Inorganica Chimica Acta, 32 (1979) 263–272

Tri-*p*-tolyl Phosphate Complexes with Metal Chlorides and Perchlorates*

CHESTER M. MIKULSKI
Department of Chemistry & Physics, Beaver College, Glenside, Pa. 19038
LOUIS L. PYTLEWSKI
Department of Chemistry, Drexel University, Philadelphia, Pa. 19104
NICHOLAS M. KARAYANNIS
Amoco Chemicals Corporation, Naperville, Ill. 60540, U.S.A.
Received June 29, 1978

*Complexes of tri-*p*-tolylphosphate (TTP) with metal chlorides and perchlorates were prepared and characterized by means of spectral, magnetic and conductance studies. Only a few of these complexes seem to be monomeric,* i.e., *those with* $M(ClO_4)_3$ *(M = Cr, Fe, Nd), which were formulated as* $[M(TTP)_4(OClO_3)_2](ClO_4)$, *involving both ionic and coordinated perchlorate, and the pseudotetrahedral* $[Zn(TTP)_2Cl_2]$. *The rest of the new complexes appear to be binuclear, containing both terminal and bridging TTP ligands,* viz.: *Hexacoordinated:* $[Cl_3(TTP)M(TTP)_2M(TTP)Cl_3]$ *(M = Cr, Fe); pentacoordinated:* $[Cl_2(TTP)M(TTP)_2M(TTP)Cl_2]$ *(M = Mn, Fe, Co, Ni, Cu); and* $[(TTP)_3M(TTP)_2M(TTP)_3](ClO_4)_4$ *(M = Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd). Most of the new binuclear metal complexes do not seem to undergo any significant structural changes in nitromethane solution; however, solutions of the* $CoCl_2$ *complex in this medium contain the monomeric pseudotetrahedral* $[Co(TTP)_2Cl_2]$ *species. The lower frequency infrared and the electronic spectral evidence suggest that TTP is a ligand almost as strong as triorganophosphine oxides and significantly stronger than trimethylphosphate. The increased donor strength of TTP, relative to that of trialkylphosphates, is probably due to a combination of inductive and steric effects. The new paramagnetic metal ion complexes are generally characterized by normal ambient temperature magnetic moments; the* d^3–d^8 *complexes are of the high-spin type.*

Introduction

Tri-alkyl or -aryl phosphine oxides easily form solid adducts with a wide variety of metal salts, coordinating through the P=O oxygen [2, 3]. In the case of neutral phosphoryl alkylesters, analogous adducts readily form in solution [4–6] or during gas-solid interactions [7, 8], but their isolation in the solid state is generally difficult, and not always possible. Thus, metal perchlorate complexes with dialkyl alkylphosphonates or trialkylphosphates are quite often precipitated in the form of viscous oils, the solidification of which (to more or less deliquescent solids) requires rather tedious procedures [5, 6, 9]. Whereas with the corresponding metal halide adducts, an additional difficulty to their isolation is their tendency to undergo C–O bond cleavage reactions(I) (especially at elevated temperatures), resulting in the elimination of one or more alkyl halide molecules per neutral ester molecule and the precipitation of polynuclear metal complexes with such anionic ligands as $R_2PO_2^-$, RPO_3^{2-}, $R_2P_2O_5^{2-}$ and PO_4^{3-} (R = alkyl or alkoxy group) [2, 10–14]. As a consequence of this, relatively few solvates of metal halides (*e.g.*, LiI [14], $TiCl_4$ [15, 16], $ZrCl_4$ [17], VCl_3 [16], $CoCl_2$ [12], SnX_2 (X = Cl, Br) and SnX_4 (X = Cl, Br, I) [15]) with neutral phosphoryl alkylesters have been obtained in adequately pure form for characterization.

Neutral phosphoryl arylesters do not seem to be too reactive toward metal halides. Thus, unlike the corresponding trialkylphosphate adducts, which are thermally unstable at room temperature [10], BX_3 (X = F, Cl, Br) adducts with triarylphosphates were found to be quite stable at 100 °C and show only small weight losses at 200–300 °C [18]; also, while, during reaction of $SiCl_4$ with trialkylphosphates, $Si_3(PO_4)_4$ is eventually formed [10], triphenylphosphate was reportedly recovered intact, after refluxing a mixture of it with $SiCl_4$ at 160 °C for 20 hr [19]. Furthermore, reactions of methyldiphenylphosphate with various metal chlorides at elevated temperatures, resulted invariably in the elimination of methyl chloride and the precipitation of diphenylphosphato metal complexes [13]. This difference in behavior of the phosphoryl arylesters (relative to the corresponding alkylesters) is due to the much greater tendency of their aryl groups to be eliminated by

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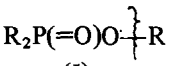
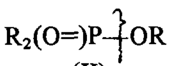
*See ref. 1.

P–O (II) rather than C–O (I) bond cleavage [20–22]; whereas alkoxyphosphoryl compounds are generally dealkylated by C–O bond fission [20], which obviously favors the formation of alkyl halide, when the reaction takes place in the presence of metal halides.



$R_2P(=O)O{\wr}R$

(I)



$R_2(O{=})P{\wr}OR$

(II)

It was of interest to us to prepare and characterize a series of transition metal chloride adducts with a neutral phosphate arylester, in view of the relative dearth of information in this field. Accordingly, synthetic and characterization work of 3d metal chloride complexes with tri-*p*-tolylphosphate (TTP; (p-$CH_3C_6H_4O)_3P{=}O$) was undertaken. Our studies revealed that these complexes are generally stable in the atmosphere. This encouraged us to extend our work to TTP complexes with 3d and a few additional (Mg^{2+}, Cd^{2+}, Nd^{3+}) metal perchlorates, which also proved to be atmospherically stable, unlike most of their neutral phosphoryl alkylester analogs. The present paper deals with TTP complexes with metal chlorides and perchlorates

Experimental

Chemicals

TTP (Eastman; m.p. 76–78 °C) was utilized as received. The metal salts and organic solvents employed in the synthetic work were reagent grade, while spectroquality grade nitromethane was generally used.

Synthetic Methods

Early synthetic attempts established that TTP forms 2:1 complexes with metal chlorides (M = Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and 4:1 complexes with metal perchlorates (M = Mg^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Nd^{3+}). Whenever ligand to metal ratios exceeding 2:1 for the metal chlorides or 4:1 for the metal perchlorates were employed, the complexes precipitated contained substantial amounts of uncoordinated TTP (as suggested by analyses and the presence of an infrared band at 1310 cm^{-1} (*vide infra*)), which was practically impossible to remove. It is, therefore, important, when precipitating the TTP complexes from a solution, to use ligand and salt at precisely 2:1 or 4:1 molar ratio. The preparation of most of the new metal complexes was effected as follows: A solution of 2 mmol TTP in 50 ml methanol is combined with a solution of 1 mmol anhydrous or hydrated metal chloride or 0.5 mmol hydrated metal perchlorate in 50 ml methanol or methanol–acetone (4:1 v/v). The resultant solution is stirred at 50 °C, until the volume is reduced to 15–20 ml, 50 ml triethyl orthoformate (a dehydrating agent [23]) are then added, and heating at 50 °C is continued until near dryness. The solid residues are subsequently separated by filtration and stored in an evacuated desiccator over $CaCl_2$. Washing of these solid products, while still wet, with anhydrous diethyl ether was found to lead to their partial decomposition, whilst washing with ligroin or hexane may cause their collapse into oils. Thus, washing was generally avoided, and the removal of any residual solvent was effected by allowing the solid complex to remain on the filter (Büchner funnel) under suction. The absence of any significant solvent impurities was later ascertained from the absence of any infrared bands attributable to the presence of alcohols, water or ketones in the spectra of the new complexes. The preceding preparative method afforded solid metal complexes in all but one of the cases investigated: The residue obtained during the interaction of TTP with $CrCl_3$, under the above conditions, was a viscous liquid. A solid $CrCl_3$ complex was prepared by a much more tedious and lengthy alternative synthetic method, which can be successfully employed for the preparation of all of the new metal chloride complexes. This method, which involves interaction of the metal salt with excess molten ligand, has been previously used by Tayim *et al.* for the preparation of triphenylphosphine oxide (TPPO) complexes with various metal chlorides [24]. During this previous work, the metal salt–TPPO melt was allowed to solidify by cooling to ambient temperature, then it was ground in a mortar and the uncoordinated ligand was washed away with a suitable solvent [24]. This type of post-interaction treatment is, nevertheless, not applicable in the case of TTP, since its metal complexes are sensitive to washing, as already mentioned. Thus, under our synthetic conditions, about 5 g TTP are allowed to melt in a beaker, by heating at *ca.* 80 °C, and 0.5 g metal chloride are added to the melt. The metal salt slowly dissolves in the molten ligand, and the temperature of the continuously stirred solution is subsequently raised at a rate of 2 °C/min. Precipitation of the complex is observed in the 150–200 °C region; the mixture is allowed to cool to *ca.* 100 °C, and the solid complex is then separated by filtration through a heated funnel. The complex is subsequently pressed between two sheets of filter paper and allowed to remain overnight between the filter paper sheets in an oven at 90 °C. The latter procedure is repeated several times, by replacing the filter paper every day, until the solid does not exhibit an infrared maximum at 1310 cm^{-1}, due to uncoordinated TTP. Finally, the complex is stored in an evacuated desiccator over $CaCl_2$. It should be noted at this point that, even when the temperature of the molten TTP–metal chloride mixture was allowed to exceed 300 °C, no decomposition of the ligand present in the

TABLE I. Tri-*p*-tolylphosphate Complexes with Metal Chlorides and Perchlorates.

Complex[a]	Color	Analysis							
		C%		H%		P%		Metal %	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$CrCl_3 \cdot 2TTP$	Green	56.47	56.91	4.73	4.97	6.92	7.23	5.81	6.02
$MnCl_2 \cdot 2TTP$	White	58.48	58.02	4.91	4.93	7.18	7.11	6.37	7.05
$FeCl_2 \cdot 2TTP$	Brown[b]	58.42	58.20	4.90	4.47	7.17	6.91	6.46	6.62
$FeCl_3 \cdot 2TTP$	Brown[b]	56.11	55.85	4.71	5.12	6.89	7.04	6.21	6.40
$CoCl_2 \cdot 2TTP$	Blue-purple	58.21	58.00	4.88	4.94	7.15	7.27	6.80	6.81
$NiCl_2 \cdot 2TTP$	Yellow	58.22	57.60	4.88	5.25	7.15	7.13	6.77	7.28
$CuCl_2 \cdot 2TTP$	Light green	57.90	58.13	4.85	4.66	7.11	6.88	7.29	7.48
$ZnCl_2 \cdot 2TTP$	White	57.78	57.24	4.85	5.26	7.09	6.91	7.47	7.85
$Mg(ClO_4)_2 \cdot 4TTP$	White	59.46	59.97	4.99	5.33	7.30	7.41	1.43	1.70
$Cr(ClO_4)_3 \cdot 4TTP$	Light grey blue	55.32	54.79	4.64	4.50	6.74	6.78	2.85	2.62
$Mn(ClO_4)_2 \cdot 4TTP$	White	58.41	58.24	4.90	5.17	7.17	6.84	3.18	3.27
$Fe(ClO_4)_2 \cdot 4TTP$	Brownish yellow	58.37	58.12	4.90	4.68	7.17	7.39	3.23	3.48
$Fe(ClO_4)_3 \cdot 4TTP$	Brown	55.20	56.12	4.63	5.13	6.72	6.31	3.05	2.73
$Co(ClO_4)_2 \cdot 4TTP$	Brownish-orange	58.27	58.44	4.89	5.10	7.16	7.26	3.40	3.61
$Ni(ClO_4)_2 \cdot 4TTP$	Light green	58.28	57.51	4.89	5.27	7.16	6.81	3.39	3.31
$Cu(ClO_4)_2 \cdot 4TTP$	Very pale green	58.12	57.75	4.87	5.02	7.14	7.18	3.66	4.03
$Zn(ClO_4)_2 \cdot 4TTP$	White	58.00	57.62	4.87	4.70	7.13	7.21	3.76	3.44
$Cd(ClO_4)_2 \cdot 4TTP$	White	56.53	56.81	4.74	4.47	6.94	7.33	6.29	6.42
$Nd(ClO_4)_3 \cdot 4TTP$	Light pink	52.93	53.34	4.42	4.71	6.50	6.22	7.56	7.77

[a] The metal perchlorate complexes exhibit sharp melting points at 70–85 °C, while the metal chloride complexes do not melt at temperatures up to 250 °C. [b] Soft solid.

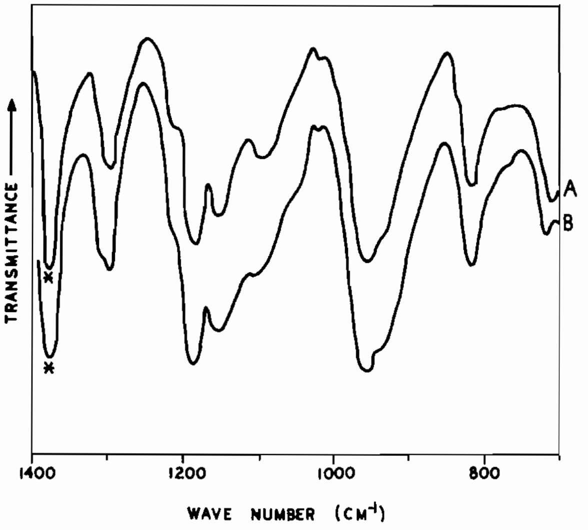


Figure 1. Infrared spectra (1400–700 cm^{-1}) of: A, $Co(ClO_4)_2 \cdot 4TTP$; B, $Cr(ClO_4)_3 \cdot 4TTP$.

solid product was observed; in fact, analytical results indicate that the C:P weight ratio in the solid obtained under these conditions is generally close to the theoretical weight ratio (8.14) for TTP.

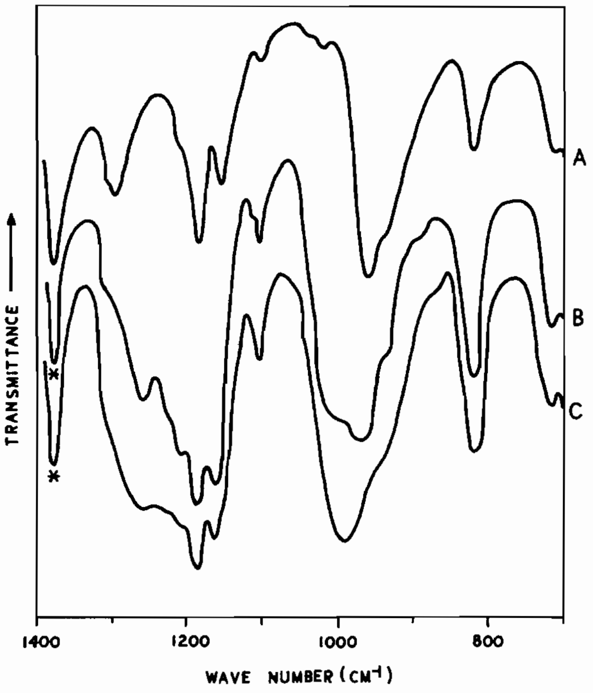


Figure 2. Infrared spectra (1400–700 cm^{-1}) of: A, $MnCl_2 \cdot 2TTP$; B, $FeCl_2 \cdot 2TTP$; C, $ZnCl_2 \cdot 2TTP$.

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

Compound	$\nu_{P=O}$ region	ClO_4 modes	ν_{M-O}(TTP)	ν_{M-X}(X = Cl or $-CClO_3$)	ν_{Ligand} (500–250 cm^{-1})
TTP	1310m, 1300m				498s, 469m,sh, 450m,b,sh, 423w, 410w,sh, 358vw, 340w, 331w, 320w, 309w, 294w, 286w, 271vw
$CrCl_3 \cdot 2TTP$	1294m, 1278sh		441m,sh, 428m, 386w,sh	346w,sh, 334w, 308w,sh	499s, 468m,sh, 450m,sh, 420mw,sh, 405w, 360vw, 340w, 330w, 322w, 310w, 296w, 287w, 272vw
$MnCl_2 \cdot 2TTP$	1300sh, 1296m		390w,b, 334w,b	277w,sh	496svs, 464ms,sh, 423mw, 410w,sh, 361vw, 340w,sh, 320w, 309w, 296w, 287w, 271vw
$FeCl_2 \cdot 2TTP$	1297m,sh, 1261m,b		389m, 337w	268w,sh	500s, 470ms,sh, 448m,sh, 422m,b, 360w,b, 342w, 330w,sh, 320w,b, 309w, 294w,sh, 288w, 272w
$FeCl_3 \cdot 2TTP$	1300sh, 1290sh, 1260m,b		433m, 419m, 380m,w	355w,b, 327w	499s, 466m,sh, 450mw,sh, 424m, 407m,sh, 361vw, 340w, 332w, 320wvw, 310w, 297w, 288w, 273vw
$CoCl_2 \cdot 2TTP$	1300sh, 1293s, 1286sh		406w,b, 333m,b	283w,sh, 261w	500svs, 465m,sh, 450m,sh, 426w, 410w,sh, 360w, 321m, 309m, 298w, 286w,b, 270w,sh
$NiCl_2 \cdot 2TTP$	1300sh, 1298m, 1281sh		413m,b, 344m	273w, 254m,b	500svs, 467s,sh, 451ms,sh, 426m, 410m,sh, 360vw, 334m,sh, 321mw, 309w, 298wvw, 286wvw,b
$CuCl_2 \cdot 2TTP$	1300sh, 1297m, 1286sh		408m,b, 381w, 334w,b	303m,b, 284m,b,	501svs, 467s,sh, 424m, 362vw, 341mw, 330mw, 320mw, 309m, 298m, 272w
$ZnCl_2 \cdot 2TTP$	1301sh, 1265m,vb		434m,b	315w,b	499s, 468m,sh, 450m,sh, 419mw,sh, 407w, 359w, 341w, 333w, 321w, 308w, 298w, 288w, 273vw
$Mg(ClO_4)_2 \cdot 4TTP$	1300sh, 1279m	1090s,b, 623m	401m, 380mw, 344w,sh	–	499s, 466m,sh, 450m, 424m, 411m, 360w, 341w, 331w, 320w, 309w, 297w, 286w,b, 271vw
$Cr(ClO_4)_3 \cdot 4TTP$	1304sh, 1294m, 1271sh	1099s,sh, 1040sh, 623m	436m,b	333w	500s, 467ms,sh, 453m,sh, 412mw,sh, 360vw, 342w, 331w,sh, 321w, 309w, 298w, 288w,b, 273vw
$Mn(ClO_4)_2 \cdot 4TTP$	1296m,b, 1276sh	1100m,b, 618m	404m, 339w,b,	–	498svs, 467s,sh, 448m,sh, 423m, 358vw, 320w, 308w, 299vw, 286vw,b, 272vw
$Fe(ClO_4)_2 \cdot 4TTP$	1300sh, 1297m, 1280sh	1101ms, 626m	410m,vb, 391mw, 337w,sh	–	499svs, 466s,sh, 453m,sh, 424m, 362vw,b, 340w, 331w, 322w, 309m, 298w, 289w, 270vw
$Fe(ClO_4)_3 \cdot 4TTP$	1299sh, 1296m, 1276sh	1107m,b, 1046sh, 621m	439m,b	328w	498s, 470s,sh, 453m,sh, 422m,sh, 410m,sh, 362vw, 342w, 332w,sh, 320w, 311w, 297w, 286w, 271vw
$Co(ClO_4)_2 \cdot 4TTP$	1298sh, 1294m, 1280sh, 1262sh	1097m,b, 625m	413m,sh, 386m,b, 338m	–	500svs, 468s,sh, 449m,sh, 423m, 408m,sh, 361vw, 340m,sh, 331m,sh, 321m, 310m, 298m, 286m, 273w
$Ni(ClO_4)_2 \cdot 4TTP$	1302sh, 1299m, 1290sh, 1270sh	1101m, 622m	415m,sh, 390m,b, 345w	–	499s, 466s,sh, 452ms,sh, 422m, 408m,sh, 358vw, 339w,sh, 331w, 320w, 310w, 297wvw, 286w, 272vw
$Cu(ClO_4)_2 \cdot 4TTP$	1302sh, 1299m, 1289sh, 1281sh	1100m, 623m	417m,b, 401m, 329w	–	496s,b, 467s,sh, 452m,sh, 425m, 410m,sh, 340w, 332w, 320w,sh, 308w, 299w,sh, 286w, 272vw
$Zn(ClO_4)_2 \cdot 4TTP$	1270m,vvb	1096m,vb, 630m	399m,sh, 347w,b	–	497s, 470s,sh, 452ms,sh, 423m, 411m, 360vw,b, 341w, 332w, 320w, 308w, 296vw, 287vw, 272vvw
$Cd(ClO_4)_2 \cdot 4TTP$	1300sh, 1295m, 1270sh	1100m,b, 620m	325w,vb, 268vw,sh	– –	499s, 469s,sh, 450m,b, 423mw, 410mw,sh, 361vw,sh, 340w,sh, 299vw, 289vw, 270vvw
$Nd(ClO_4)_3 \cdot 4TTP$	1301sh, 1296m, 1286sh, 1269sh	1104m,b, 1024w, 619m	362w,vb	327w	499s, 470ms,sh, 447m,sh, 422mw, 410w,sh, 341w, 330w,sh, 321vw, 309w, 296w, 290vw,b, 271vvw

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder.

TABLE III. Electronic Spectra of TTP Transition Metal Complexes.[a]

Complex	Medium	λ_{max}, nm(ϵ_{max})
$CrCl_3 \cdot 2TTP$	Nujol	440s,sh, 482s,sh, 620s, 661s,sh, 693sh
	5.6×10^{-3} M in $CH_3NO_2 + CH_3OH$	463(47), 619sh(24), 650(29), 661(29), 689sh(25)
$Cr(ClO_4)_3 \cdot 4TTP$	Nujol	393s, 404s, 450s,sh, 565s,sh, 633m,sh, 671m,sh
	3.3×10^{-3} M in CH_3NO_2	393(44), 404(44), 569(29), 608sh(26)
$MnCl_2 \cdot 2TTP$	Nujol	308m-s, 379m,sh, 411w-m, 450w,sh, 488w
$Mn(ClO_4)_2 \cdot 4TTP$	Nujol	321m-s, 381m,sh, 400m-w,sh, 440w,sh, 482w
$FeCl_2 \cdot 2TTP$	Nujol	<300vs, 820s,sh, 950s,sh
	2.9×10^{-3} M in CH_3NO_2	<400vvs, 882(15), 921sh(12), 990b(11)
$Fe(ClO_4)_2 \cdot 4TTP$	Nujol	<300vs, 480s,sh, 902m,b,sh, 1350w-m,vb,sh
	2×10^{-3} M in CH_3NO_2	<400vvs, 900b(31), 1375(23)
$FeCl_3 \cdot 2TTP$	Nujol	327vs
$Fe(ClO_4)_3 \cdot 4TTP$	Nujol	324vs,sh
$CoCl_2 \cdot 2TTP$	Nujol	498s, 530s,sh, 582s,sh, 772m,sh, 883m,sh, 1330w,b,sh
	1.7×10^{-3} M in CH_3NO_2	585sh(312), 611(380), 639sh(341), 662sh(289), 1450vb(58), 1704(60)
$Co(ClO_4)_2 \cdot 4TTP$	Nujol	504s, 536s,sh, 795m,b,sh, 1100w,b
	1.7×10^{-3} M in $CH_3NO_2 + CH_3OH$	495(154), 560sh(106), 749(63), 1030b(46)
$NiCl_2 \cdot 2TTP$	Nujol	393s, 486s,sh, 638m, 700m,sh, 830m,b, 1120m,b
	6.3×10^{-3} M in $CH_3NO_2 + CH_3OH$	409(31), 477sh(17), 560(16), 655sh, 673(12), 732(9), 1085sh(8)
$Ni(ClO_4)_2 \cdot 4TTP$	Nujol	406s, 493s,sh, 620m,b, 815w,sh, 1070w, 1410w,b
	2.9×10^{-3} M in CH_3NO_2	400sh(65), 500sh(35), 545(31), 631sh(24), 1163(13), 1400b(9)
$CuCl_2 \cdot 2TTP$	Nujol	<300vs, 740s,sh, 815s,sh, 1002m,sh
	5.7×10^{-3} M in $CH_3NO_2 + CH_3OH$	848b(46), 1011sh(36)
$Cu(ClO_4)_2 \cdot 4TTP$	Nujol	<300vs, 470s,sh, 623s,sh, 750s,sh, 830s,sh, 935m,sh
	2.6×10^{-3} M in CH_3NO_2	652sh(70), 739(77), 817sh(72), 920sh(58)
$Nd(ClO_4)_3 \cdot 4TTP$	Nujol	<300vs, 520m,b, 570m,b, 620w,b

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder.

TABLE IV. Magnetic Moments (300 K) and Molar Conductivities (10^{-3} M Nitromethane Solutions at 25 °C) of Tri-*p*-tolylphosphate Metal Complexes.

Complex	$10^6 \chi_M^{Cor}$, cgsu	μ_{eff}, BM	Λ_M, Ω^{-1} cm^2 mol^{-1} [a]
$CrCl_3 \cdot 2TTP$	6,239	3.88	18
$MnCl_2 \cdot 2TTP$	14,531	5.93	24
$FeCl_2 \cdot 2TTP$	12,370	5.47	33
$FeCl_3 \cdot 2TTP$	15,667	6.15	30
$CoCl_2 \cdot 2TTP$	10,007	4.92	26
$NiCl_2 \cdot 2TTP$	4,330	3.24	25
$CuCl_2 \cdot 2TTP$	1,998	2.19	32
$Cr(ClO_4)_3 \cdot 4TTP$	6,193	3.87	124
$Mn(ClO_4)_2 \cdot 4TTP$	14,320	5.89	151
$Fe(ClO_4)_2 \cdot 4TTP$	12,201	5.43	154
$Fe(ClO_4)_3 \cdot 4TTP$	15,480	6.11	115
$Co(ClO_4)_2 \cdot 4TTP$	9,901	4.90	147
$Ni(ClO_4)_2 \cdot 4TTP$	4,265	3.21	141
$Cu(ClO_4)_2 \cdot 4TTP$	1,880	2.13	164
$Nd(ClO_4)_3 \cdot 4TTP$	5,393	3.60	128

[a] Note: Λ_M values for the diamagnetic new complexes, Ω^{-1} cm^2 mol^{-1}: $ZnCl_2 \cdot 2TTP$ 21; $Mg(ClO_4)_2 \cdot 4TTP$ 160; $Zn(ClO_4)_2 \cdot 4TTP$ 157; $Cd(ClO_4)_2 \cdot 4TTP$ 158.

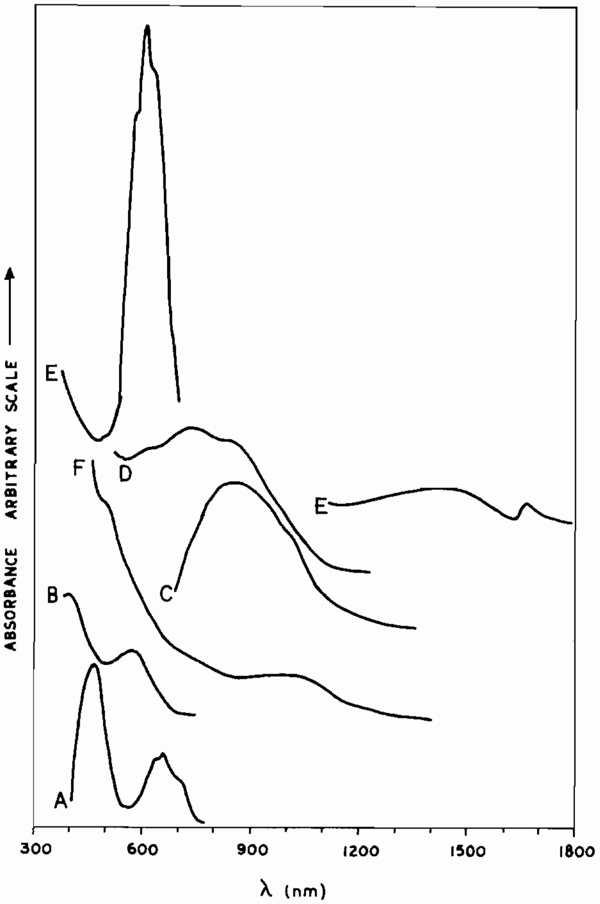


Figure 3. Electronic spectra of some TTP metal complexes in nitromethane solution: A, $CrCl_3 \cdot 2TTP$; B, $Cr(ClO_4)_3 \cdot 4TTP$; C, $CuCl_2 \cdot 2TTP$; D, $Cu(ClO_4)_2 \cdot 4TTP$; E, $CoCl_2 \cdot 2TTP$; F, $Co(ClO_4)_2 \cdot 4TTP$.

Analytical data (A. Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, W. Germany) for the new metal complexes are given in Table I. These complexes are generally stable in the atmosphere and soluble in various organic solvents (*e.g.*, nitromethane, alcohols, acetone). The metal chloride complexes are high-melting, while the metal perchlorate analogs show quite sharp melting points (Table I).

Spectral, Magnetic and Conductance Studies

Infrared spectra (Table II, Figures 1 and 2) of the new metal complexes were obtained on Nujol mulls between IRTRAN 2 (zinc sulfide) (4000–700 cm^{-1}) and high-density polyethylene (800–200 cm^{-1}) windows, in conjunction with a Perkin-Elmer 621 spectrophotometer. Solid-state (Nujol mull) and nitromethane solution electronic spectra (Table III, Figure 3), magnetic susceptibility and molar conductance measurements (Table IV) were obtained by methods described elsewhere [5, 25].

Discussion

Infrared and Conductance Data

In the ir spectra of the only previously reported complexes of TTP with boron trihalides, the $\nu_{P=O}$ mode appeared as a very broad absorption, exhibiting shifts of 90–145 cm^{-1} to lower wavenumbers, relative to the $\nu_{P=O}$ position in uncomplexed TTP [18]. The $\nu_{P=O}$ region [26] of free TTP is characterized by two maxima at 1310 and 1300 cm^{-1}. One of these bands is due to the $\nu_{P=O}$ mode [26], whilst the other is associated with vibrational modes of the tolyl group (toluene, for instance, exhibits absorptions at 1312 and 1305 cm^{-1}, assigned, respectively, as the $B_1(\nu_3)$ and $A_1(\nu_1 + \nu_6)$ modes) [27]. The spectra of the new metal complexes show almost invariably one or more bands at 1302–1293 cm^{-1}, which are most probably due to the above modes of the tolyl group, and a second set of one or more bands at 1290–1260 cm^{-1}, which may be attributed to negative frequency shifts and splittings of $\nu_{P=O}$ upon complex formation [28] (Table II). If we tentatively assign $\nu_{P=O}$ in free TTP at 1310 cm^{-1} (*i.e.*, the absorption which is absent in the spectra of the metal complexes), the magnitude of the negative frequency shifts in the spectra of the new metal complexes would range between 20–50 cm^{-1}. It should be mentioned at this point that the $\nu_{P=O}$ shifts in organophosphoryl ligand complexes with the metal ions under study are generally much smaller than those observed in boron halide adducts with these ligands [2, 3, 18]. The $\Delta\nu_{P=O}$ values in the spectra of the new complexes are in the same range observed for analogous complexes with trialkylphosphates (*e.g.*, Mg^{2+}, 3d metal ion and Ce^{3+} perchlorate complexes with trimethylphosphate show $\Delta\nu_{P=O}$ values ranging between 23–76 cm^{-1}) [6] or p-tolyl-substituted phosphoryl ligands (the 2:1 tri-*p*-tolylphosphine oxide (TTPO) complex with $NiCl_2$ shows a $\Delta\nu_{P=O}$ of 41 cm^{-1}) [29].

Among the fundamental vibrational modes of the perchlorate group, the ν_3 and ν_4 modes of ionic ClO_4^- were easily recognized in the ir spectra of the new metal complexes [30] (Table II). However, strong ligand absorptions at 1200–1160, 920, 650, 560 and 495 cm^{-1} prevented the identification of any splittings in the ν_3 or $\nu_4(ClO_4)$ modes or ir-active ν_1 or $\nu_2(ClO_4)$ absorptions, attributable to the simultaneous presence of coordinated perchlorato ligands [30, 31]. Only in the case of the M(III) perchlorate complexes (M = Cr, Fe, Nd) was a band, that might be assigned to a ν_3 splitting, observed at 1046–1024 cm^{-1} (Table II, Fig. 1) [30, 31]. Figure 2, showing the ir spectra of some of the new metal chloride complexes at 1400–700 cm^{-1}, is also illustrative of the difficulties encountered during attempts at identifying absorptions of the ClO_4 group in the spectra of the corresponding metal perchlorate complexes.

Tentative ν_{M-O} (TTP and perchlorato) band assignments in the low frequency ir spectra of the $M(ClO_4)_3$ (M = Cr, Fe, Nd) complexes (Table II) are consistent with hexacoordinated configurations for the central metal ions [25, 32–35]. It should be mentioned at this point that there is significant overlap between metal-sensitive and ligand [36] absorptions at 500–250 cm^{-1} in the spectra of all of the new complexes; however, the identification of metal–ligand bands is facilitated by a considerable intensification of the overall absorption in the regions of their occurrence, relative to the absorption in the spectra of complexes not exhibiting metal–ligand bands in the same regions. The metal(II) perchlorate complexes show one or two ν_{M-O}(TTP) bands at 417–380 cm^{-1} (or 325 cm^{-1} for Cd^{2+}), which are suggestive of coordination numbers lower than six (most probably five) [25, 32, 33]. Additional metal-sensitive bands at 347–329 cm^{-1}, also observed in these spectra, might be attributed to either ν_{M-O}(TTP) for bridging TTP ligands [25, 32, 33, 37] or ν_{M-O}(perchlorato) [33, 34, 38] modes. Since most of the corresponding metal(II) chloride complexes (M = Mn, Fe, Co, Ni, Cu) show very similar to the preceding metal-ligand absorptions (*i.e.*, one or two bands at 413–381 and one band at 344–333 cm^{-1}), the assignment of the bands at 350–325 cm^{-1} as ν_{M-O}(bridging TTP) in both the MCl_2 and the $M(ClO_4)_2$ complexes is considered as reasonable. In fact, the occurrence of ν_{M-O}(terminal TTP) at 413–381 cm^{-1} in the spectra of the preceding MCl_2 complexes favors coordination number five [25, 32, 33], thus ruling out the possibility that the absorptions at 344–333 cm^{-1} are due to ν_{M-Cl} modes, which were identified in the 303–254 cm^{-1} region [39, 40]. Similar ν_{M-O}(TTP) splittings as above occur also in the spectra of the two MCl_3 (M = Cr, Fe) complexes, which presumably are of the same type, involving both terminal and bridging TTP. In these cases the ν_{M-O} [25, 32, 33] and ν_{M-Cl} [41] band assignments favor coordination number six for the central metal ions. Finally, the ν_{Zn-O} and ν_{Zn-Cl} modes in the new $ZnCl_2$ complex appear at wavenumbers suggestive of a tetrahedral configuration for this compound [32, 33, 37, 41–43].

The molar conductance data (Table IV) for the new metal(II) perchlorate complexes indicate that these compounds behave as 1:2 electrolytes in nitromethane [44], and are in agreement with the ir evidence, which favors the exclusive presence of ionic ClO_4 in these complexes. Whereas in the case of the metal(III) perchlorate complexes, the presence of both coordinated and ionic perchlorate, suggested by the ir data, is also supported by the fact that the Λ_M values are intermediate between those corresponding to 1:1 and 1:2 electrolytes [44]. It is most likely that in the solid-state these complexes are of the type $[M(TTP)_4(OClO_3)_2](ClO_4)$ (M = Cr, Fe, Nd; with two coordinated and one ionic ClO_4), which seems to be quite common in tripositive 3d or 4f metal perchlorate complexes with phosphoryl ligands [2, 3, 32, 35, 45], and that, during their dissolution in nitromethane, exchange between perchlorato and CH_3NO_2 ligands occurs to some extent. Small exchange between chloride and nitromethane ligands seems to also occur in solutions of the presumably neutral new metal chloride complexes, which generally show Λ_M values closer to those corresponding to "non"-rather than 1:1 electrolytes [44].

Electronic Spectra and Magnetic Properties

The Nujol mull or solution electronic spectra of both of the new Cr^{3+} complexes (Table III, Figure 3) are consistent with low symmetry hexacoordinated configurations, suggested by the splittings of the $^4A_{1g}(F) \rightarrow {}^4T_{1g}(F)$ (400–482 nm) and $\rightarrow {}^4T_{2g}(F)$ (565–693 nm) transitions. The solid-state electronic spectra of the Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) chloride or perchlorate complexes can be interpreted in terms of coordination number five for these compounds, in view of their similarities to the spectra of previously reported pentacoordinated complexes of these metal ions with various R_nXO (X = P, As, N, *etc.*) ligands [5, 25, 46–53]. Specifically: the Mn(II) complexes exhibit a characteristic medium to strong band at 308–321 nm, as was also the case with the triphenylphosphine oxide [47] and diisopropyl methylphosphonate [5, 25] complexes with $Mn(ClO_4)_2$, which involve coordination number five. The new Co(II) compounds exhibit medium d–d bands at 749–883 nm, which appear to be common in pentacoordinated cobaltous complexes [5, 25, 46, 48]. Whereas the spectra of the Ni(II) new complexes are characterized by six d–d maxima at 390–1450 nm; similar spectra were reported for several square pyramidal Ni(II) complexes, [5, 25, 48–50], including $[Ni(TMAsO)_5](ClO_4)_2$ (TMAsO = trimethylarsine oxide), which was recently fully characterized by crystal structure determination [51]. The two Cu(II) complexes show the main d–d maximum at 740–750 nm, with one or two shoulders at lower energies; these spectra are also compatible with coordination number five for the central Cu^{2+} ions [5, 25, 48, 52, 53]. Finally, the appearance of two d–d bands in the spectra of the Fe(II) complexes may be attributed to either a penta- [53] or a hexa-coordinated configuration.

The solution electronic spectra of the new complexes (Table III, Figure 3) do not show any significant differences from the corresponding solid-state spectra, in most cases. There are two exceptions: in the solution spectrum of the $Cr(ClO_4)_3$ complex, the absorption at 630–671 nm seems to disappear (or is completely masked by the stronger absorption at 569–608 nm). Whereas the coordination number of the $CoCl_2$ complex obviously changes from five to four (tetrahedral) [54], in nitromethane solution. This is not surprising, since the great majority of CoX_2L_2 (X = Cl, Br, I) complexes with organophosphoryl ligands are monomeric pseudotetrahedral [12, 54, 55]; however, the existence of higher-coordinated bi- or poly-nuclear $Co(TMAsO)_2X_2$ (X = Cl, Br, NCS) complexes has been also established [37].

Finally, the ambient temperature magnetic moments (Table IV) of the new complexes are generally within the range of normal values corresponding to high-spin $3d^3$–$3d^8$ compounds, the d^9 configuration or Nd^{3+} [56].

Conclusion

The overall evidence suggests that only a few of the new metal complexes are monomeric compounds, namely, the pseudotetrahedral $[Zn(TTP)_2Cl_2]$ and the hexacoordinated $[M(TTP)_4(OClO_3)_2](ClO_4)$ (M = Cr, Fe, Nd). The rest of the new complexes seem to be binuclear TTP-bridged and pentacoordinated. It should be mentioned at this point that several pentacoordinated $ML_4(ClO_4)_{2\text{ or }3}$ complexes with organophosphoryl ligands have been considered (by different groups) to be either monomeric with one coordinated perchlorato ligand ($[ML_4(OClO_3)](ClO_4)_{1\text{ or }2}$) [48, 50] or binuclear with double L bridges ($[L_3M\genfrac{}{}{0pt}{}{\diagup L \diagdown}{\diagdown L \diagup}ML_3](ClO_4)_{4\text{ or }6}$) and exclusively ionic perchlorate [33, 49] (see also ref. 25). The fact that several of the new metal(II) chloride and metal(II) perchlorate new complexes appear to be of the same structural type is definitely in favor of the presence of $M\genfrac{}{}{0pt}{}{\diagup TTP \diagdown}{\diagdown TTP \diagup}M$ bridges in all of these compounds. It should be also noted, in this connection, that the crystal structure determinations of several triorganoarsine oxide complexes, involving bridging of this type, have been reported [57–59]. Moreover, analogous bi- or poly-nuclear ligand-bridged triorganophosphine oxide or sulfide complexes with metal halides reportedly also appear to exist [37, 60]. Hence, on the basis of the available evidence and the preceding discussion, the non-monomeric new complexes are formulated as binuclear of the types $[Cl_2(TTP)M(TTP)_2M(TTP)Cl_2]$ (M = Mn, Fe, Co, Ni, Cu), $[Cl_3(TTP)M(TTP)_2M(TTP)Cl_3]$ (M = Cr, Fe), and $[(TTP)_3M(TTP)_2M(TTP)_3](ClO_4)_4$ (M = Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd). It is generally assumed that only the phopshoryl oxygen of TTP functions as a ligand site in all of its complexes; in fact the aryloxy or alkoxy oxygens of neutral phosphate or phosphonate esters do not participate in coordination [2, 3].

Regarding the proposed presence of $M\genfrac{}{}{0pt}{}{\diagup O \diagdown}{\diagdown O \diagup}M$ bridges in the new binuclear metal complexes, it should be mentioned that, among several paramagnetic 3d metal ion complexes with $R_3P{=}O$ ligands, that have been characterized as involving bridging of this type, none was found to exhibit subnormal ambient temperature magnetic moments [25, 33, 37, 61]. Actually, there are only a few known bi- or poly-nuclear Cu(II) complexes with TPPO(L), showing either subnormal room temperature magnetic moments (*e.g.*, $[CuL(CH_3COO)_2]_2$) [62] or evidence in favor of antiferromagnetic exchange at low temperatures (*e.g.*, $Cu_4OL_4X_6$ (X = Cl, Br)) [63]; these compounds are not phosphine oxide-bridged, the former involving acetato bridges [62] and the latter oxo-oxygen and halogen bridges [63]. Although the presence of R_3-$P{=}O$ bridging ligands does not seem to cause subnormal paramagnetism at room temperature, it would be of interest to investigate the temperature-dependence of the magnetic susceptibilities of bi- or poly-nuclear metal complexes with bridging phosphoryl ligands. In fact, among analogous ligand-bridged aromatic amine N-oxide metal complexes, those with Cu(II) usually show low room temperature μ_{eff} values, which dramatically decrease at lower temperatures [64], whilst those with the other 3d metal ions of interest show clearcut evidence in favor of spin–spin coupling at lower temperatures [65]. A study in this direction for the new TTP complexes is planned for the future.

Another interesting point is that, rather unexpectedly, TTP seems to be a ligand of comparable strength to that of triorganophosphine oxides rather than that of trimethylphosphate. Thus, the bands assigned as $\nu_{M-O}(TTP)$ (Table II) occur at only slightly lower wavenumbers than those reported for hexa-($M{=}Cr^{3+}$, Fe^{3+}, Ln^{3+}) [32, 33] or penta-(M=dipositive 3d metal ion) [48] coordinated complexes of the same metal ions with triorganophosphine oxides. Whereas $[ML_5](ClO_4)_2$ (M = Mn–Zn) complexes with trimethylphosphate show the ν_{M-O} modes at significantly lower wavenumbers (382–350 cm^{-1} region) [25] than those in the spectra of the new pentacoordinated TTP metal complexes. On the other hand, although Dq calculations for the new Cr^{3+} complexes are impeded by the multiple splittings of the d–d transitions, it is clear from the bands assigned to the $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transition in $[Cr(TTP)_4(OClO_3)_2](ClO_4)$ (565, 633, 671 nm) that the Dq for this compound is most probably larger than the corresponding Dq values in the TPPO and tri-n-butylphosphine oxide analogues, which show four maxima at 598–706 nm [32]. Spectrochemical parameters can be obtained from the solution spectrum of the $CoCl_2$ complex, which is presumably due to the monomeric pseudotetrahedral $[Co(TTP)_2Cl_2]$ species. By assigning ν_2 at 6341 and ν_3 at 16,077 cm^{-1} in this spectrum (Table III, Figure 3), the following parameters are calculated [54, 66]: $\Delta = 3637\ cm^{-1}$; $B' = 767\ cm^{-1}$; $\beta = (B'/967) = 0.79$.

The corresponding values reported for pseudotetrahedral $[CoL_2Cl_2]$ analogues with phosphine oxides (L = TPPO: $\Delta = 3270\ cm^{-1}$; $\beta = 0.79$; L = trimethylphosphine oxide: $\Delta = 3730\ cm^{-1}$; $\beta = 0.76$) [54] are comparable to the parameters for TTP.

The generation of a significantly stronger ligand-field by TTP, relative to trimethylphosphate, may be due to a synergistic contribution of the three *p*-tolyloxysubstituents on phosphorus to the donor strength of this ligand. In fact, the values of the σ^{Φ} substituent constants [67] (which seem to correlate satisfactorily with donor ability [13, 68]) for aryl-substituted organophosphorus compounds reportedly increase with increasing number of aryl substituents on phosphorus, while σ^{Φ} is the same for either one or two alkyl or alkoxy substituents [67]. It is not inconceivable that the σ^{Φ} of aryloxy groups increases with the number of substituents. If such is the case, although the σ^{Φ} values for one methoxy (–0.124) and for one *p*-tolyloxy (–0.141) substituent are very similar [67], $\Sigma\sigma^{\Phi}$ for TTP would be significantly greater than –0.423 ($3\sigma^{\Phi}$), while $\Sigma\sigma^{\Phi}$ for trimethylphosphate is –0.372. However, even a substantially increased $\Sigma\sigma^{\Phi}$ value for TTP can certainly not account for the fact that it is almost as strong a ligand as triorganophosphine oxides (*e.g.*, $\Sigma\sigma^{\Phi}$ for trimethylphosphine oxide is –2.895 [67]). Steric factors may be causing the further increase of the donor strength of TTP during its function as a ligand. Several examples of enhanced strength of ligand-to-metal coordinate bonds, owing to steric hindrance introduced by substituents on the ligand, have been reported [33, 69]. The three bulky *p*-tolyloxy-substituents in TTP undoubtedly introduce severe steric hindrance during the coordination of this ligand. This is also obvious from the fact that our synthetic attempts established that no higher than 4:1 TTP to metal ratios can be realized in its complexes with metal perchlorates. In this respect TTP resembles TPPO and tri-n-butylphosphine oxide, which also form 4:1 complexes with M(II) and even M(III) perchlorates, owing to their bulkiness [32, 47], rather than phosphate or phosphonate alkylesters, which reportedly can yield $[ML_6]^{n+}$, $[ML_5]^{n+}$ or $[ML_4(OH_2)_x]^{n+}$ (n = 2, 3; x = 1, 2) cationic complexes with 3d metal ions [5, 6, 9].

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