

Neutral Phosphate and Phosphonate Butylesters as Ligands

N.M. Karayannis, C.M. Mikulski, M.J. Strocko, L.L. Pytlewski,
and M.M. Labes

Received June 3, 1970

Interaction of tri-n-butyl phosphate (TBP), tri-iso-butyl phosphate (TIBP) or di-n-butyl n-butylphosphonate (DBBP) with hydrated 3d metal perchlorates in triethyl orthoformate leads to the formation of crystalline complexes of the general type $ML_4(ClO_4)_2 \cdot xH_2O$ ($x = 1, 2$). Characterization of these complexes by means of spectral, magnetic and conductance studies led to the following tentative formulations: $[M(TBP)_4(OH_2)(OClO_3)](ClO_4)$; $[M(TIBP)_4(OH_2)](ClO_4)_2$; $[M(DBBP)_4(OH_2)_2](ClO_4)_2$ ($M = Mn, Co, Ni$); $[Cu(DBBP)_4(OH_2)](ClO_4)_2$. According to these assignments, the TIBP complexes and that of Cu^{II} with DBBP involve pentacoordinated complex cations, while in the other DBBP complexes the cation is hexacoordinated. The cationic TBP complexes are hexacoordinated, probably involving one coordinated monodentate perchlorato group. The factors influencing the stabilization of mono- or di-aquo adducts rather than the $[ML_4](ClO_4)_2$ solvates are discussed.

Introduction

Metal complexes of neutral phosphate and phosphonate esters have been reported in a number of recent studies.¹⁻⁵ These include complexes of lanthanide(III) nitrates with tri-n-butyl phosphate (TBP),¹ lanthanide(III) perchlorates with trimethyl phosphate (TMP),⁴ various metal perchlorates, halides, nitrates and thiocyanates with diisopropyl methylphosphonate (DIMP),² and metal perchlorates with dimethyl methylphosphonate (DMMP)^{2,3} and TMP.^{3,5} Neutral phosphate and phosphonate esters, and especially those containing bulky substituents (butyl or higher alkyl), have been used as extracting agents for metal ions for many years.⁶ The species formed in solution between metal salts and neutral phosphate or phosphonate butylesters have been characterized in many cases.⁷⁻¹² Isolation

of pure solvates of metal salts with these ligands is generally difficult, however, and has been accomplished only in a few cases.^{1,13} The synthesis of metal complexes with alkoxyphosphoryl compounds is greatly facilitated in the presence of dehydrating agents, such as triethyl orthoformate or 2,2-dimethoxypropane.^{2,5} In view of the importance of neutral phosphate and phosphonate butylesters as extractants, it seemed appropriate to explore the possibility of preparing and studying some of their metal complexes, by using triethyl orthoformate as the dehydrating agent.¹⁴ The present paper deals with the synthesis and characterization of TBP, tri-iso-butyl phosphate (TIBP) and di-n-butyl n-butylphosphonate (DBBP) complexes with a number of metal perchlorates.

Experimental Section

Synthetic Procedure. TBP (Eastman), TIBP (K&K), and DBBP (Mobil Chemical Co.) were utilized as received. The syntheses were accomplished by methods analogous to those employed for the preparation of DIMP, DMMP, and TMP complexes with metal perchlorates.^{2,5} Thus, the hydrated metal perchlorates were treated with triethyl orthoformate at 40-50 °C,^{2,5} excess ligand was then added, and the resulting mixture was heated at 50 °C under stirring for 3-4 hrs., and then allowed to cool slowly. The new complexes were obtained in crystalline form either by stirring the viscous reaction mixture at room temperature for 1-6 hrs. (Mn, Co, Ni-TIBP; Mn, Co-DBBP complexes) or by treatment of the mixture with several portions of anhydrous ether and subsequent stirring of the very viscous solid residue (Ni, Cu-DBBP; Mn, Co, Ni-TBP complexes). $Cu(ClO_4)_2$ complexes with TBP or TIBP could not be obtained in crystalline form by either of these procedures. The viscous liquid final products obtained in these cases were not studied any further.

The compounds obtained as described above were generally sensitive to atmospheric moisture. They were filtered and thoroughly washed with ether in the dry-box and subsequently dried over calcium chloride in an evacuated desiccator. The TBP complexes col-

(1) J. R. Ferraro, C. Cristallini, and I. Fox, *J. Inorg. Nucl. Chem.*, **29**, 139 (1967).

(2) N. M. Karayannis, C. Owens, L. L. Pytlewski, and M. M. Labes, *ibid.*, **31**, 2059, 2767 (1969); **32**, 83 (1970).

(3) L. S. Frankel, *Inorg. Chem.*, **8**, 1784 (1969).

(4) P. Graham and M. Joesten, *J. Inorg. Nucl. Chem.*, **32**, 531 (1970).

(5) N. M. Karayannis, E. E. Bradshaw, L. L. Pytlewski, and M. M. Labes, *ibid.*, **32**, 1079 (1970).

(6) D. F. Peppard, *Adv. Inorg. Chem. Radiochem.*, **9**, 1 (1966), and references therein

(7) T. V. Healy and J. Kennedy, *J. Inorg. Nucl. Chem.*, **10**, 128 (1959); T. V. Healy, J. Kennedy, and G. M. Waind, *ibid.*, **137**; H. Irving and D. N. Edgington, *ibid.*, **306**.

(8) D. C. Madigan and R. W. Catrall, *ibid.*, **21**, 334 (1961).

(9) D. F. C. Morris, E. L. Short, and D. N. Slater, *Electrochim. Acta*, **8**, 289 (1963); D. F. C. Morris and D. N. Slater, *J. Inorg. Nucl. Chem.*, **27**, 250 (1965).

(10) C. Günzler and P. Mühl, *Z. Chem. (Leipzig)*, **5**, 148 (1965); K. Schaarschmidt, G. Mende, and G. Emrich, *ibid.*, **6**, 275 (1966).

(11) E. Chifu and G. Gabrielli, *Gazz. Chim. Ital.*, **98**, 1213 (1968).

(12) B. Jezowska-Trzebiatowska, A. Bartecki, and S. Kopacz, *Zhur. Neorg. Khim.*, **13**, 864 (1968); P. G. Berezko, S. S. Korovin, K. I. Petrov and A. M. Reznik, *ibid.*, **1058**; V. N. Startsev, Yu. I. Sannikov, G. N. Ben'ash and E. I. Krylov, *ibid.*, **1122**.

(13) J. R. Ferraro, *J. Inorg. Nucl. Chem.*, **10**, 319 (1959).

(14) P. W. N. M. van Leeuwen and W. L. Groeneveld, *Inorg. Nucl. Chem. Lett.*, **3**, 145 (1967).

Table I. Analyses of TBP, TIBP and DBBP Metal Complexes ^a

Complex	Color	C %		H %		Metal %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
[Mn(TBP) ₄ (OH ₂)(OCIO ₃)](ClO ₄)	White	43.10	43.42	8.29	7.90	4.11	4.60
[Co(TBP) ₄ (OH ₂)(OCIO ₃)](ClO ₄)	Purple-pink	42.99	43.26	8.27	8.12	4.39	4.82
[Ni(TBP) ₄ (OH ₂)(OCIO ₃)](ClO ₄)	Yellow green	43.00	42.60	8.27	8.46	4.38	4.45
[Mn(TIBP) ₄ (OH ₂)](ClO ₄) ₂	White	43.10	42.66	8.29	8.02	4.11	4.38
[Co(TIBP) ₄ (OH ₂)](ClO ₄) ₂	Violet	42.99	43.46	8.27	8.31	4.39	4.60
[Ni(TIBP) ₄ (OH ₂)](ClO ₄) ₂	Yellow	43.00	43.29	8.27	8.44	4.38	4.16
[Mn(DBBP) ₄ (OH ₂)](ClO ₄) ₂	White	44.63	44.29	8.74	8.72	4.25	4.53
[Co(DBBP) ₄ (OH ₂)](ClO ₄) ₂	Purple-pink	44.50	44.30	8.71	8.69	4.55	4.38
[Ni(DBBP) ₄ (OH ₂)](ClO ₄) ₂	Green	44.50	44.11	8.71	8.85	4.53	4.71
[Cu(DBBP) ₄ (OH ₂)](ClO ₄) ₂	Green	44.96	44.60	8.69	8.90	4.95	5.02

^a P analyses performed in some cases were satisfactory, i.e.: Mn^{II}-DBBP complex, calcd.: 9.59%, found 9.44%; Ni^{II}-TBP complex, calcd.: 9.24%, found 9.08%.

Table II. Pertinent Infrared Data for TBP, TIBP and DBBP Metal Complexes (cm⁻¹)

Compound	$\nu_{P-O}(\Delta\nu_{P-O})$	ν_{OH}	δ_{H-O-H}	Aquo bands $\nu_3(\text{ionic ClO}_4^-)$	$\nu_2(\text{monodentate } -\text{OCIO}_3)$	ν Ligand (950-870 cm ⁻¹)
TBP	1275 vs					898 m
[Mn(TBP) ₄ (OH ₂)(OCIO ₃)](ClO ₄)	1228 vs (-47)	3478 vs, b	1622 s	1103 vs, b, sh	913 m-s	920 sh, 900 sh
[Co(TBP) ₄ (OH ₂)(OCIO ₃)](ClO ₄)	1238 vs (-37)	3480 vs, b	1628 s	1090 vs, b, sh	912 m-s	920 sh, 897 sh
[Ni(TBP) ₄ (OH ₂)(OCIO ₃)](ClO ₄)	1240 vs (-35)	3440 vs, b	1635 s	1108 vs	917 m-s	923 sh, 901 sh
TIBP	1266 vs					913 w, 870 s-m
[Mn(TIBP) ₄ (OH ₂)](ClO ₄) ₂	1230 vs (-36)	3405 vs, b	1634 s	1105 vs		921 m-w, 882 s-m
[Co(TIBP) ₄ (OH ₂)](ClO ₄) ₂	1235 vs (-31)	3425 vs, b	1631 s	1090 vs		918 m-w, 878 s-m
[Ni(TIBP) ₄ (OH ₂)](ClO ₄) ₂	1235 vs (-31)	3400 vs, b	1633 s	1100 vs, b, sh		920 m-w, 880 s-m
DBBP	1244 vs					903 s-m
[Mn(DBBP) ₄ (OH ₂)](ClO ₄) ₂	1194 vs (-50)	3480 vs, b	1622 s	1095 vs, sh		913 m
[Co(DBBP) ₄ (OH ₂)](ClO ₄) ₂	1203 vs (-41)	3430 vs, b	1630 s	1090 vs, b, sh		910 m
[Ni(DBBP) ₄ (OH ₂)](ClO ₄) ₂	1199 vs (-45)	3450 vs, b	1628 s	1085 vs, b, sh		910 m
[Cu(DBBP) ₄ (OH ₂)](ClO ₄) ₂	1190 vs, b sh (-54)	3400 vs, b	1628 s	^a		905 m

^a Overlaps with the ligand band at 1055 cm⁻¹. Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder.

lapsed to viscous liquids in the desiccator, and could not be recrystallized from a number of solvents. Analytical data (Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.) and some properties of the new complexes are given in Table I.

Purity of the New Complexes. A serious problem arising during attempts at the synthesis of metal complexes with neutral alkoxyphosphoryl compounds is the possibility of their contamination with substantial amounts of polymeric complexes of the corresponding monoacidic phosphoryl compounds.¹⁵ The solubility of the new complexes in many organic solvents^{2,5,15} and the absence of IR bands attributable to ν_{POO} vibrations¹⁶ demonstrate that these compounds are authentic complexes of the neutral phosphate and phosphonate butylesters under study.

Spectral, Magnetic and Conductance Studies. IR spectra (Table II, Figure 1), electronic spectra (Table III, Figures 2, 3) and magnetic and conductance mea-

surements (Table IV) were obtained as previously described.^{2,5,17}

Discussion

Infrared and Conductance Studies. The negative ν_{P-O} shifts (Table II, Figure 1) demonstrate that coordination to the metal ion occurs through the phosphoryl oxygen of the ligands.¹⁸ Coordinated water bands at 3500-3400 (ν_{OH}) and 1640-1620 (δ_{H-O-H}) cm⁻¹¹⁹ are invariably present in the IR spectra of the complexes (Table II). The ligands exhibit rich IR spectra

(15) V. Gutmann and G. Beer, *Inorg. Chim. Acta*, **3**, 87 (1969); C. M. Mikulski, N. M. Karayannis, J. V. Minkiewicz, L. L. Pytlewski, and M. M. Labes, *ibid.*, 523.

(16) N. M. Karayannis, C. M. Mikulski, L. L. Pytlewski, and M. M. Labes, *Z. anal. Chem.*, **249**, 380 (1970).

(17) L. L. Pytlewski, J. V. Minkiewicz, N. M. Karayannis, and M. M. Labes, *ibid.*, **244**, 390 (1969).

(18) F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

(19) I. Gamo, *Bull. Chem. Soc. Japan*, **34**, 760 (1961).

Table III. Electronic Spectra of TBP, TIBP and DBBP Metal Complexes

Complex	Medium	λ_{\max} , nm (ϵ_{\max})
[Mn(TBP) ₄ (OH) ₂ (OCIO ₃) ₂](ClO ₄)	Nujol	260 vs, 302 s, sh
[Co(TBP) ₄ (OH) ₂ (OCIO ₃) ₂](ClO ₄)	Nujol	259 vs, 490 sh, 536 s, 750 sh, 1280 m-w, b
	$5 \times 10^{-3} M$ in CH ₃ NO ₂	498 sh(21), 530(22.5), 1280(4)
	$7.8 \times 10^{-3} M$ in TBP	471 sh(4.5), 536(10.5), 635(4.5), 1350(2.5)
[Ni(TBP) ₄ (OH) ₂ (OCIO ₃) ₂](ClO ₄)	Nujol	260 vs, 388 s, sh, 660 m, b, sh, 1210 m-w, b
	$4.3 \times 10^{-3} M$ in CH ₃ NO ₂	371(47), 686(21), 1034(12)
	$6.3 \times 10^{-3} M$ in TBP	392(41), 764(23), 1268(17)
[Mn(TIBP) ₄ (OH) ₂](ClO ₄) ₂	Nujol	259 vs, 300 s, sh
[Co(TIBP) ₄ (OH) ₂](ClO ₄) ₂	Nujol	<270 vs, 485 s, sh, 549 s, sh, 629 sh, 790 sh, 1010 sh, 1240 m-w, b
	$10^{-2} M$ in CH ₃ NO ₂	471 sh(14), 497sh(17), 532(20), 618 sh(10.5) 1280 b(3)
	$6.6 \times 10^{-3} M$ in TIBP	484 sh(15), 537(27.5), 628(8.5), 1322(5.5)
[Ni(TIBP) ₄ (OH) ₂](ClO ₄) ₂	Nujol	<270 vs, 412 s, 539 sh, 690 m, sh, 785 m, 1270 m-w, b
	$8 \times 10^{-3} M$ in CH ₃ NO ₂	382(15), 649(6), 712(5), 1100 b(4)
	$1.7 \times 10^{-2} M$ in TIBP	408(8), 672(2.5), 745(3), 1250(3)
[Mn(DBBP) ₄ (OH) ₂](ClO ₄) ₂	Nujol	260 vs, 298 s, sh
[Co(DBBP) ₄ (OH) ₂](ClO ₄) ₂	Nujol	259 vs, 539 s, 690 sh, 950 sh, 1250 m-w, vb
	$1.9 \times 10^{-2} M$ in CH ₃ NO ₂	500 sh(20), 547 sh(61), 554(63), 576(76), 594(78), 621(80), 1321(14), 1550(13), 1720(13.5)
[Ni(DBBP) ₄ (OH) ₂](ClO ₄) ₂	Nujol	245 sh, 263 vs, 392 s, 700 m, b, 1281 m-w, b
	$1.4 \times 10^{-2} M$ in CH ₃ NO ₂	385(20), 550 sh(2), 665(7), 734(6), 1189(6.5)
[Cu(DBBP) ₄ (OH) ₂](ClO ₄) ₂	Nujol	330 vs, 785 vs, b
	$8.5 \times 10^{-3} M$ in CH ₃ NO ₂	782(53)

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

Table IV. Magnetic Moments (300°K) and Electrical Conductivities ($10^{-3} M$ Nitromethane Solutions at 25°C) of TBP, TIBP and DBBP Metal Complexes

Complex	$10^6 \chi_M^{\text{corr}}$, cgsu	μ_{eff} , BM	Λ_M , $\Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$
[Mn(TBP) ₄ (OH) ₂ (OCIO ₃) ₂](ClO ₄)	14.622	5.96	177
[Co(TBP) ₄ (OH) ₂ (OCIO ₃) ₂](ClO ₄)	9.721	4.85	161
[Ni(TBP) ₄ (OH) ₂ (OCIO ₃) ₂](ClO ₄)	3.850	3.05	153
[Mn(TIBP) ₄ (OH) ₂](ClO ₄) ₂	14.675	5.96	166
[Co(TIBP) ₄ (OH) ₂](ClO ₄) ₂	9.242	4.73	157
[Ni(TIBP) ₄ (OH) ₂](ClO ₄) ₂	4.231	3.23	153
[Mn(DBBP) ₄ (OH) ₂](ClO ₄) ₂	14.768	5.98	172
[Co(DBBP) ₄ (OH) ₂](ClO ₄) ₂	10.251	4.98	170
[Ni(DBBP) ₄ (OH) ₂](ClO ₄) ₂	4.164	3.17	159
[Cu(DBBP) ₄ (OH) ₂](ClO ₄) ₂	1.595	1.96	184

in the 1350-800 cm^{-1} region (Figure 1),^{20,21} and any splittings of the ν_3 mode of ionic ClO_4^- ²² cannot be identified with certainty (Figure 1). In particular the ν_1 mode of $-\text{OCIO}_3$ (C_{3v} symmetry), which occurs at ca. 1030 cm^{-1} ,²² would be completely masked by the $\nu_{\text{P-O-(C)}}$ bands of the ligands in this region.²⁰ Nevertheless, some indication concerning the presence of coordinated perchlorate may be obtained by examination of the spectra in the 930-900 cm^{-1} region. The ν_1 mode of ionic perchlorate (T_d) is IR inactive,²² but may occur in certain cases as a weak band at ca. 920 cm^{-1} in crystalline compounds, owing to lowering of the symmetry of this anion in the crystal lattice.²³ The ν_2 mode of coordinated monodentate perchlorate is IR active and appears at ca. 920 cm^{-1} as a medium intensity band.²² TBP exhibits a medium band at 898 cm^{-1} . Its complexes exhibit a stronger absorption at 917-913 cm^{-1} , with shoulders at ca. 920 and 900 cm^{-1} . It is, thus, possible that these compounds contain one co-

ordinated monodentate perchlorate group (Table II, Figure 1). TIBP exhibits a weak band at 913 cm^{-1} , while DBBP shows a strong to medium absorption at 903 cm^{-1} . In the complexes of these ligands these bands exhibit small positive shifts (Table II, Figure 1),

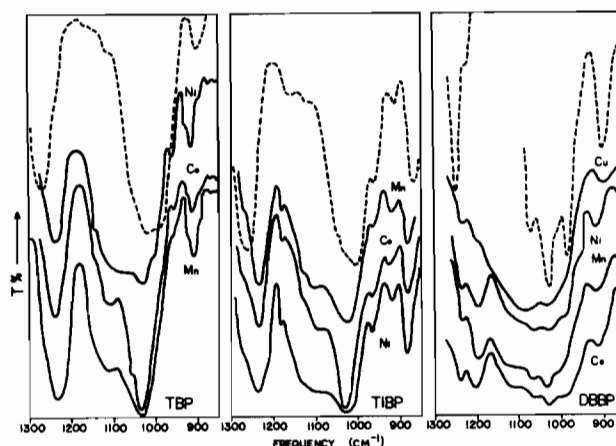


Figure 1. Infrared spectra (1300-850 cm^{-1}) of TBP, TIBP and DBBP (---) and their metal perchlorate complexes (—).

(20) L. C. Thomas and R. A. Chittenden, *Spectrochim. Acta*, 20, 467, 489 (1964); 21, 1905 (1965).

(21) L. L. Burger, *J. Phys. Chem.*, 62, 590 (1958); A. L. Mills and W. R. Logan, *J. Inorg. Nucl. Chem.*, 26, 2191 (1964)

(22) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961); B. J. Hathaway, D. G. Holah and M. Hudson, *ibid.*, 4586 (1963)

(23) S. D. Ross, *Spectrochim. Acta*, 18, 225 (1962); A. Hezel and S. D. Ross, *ibid.*, 22, 1949 (1966).

but are not significantly intensified or split. Comparison of these cases to that of the TBP complexes leads to the tentative conclusion that the TIBP and DBBP complexes involve only ionic perchlorate. Conductance data show that the complexes are 2:1 electrolytes in solution (Table IV). In the TBP complexes the coordinated perchlorate group is, presumably, displaced by a solvent molecule (nitromethane) in solution. A similar behavior has been reported for a number of 3d metal complexes with phosphine oxides, involving coordinated perchlorate in the solid state.²⁴ On the basis of the above evidence and the analytical data (Table I) the new complexes are formulated as follows: $[M(\text{TBP})_4(\text{OH}_2)(\text{OClO}_3)](\text{ClO}_4)$; $[M(\text{TBP})_4(\text{OH}_2)](\text{ClO}_4)_2$, $[M(\text{DBBP})_4(\text{OH}_2)_2](\text{ClO}_4)_2$ ($M = \text{Mn, Co, Ni}$) and $[\text{Cu}(\text{DBBP})_4(\text{OH}_2)](\text{ClO}_4)_2$.

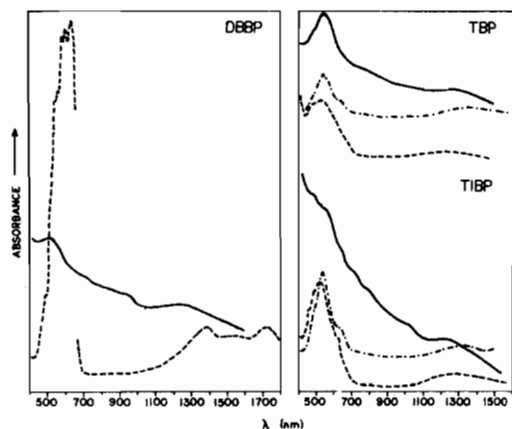


Figure 2. Electronic spectra of Co^{II} complexes with TBP, TIBP and DBBP. (—), Nujol mull; (---), nitromethane solution; (-.-), solution in excess ligand.

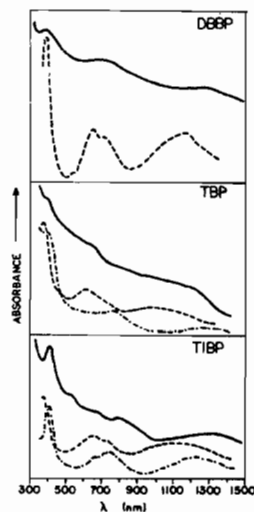


Figure 3. Electronic spectra of Ni^{II} complexes with TBP, TIBP and DBBP. (—), Nujol mull; (---), nitromethane solution; (-.-), solution in excess ligand.

Electronic Spectra and Magnetic Moments. Resolution of the mull electronic spectra of the moisture-

(24) N. M. Karayannis, C. M. Mikulski, L. L. Pytlewski, and M. M. Labes, *Inorg. Chem.*, **9**, 582 (1970).

sensitive new complexes was rather poor (Figures 2, 3). The Co^{II} and Ni^{II} -TIBP complexes exhibit a greater number of (d-d) bands than the corresponding TBP and DBBP complexes. This may be attributed to pentacoordinated configurations^{5,25} for the TIBP and hexacoordinated for the TBP and DBBP compounds.²⁶ Further, the magnetic moments (Table IV) of the Co^{II} and Ni^{II} -TIBP complexes are within the region of values reported for high-spin pentacoordinated compounds,²⁷ while those of the corresponding TBP and DBBP complexes are typical of hexacoordinated Co^{II} and Ni^{II} compounds.²⁸ The energy of the (d-d) band in the Cu^{II} -DBBP complex is rather low for a tetra- and high for a hexa-coordinated configuration.^{24,28} This compound involves, most probably, a pentacoordinated complex cation of the type $[\text{Cu}(\text{DBBP})_4(\text{OH}_2)]^{2+}$.^{5,25} Thus, solid-state spectral and magnetic evidence appears to be in favor of the above formulations.

Solution spectra of the TBP complexes in nitromethane (Table II, Figures 2, 3) do not show appreciable changes from the corresponding mull spectra. Hexacoordinated cationic species of the type $[\text{M}(\text{TBP})_4(\text{OH}_2)(\text{CH}_3\text{NO}_2)]^{2+}$ are probably formed under these conditions (*vide supra*). Solutions of the above complexes in TBP exhibit notable differences from their mull spectra. Thus, the Co^{II} complex exhibits a new band at 635 nm (Figure 2), while the (d-d) bands of the Ni^{II} complex show a general shift toward lower energies (Figure 3). These changes are most probably due to competition between TBP, aquo and perchlorate groups in the first coordination sphere of the metal ion. The TBP solution spectrum of the Co^{II} complex, as well as those of the Co^{II} and Ni^{II} -TIBP complexes in TIBP exhibit patterns similar to those reported for high-spin pentacoordinated compounds (Table III, Figs. 2, 3).^{5,25,27} The intensities of the visible (d-d) bands in these spectra are, however, too low to be attributed to the exclusive presence of pentacoordinated species. The most reasonable conclusion is that these solutions contain, penta- and hexa-coordinated species in equilibrium. The TIBP complexes in nitromethane exhibit very similar spectra to those of the corresponding TBP complexes. This is apparently due to solvation of the TIBP complexes and formation of hexacoordinated species.

Solution spectra of the DBBP complexes in excess ligand are practically similar to the corresponding solid state spectra. The spectrum of the Cu^{II} complex does not change in nitromethane, but a dramatic change is observed in that of the Co^{II} complex (Table III, Figure 2). $[\text{Co}(\text{DBBP})_4(\text{OH}_2)_2]^{2+}$ is, presumably, dissociated in nitromethane and an essentially tetrahedral cationic species (most probably $[\text{Co}(\text{DBBP})_4]^{2+}$)²⁴ is stabilized in this solvent. A similar behavior is observed in nitromethane solutions of the Ni^{II} -DBBP complex (Table III, Figure 3). In fact, the predominant species present under these conditions appears

(25) A. M. Brodie, S. H. Hunter, G. A. Rodley, and C. J. Wilkins, *Inorg. Chim. Acta*, **2**, 195 (1968); S. H. Hunter, R. S. Nyholm and G. A. Rodley, *ibid.*, **3**, 631 (1969).

(26) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966); M. Ciampolini and G. Sponeri, *ibid.*, **5**, 45 (1966).

(27) D. W. Meek, R. S. Drago, and T. S. Piper, *ibid.*, **1**, 285 (1962).

(28) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).

(29) W. Byers, A. B. P. Lever and R. V. Parish, *Inorg. Chem.*, **7**, 1835 (1968).

to be pentacoordinated.^{5,25} As is the case with most $\text{Ni}(\text{L})_4(\text{ClO}_4)_2$ complexes with phosphoryl ligands,^{24,25} $\text{Ni}(\text{DBBP})_4(\text{ClO}_4)_2$ might be expected to involve coordination number five for the Ni^{II} ion. Nitromethane presumably causes at least partial dissociation of $[\text{Ni}(\text{DBBP})_4(\text{OH}_2)_2]^{2+}$ and favors the stabilization of the dehydrated cationic species.

Conclusion

With the exception of some methyl substituted derivatives,^{2,5,25} organophosphoryl compounds yield cationic metal complexes involving coordination of four ligands per metal ion (*i.e.* $[\text{ML}_4]^{n+}$).^{2,24,25,30} In complexes of this type the bulky ligand groups make the central metal ion inaccessible for coordination to additional bulky ligand groups (*e.g.* a fifth organophosphoryl group). «Smaller» ligands, such as aquo and perchlorato groups can, however, coordinate to the metal ions and many organophosphoryl complexes of the types $[\text{ML}_4(\text{OCIO}_3)]^{2+}$, $[\text{ML}_4(\text{OCIO}_3)(\text{OH}_2)]^{2+}$, $[\text{ML}_4(\text{OCIO}_3)_2]^{3+}$ and $[\text{ML}_4(\text{OH}_2)_2]^{2+}$ have been reported.^{2,24,25,31} Mono- or di-aquo adducts usually revert to the $[\text{ML}_4]^{n+}$ species upon drying.^{2,25,31} The complexes reported here are isolated in the form of mono- or di-hydrates, which cannot be dehydrated in the presence of a number of effective drying agents (CaCl_2 ,

$\text{Mg}(\text{ClO}_4)_2$, P_2O_5). Stabilization of mono- or di-aquo adducts rather than the anhydrous $[\text{ML}_4]^{2+}$ complex cations in the case of alkoxyphosphoryl ligands may be attributed to the decreasing donor strength of R_3PO compounds with increasing substitution of alkoxy for alkyl groups.³² Thus, phosphine oxides would be less susceptible to the formation of adducts with small ligands than the corresponding complexes of the above esters. This is corroborated by the fact that $[\text{ML}_4]^{n+}$ complexes with phosphine oxides are only slightly hygroscopic,^{24,30} while the neutral phosphate and phosphonate ester analogs are extremely hygroscopic, and always form aquo adducts when exposed to atmospheric moisture.^{2,5} The fact that the crystalline butylester complexes reported cannot be dehydrated is most probably due to effective shielding of the aquo and, in the case of TBP complexes, perchlorato groups by the bulky organophosphoryl ligands, leading to increased stabilization of the hexa- or penta-coordinated complex cation. Stabilization of a pentacoordinated configuration in the case of the solid TIBP complexes may be attributed to the steric effect of the branched alkyl substituents, which presumably leads to effective shielding of the central metal ion.

In conclusion, although the authentic $[\text{ML}_4](\text{ClO}_4)_2$ solvates of neutral phosphate and phosphonate butylesters with 3d metal perchlorates could not be isolated, their mono- or di-aquo adducts have been obtained in crystalline form and characterized.

(30) F. A. Cotton and E. Bannister, *J. Chem. Soc.*, 1875 (1960); E. Bannister and F. A. Cotton, *ibid.*, 1878 (1960); K. Issleib and B. Mitscherling, *Z. anorg. allgem. Chem.*, 304, 73 (1960).

(31) A. M. Brodie, S. H. Hunter, G. A. Rodley, and C. J. Wilkins, *J. Chem. Soc.*, (A), 2039 (1968).

(32) S. Nomura and R. Hara, *Anal. Chim. Acta*, 25, 212 (1961).