rightarrow 4A_{2g}(F)$ 517; $\rightarrow {}^4T_{2g}(F)$ 1200 nm), $Ni(detp)ClO_4 \cdot 4H_2O$ ($^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 424; $\rightarrow {}^3T_{1g}(F)$ 612, 700; $\rightarrow {}^3T_{2g}(F)$ 1135 nm; $Dq = 881$ cm^{-1}) and $Cu(detp)_2 \cdot 2H_2O$ (main maximum of the split $^2E_g \rightarrow {}^2T_{2g}$ transition at 702 nm) [36], five for $Fe(detp)ClO_4 \cdot 2H_2O$ (several maxima at 600–1360 nm) [4, 42] and four (distorted tetrahedral) for $Cu(detp)_2$ (main d–d maximum at 820 nm) [14, 15]. The corresponding spectra of the hexacoordinated $M(detp)_3$ (M = Cr, Fe) samples prepared during this work are identical to those observed for the samples of the same complexes prepared by reaction of the metal chlorides with tetp [4]. The spectra of $Ni(detp)ClO_4 \cdot 3H_2O$ ($Dq = 870$ cm^{-1}), $Cu_2(detp)(ClO_4)_3 \cdot 4H_2O$ and $Fe(detp)_2 \cdot 2H_2O$, which are, respectively, indicative of coordination numbers six, four (flattened tetrahedral, closer to square-planar than $Cu(detp)_2$) [14, 15] and five, were discussed elsewhere [4, 20].

With the exception of $Cu(detp)_2 \cdot 2H_2O$ and $Cu(detp)_2$, the complexes of Table IV exhibit normal ambient temperature (294 K) magnetic moments [43]. Although the di- or poly-meric nature of most of these complexes would conceivably result in subnormal paramagnetism even at room temperature, owing to magnetic exchange between adjacent metal ions in the detp-bridged structure [16, 44, 45], several polymeric complexes with bridging $-OP(R)_2O-$ ligands showing normal room temperature magnetic moments and evidence favoring magnetic exchange only at lower temperatures have been reported [12, 44, 46–48]. Moreover, our earlier studies have shown polymeric dialkyl phosphato metal complexes having subnormal ambient temperature magnetic moments in many occasions [49, 50], while most of the $M(detp)_n$ complexes we studied in the past exhibit normal μ_{eff} values at room temperature [2–4, 20]. The fact that $Cu(detp)_2 \cdot 2H_2O$ and $Cu(detp)_2$ exhibit subnormal magnetic moments even at 294 K (1.63 and 1.52 μ_B, respectively) is attributed to the trend of 3d metal ion polynuclear complexes to show increased spin–spin interactions along the series $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cr^{3+}, Fe^{3+} \ll Cu^{2+}$ [51–54].

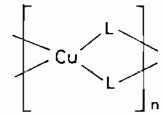
Among the various detp metal complexes studied, several appear to be monomers or dimers. With the exceptions of $Fe(detp)_2 \cdot 2H_2O$ [4] and $Cu_2(detp)(ClO_4)_3 \cdot 4H_2O$ [20], these complexes dissolve in organic solvents, including nitromethane. The fact that the detp-perchlorato complexes exhibit in this solvent behaviour intermediate between those of 'non'- and 1:1-electrolytes $\Lambda_M = 26–43$ Ω^{-1} cm^2 mol^{-1}) [55] may be due to partial substitution of $-OClO_3$ by nitromethane ligands in solution [20]; regarding the same complexes in the solid state, the IR evidence favoring the presence of $-OClO_3$ ligands is clearcut [34, 35]. The new mono- or di-meric complexes prepared during this work are, thus, formulated as follows, on the basis of the overall evidence (L: bidentate bridging O,S-bonded detp; L_s: unidentate terminal S-bonded detp): $[M(L_s)(OClO_3)(OH_2)_4]$ (M = Co, Ni); $[M(L_s)_2(OH_2)_4]$ (M = Zn, Cd); and $[(H_2O)_2(O_3ClO)FeL_2Fe(OClO_3)(OH_2)_2]$. Previously characterized analogous complexes (L_o: unidentate terminal O-bonded detp): $[(H_2O)_2(L_o)FeL_2Fe(L_o)(OH_2)_2]$ [4], $[(H_2O)_3(O_3ClO)NiL_2Ni(OClO_3)(OH_2)_3]$ and $[(H_2O)_2Cu(L)OCl(O)_2OCu(OH_2)_2](ClO_4)_2$ (the latter complex involves bidentate bridging perchlorate) [20]. The remaining detp complexes studied are presumably linear chainlike polymeric species with triple (M = Al^{3+}, Cr^{3+}, Fe^{3+}; structure **III**) or double (M = Cu^{2+}, structures **IV** and **V**) bridges of bidentate bridging detp between adjacent metal ions [4, 6–16].



III



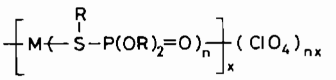
IV



V

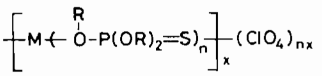
Under our experimental conditions, tetp adducts with the metal perchlorates are initially formed, regardless of whether they can or cannot be isolated at 35–40 °C (Condition I). Coordination of tetp occurs either through O (teptl form for M = Al^{3+}, Cr^{3+}, Fe^{3+}, Mg^{2+}) or through S (tcptn form for M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}) [25, 26, 28, 30, 56–58]. As the temperature is raised, a second bond is probably formed by coordination of the SC_2H_5 sulfur of teptl or one of the OC_2H_5 oxygens of teptn to the metal ion, as shown in **VI** and **VII**, respectively (R = C_2H_5) [2–5, 22, 24, 27, 29, 49, 50, 59–61]. Subsequently, the ethyl group attached to the coordinated S or O of intermediates **VI** or **VII** is eliminated in the form of $C_2H_5OClO_3$, leaving the metal ion coordinated to the anionic detp ligand [2–5, 22, 24, 27, 29, 49, 50, 59–61]. It is assumed that teptl will form intermediate **VI** and not a tautomer of type **VIII**, with an OC_2H_5 oxygen coordinating to the metal ion, since detp is in the $(C_2H_5O)_2POS^-$ and not the $(C_2H_5O)(C_2H_5S)POO^-$ tautomeric form, as demonstrated by the strong ν_{P-S} bands (Table IV) and the absence of weak

ν_{P-S-C} absorptions [31–33] in the spectra of the various detp complexes. Furthermore, thermal or hydrolytic cleavage of the C–X bond in a C–X–P grouping seems to be easier with X = S rather than O [24, 62–64]. Regarding the ethyl perchlorate formed as by-product of detp formation, it should be mentioned that the rather uncommon alkyl perchlorates have been prepared in the past by reacting $AgClO_4$ with alkyl halides [65, 66] or alcohols with anhydrous $HClO_4$ [67]. No attempts at isolating and identifying $C_2H_5OClO_3$ were made, in view of its reportedly extremely explosive nature [27, 66, 68].



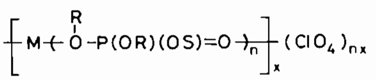
$$\left[M(\leftarrow \overset{\overset{R}{|}}{S}-P(OR)_2{=}O)_n\right]_x(ClO_4)_{nx}$$

VI



$$\left[M(\leftarrow \overset{\overset{R}{|}}{O}-P(OR)_2{=}S)_n\right]_x(ClO_4)_{nx}$$

VII



$$\left[M(\leftarrow \overset{\overset{R}{|}}{O}-P(OR)(OS){=}O\rightarrow)_n\right]_x(ClO_4)_{nx}$$

VIII

In conclusion, adducts of tetp in either of its tautomeric forms (**I** and **II**) with metal perchlorates are generally formed upon interaction of these two compounds at mild temperatures (35–40 ℃) in ethanol–teof. However, these adducts are labile, undergoing reactions leading to elimination of one ethyl group per tetp molecule and formation of the corresponding detp or detp-perchlorato metal complexes and ethyl perchlorate. These reactions start at 35–50 ℃, depending on the metal ion present in the system and are complete, as far as disappearance of tetp ligands is concerned, at 80–90 ℃. In some cases, $M(detp)_n \cdot xH_2O$ complexes are precipitated at 80–90 ℃, whilst in other cases mixed-ligand (detp–perchlorato) complexes are obtained instead. Temperature increase apparently favors elimination of more ClO_4 groups per metal ion, as suggested by the formation of $Cu_2(detp)(ClO_4)_3 \cdot 4H_2O$ at 50 ℃ and $Cu(detp)_2 \cdot xH_2O$ ($x = 0$ or 2) at 80–90 ℃. The 7:3 (ν/ν) mixture of ethanol–teof was not adequate in many cases for complete dehydration of the detp complexes by teof [69]. Actually, in several cases the detp complexes precipitated contained excess aqua ligands, which forced detp to function as terminal unidentate S-bonded rather than bridging bidentate O,S-bonded ($M = Co^{2+}$, Ni^{2+}, Zn^{2+}, Cd^{2+}). Operating at lower ethanol to teof ratios or teof alone can reduce or eliminate the aqua ligands in the complexes precipitated (*e.g.*, $Ni(detp)ClO_4$ with 3 *versus* 4 aqua ligands per Ni^{2+} ion, and $Cu(detp)_2$ *vs.* $Cu(detp)_2 \cdot 2H_2O$). Among the detp complexes studied, $Fe(detp)_2 \cdot 2H_2O$ is rather puzzling in that it seems to involve terminal unidentate O-bonded detp; the borderline nature of the Fe^{2+} ion in the hard-soft acid scale [30], combined with the obvious presence of S-bonded terminal detp in the new Co^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} complexes, would lead one to expect that the terminal detp ligand in the above ferrous complex would be also S-bonded, but this is not the case since ν_{P-O} appears at 1167 cm^{-1} in this compound. The occurrence of reactions leading to elimination of more than one ethyl groups per tetp molecule under Condition II was not firmly established, but seems likely for $M = Mg^{2+}$, Mn^{2+}. These reactions would require partial catalytic disproportionation of the $C_2H_5OClO_3$ produced during $M(detp)_x$ formation to ethylene and $HClO_4$ [70–72], followed by attack of the detp metal complex by perchloric acid [5, 24, 73, 74], and then condensation of the ethyl hydroxythiophosphate produced to ethyl pyrothiophosphate and H_2S [5, 24, 75]. A final point of interest is that tetp has been used successfully as modifier for the stereospecificity control of heterogeneous propylene catalyst systems, based on $TiCl_3$ and $(C_2H_5)_2AlCl$ [76]. The behavior of tetp and other neutral thiophosphate esters as modifiers was interpreted in terms of combination of adduct formation with the inorganic or organometallic metal chloride components of the catalyst system, and reactions of the neutral ester with the same components, leading to the production of dialkyl thiophosphato metal complexes and alkyl chloride, at the temperature (70 ℃) used in the polymerization process [76].

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