For M((*S*)-pn)$_3$, when the methyl groups are equatorial, the significant interaction system is identical with that for M(en)$_3$, and, therefore, the energy difference between the D($\delta\delta\delta$) and L($\delta\delta\delta$) configurations using the empirical equation is about 0.9 kcal mol^{-1}. For a complex of the type M((*S*)-pn)(NH$_3$)$_4$, interactions between the methyl group in an axial orientation and the ammonia groups can be somewhat relieved by the rotation of the NH$_3$ about the M–N bond.[9] This alleviation of the van der Waals interaction of the axial methyl group is not possible to the same extent in M((*S*)-pn)$_3$. Thus, the preference for the equatorial conformation (δ) will be greater for the tris than for the mono complex.

According to the present geometrical model, the relative energies of the three configuration types of the *cis*-bis-ethylenediamine complexes are (kcal mol^{-1}): D($\delta\delta$) = L($\lambda\lambda$), 0; D($\delta\lambda$) = L($\lambda\delta$), −0.05; D($\lambda\lambda$) = L($\delta\delta$), 0.3. However, it must be emphasized that this model probably overestimates the interactions because, for these complexes, nonbonded interactions with a third puckered conformation are missing, and the two chelate rings should be able to distort more than for the tris complex to alleviate any interactions between them. In fact, it is conceivable that the order of preference is in error because of this facility for distortion. Nevertheless it can be concluded from this study that the actual energy differences between the configurations is very small.

As stated in the Results the chiral and *meso* configurations of the *trans*-bis-ethylenediamine complexes have equivalent energies when Bartell's or the empirical equations are used. Corey and Bailar calculated an energy difference of about 1 kcal mol^{-1} using the Mason and Kreevoy H···H interaction expression without allowing for distortions of the chelate rings, which could considerably reduce even this energy. Therefore, conformational analysis suggests that the chelate rings are free to adopt either the chiral or *meso* configurations.

Finally, as the medium-energy interaction equations have been found to be the more realistic, it is possible to comment further on the energy differences between the axial and equatorial orientations of a methyl group in mono(N- and C-substituted ethylenediamine) complexes. The energies would approximate to those published using the Bartell equation.[9] For tetraammine((*R*)-propylenediamine)cobalt(III) the energy difference would be of the order of 0.7 kcal mol^{-1}, and, for the equivalent N-methylethylenediamine complex about 0.8 kcal mol^{-1} in favor of the equatorial orientation.

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Complexes of Tri-*n*-butylphosphine Oxide with Metal Perchlorates

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Complexes of tri-*n*-butylphosphine oxide (TBPO) with metal perchlorates were synthesized and characterized by means of spectral, magnetic, conductance, and X-ray powder diffraction studies. Coordination of monodentate perchlorate groups has been established for the Cr(III), Fe(II), Fe(III), and Ce(III) compounds, which are of the novel types [M(TBPO)$_4$(OClO$_3$)$_2$](ClO$_4$) (M = Cr(III), Fe(III), Ce(III)) and [Fe(TBPO)$_4$(OClO$_3$)$_2$]. Mg(II), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) yield cationic complexes of the type M(TBPO)$_4^{2+}$. The Co(II) and Zn(II) complexes are tetrahedral. The Cu(II) complex may be assigned either a symmetry intermediate between distorted T$_d$ and D_{4h} or a polymeric hexacoordinated tetragonal structure, involving both terminal and bridging ligand molecules. Of interest are the Ni(II) and Mn(II) complexes, which, unlike their analogs with other phosphine oxides, have a distorted tetrahedral ligand field symmetry with essentially T$_d$ MO$_4$ moieties. The steric and inductive effects influencing the stereochemistry of metal complexes of neutral organophosphoryl compounds are discussed.

Introduction

Although metal complexes with phosphine oxides (R$_3$PO) are among the first complexes of monodentate oxo ligands to be synthesized,[1] systematic characterization studies of compounds of this type have appeared only in recent years. Several of these recent studies dealt with phosphine oxide complexes of metal perchlorates.[2-5] Cationic complexes of the general type ML$_4^{n+}$ (M = Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II)) have been reported for triphenyl-, trimethyl-, and triethylphosphine oxides (TPPO, TMPO, and TEPO, respectively).[2-4] Co(II) and Zn(II) complexes

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[1] A. W. Hofmann, *Ann. Chem. Pharm., Suppl.*, **1**, 7 (1861); L. Pebal, *Ann. Chem. Pharm.*, **120**, 194 (1862); F. Fleissner, *Ber. Deut. Chem. Ges.*, **13**, 1665 (1880); R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **89**, 262 (1906).

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TABLE I

PROPERTIES AND ANALYSES OF TBPO–METAL COMPLEXES

			Analyses, %							
			C		H		P		Metal	
Complex	Color	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Mg(TBPO)_4]ClO_4)_2$	White	192.5–193	52.58	52.83	9.93	10.02	11.30	11.48	2.22	2.06
$[Cr(TBPO)_4(OClO_3)_2](ClO_4)$	Bright green	131–132	47.12	46.67	8.90	9.23	10.13	9.83	4.25	4.35
$[Mn(TBPO)_4](ClO_4)_2$	White	149.5–150	51.15	50.91	9.66	9.46	10.99	11.20	4.87	4.72
$[Fe(TBPO)_4(OClO_3)_2]$	Light beige	102–103	51.11	50.77	9.65	9.62	10.98	10.62	4.95	4.85
$[Fe(TBPO)_4(OClO_3)_2](ClO_4)$	Pale orange	116–117	46.98	46.49	8.87	9.21	10.10	9.91	4.55	4.63
$[Co(TBPO)_4](ClO_4)_2$	Dark blue	189–190	50.97	50.72	9.62	9.55	10.95	10.92	5.21	5.28
$[Ni(TBPO)_4](ClO_4)_2$	Red rose	141.5–142	50.98	51.05	9.66	9.81	10.96	11.10	5.19	5.30
$[Cu(TBPO)_4](ClO_4)_2$	Light green	125.5–126	50.76	50.48	9.59	9.60	10.91	10.94	5.59	5.50
$[Zn(TBPO)_4](ClO_4)_2$	White	128–129	50.68	50.40	9.57	9.51	10.89	10.70	5.75	5.98
$[Ce(TBPO)_4(OClO_3)_2](ClO_4)$	White	175.5–176	43.95	43.52	8.29	8.42	9.44	9.43	10.68	10.24

of this type are tetrahedral, while Mn(II), Ni(II), and Cu(II) analogs have been assigned ligand field symmetries intermediate between distorted tetrahedral and square planar.[2] More recently, square-pyramidal cationic complexes of the types ML_5^{2+} (M = Mn, Co, Ni) and $ML_4(ClO_4)^+$ (M = Fe, Cu) with TMPO were reported.[5]

In a recent communication we reported the synthesis and characterization of a tetrahedral cationic complex of Ni(II) with tri-*n*-butylphosphine oxide (TBPO).[6] This compound, unlike the yellow NiL_4^{2+} complexes mentioned above,[2–4] is red rose in color and has a magnetic moment (3.68 BM) and electronic spectrum indicative of a tetrahedral symmetry.[6] In fact, the electronic spectrum of this complex[6] shows great similarity to those reported for the tetrahedral cationic complexes of Ni(II) with trimethylamine N-oxide (TMNO)[7] and hexamethylphosphoramide (HMPA).[8] The adoption of a tetrahedral configuration by Ni(II) in $Ni(TBPO)_4^{2+}$ was attributed[6] to the bulkiness of the ligand.[9] In view of the difference in configuration between $Ni(TBPO)_4^{2+}$[6] and its analogs with other phosphine oxides,[2–4] it seemed appropriate to study the complexes of TBPO with other metal ions. The present paper deals with synthetic and characterization studies of TBPO–metal perchlorate complexes.

Experimental Section

Chemicals.—TBPO (Carlisle Chemical Works) was utilized as received. The purest commercially available metal salts, triethyl orthoformate, and solvents were used.

Synthetic Procedure.—Triethyl orthoformate solutions of ligand and hydrated salt (in *ca.* 6:1 molar ratio) are mixed and warmed at 40–50° under stirring. The Ni(II),[6] Mn(II), Fe(III), Co(II), and Mg(II) complexes were precipitated after 5–15 min. The rest of the complexes reported were precipitated by warming the mixture for *ca.* 20 min, allowing to cool, and adding an excess of ether (Fe(II), Ce(III)) or petroleum ether (bp 63–75°) (Cr(III), Cu(II), Zn(II)). The complexes were filtered, washed with anhydrous ether, and kept over $Mg(ClO_4)_2$ in an evacuated desiccator. The Mn(II), Co(II), Ni(II), and Zn(II) complexes are slightly hygroscopic, but the other new complexes are stable in the atmosphere. The syntheses were repeated several times with excellent reproducibility. Analyses (Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.) and properties of the new complexes are given in Table I.

Spectral, Magnetic, Conductance, and X-Ray Studies.—Infrared spectra (Table II), electronic spectra (Table III), and magnetic and conductance measurements (Table IV) were obtained as described elsewhere.[10] The ir spectra of the new complexes are characterized by the absence of water bands. Far-ir spectra (Table II) were obtained in Nujol mulls between high-density polyethylene windows on a Perkin-Elmer 621 spectrophotometer. A North American Philips X-ray diffractometer was utilized for X-ray powder diffraction patterns. The main lines and relative intensities of the X-ray patterns are represented schematically in Figure 1.

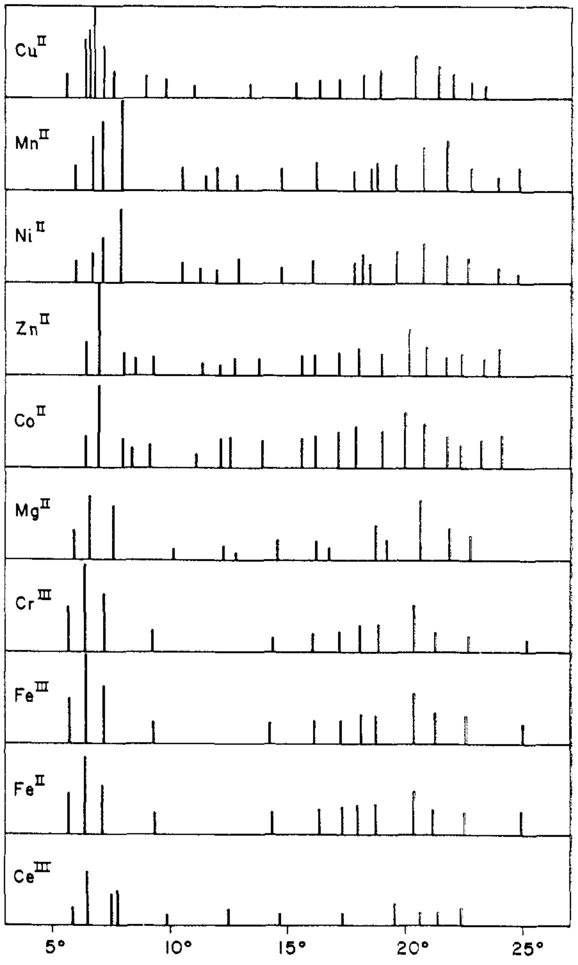

Figure 1.—Schematic representation of the X-ray powder diffraction patterns of tri-*n*-butylphosphine oxide–metal complexes.

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TABLE II

INFRARED DATA FOR TRI-*n*-BUTYLPHOSPHINE OXIDE–METAL COMPLEXES (CM^{-1})[d]

			Ionic T_d ClO_4^-		Vibrational modes of coordinated	ν_{M-O}		ν_{ligand} in the far-ir
Compound	ν_{P-O}	$\Delta\nu_{P-O}$	ν_3	ν_4	C_{3v} $OClO_3$[a]	M–ligand	M–$OClO_3$	spectrum
TBPO	1157 s							585 m, 550 m, 505 sh, 475 m, 402 m, 380 m, 363 m, 346 w, 310 w, b
$[Mg(TBPO)_4](ClO_4)_2$	1132 s	−25	1069 vs	619 vs		460 m		582 sh, 554 w, 506 sh, 470 sh, 402 sh, 388 s, 350 sh, 305 m
$[Cr(TBPO)_4(OClO_3)_2](ClO_4)$	1120 s	−37	1076 s	622–610 vs,[b] b	1150 s, 1030 s, 930 s, 642 sh, 622–610 vs, b,[b] 600 sh, 480 sh, 460 s	450 s	337 s	575 sh, 550 sh, 508 sh, 470 sh, 402 sh, 375 s, 310 sh
$[Mn(TBPO)_4](ClO_4)_2$	1130 vs	−27	1078 vs	623 vs		454 vs		580 sh, 550 w, 502 sh, 475 s, 402 sh, 380 s, 345 sh, 305 w
$Fe(TBPO)_4(OClO_3)_2$	1128 vs	−29	*c*		1150 s, 1030 s, 930 sh, 640 sh, 620 vs, b, 602 sh, 480 sh, 460 s	438 s, sh	290 m–s	575 sh, 550 sh, 504 sh, 470 sh, 402 s, 330 s, 345 sh
$[Fe(TBPO)_4(OClO_3)_2](ClO_4)$	1106 s, b	−51	1068 s, b	630 s	1140 s, 1030 s, 910 sh, 635 s, sh, 619 vs, 599 sh, 480 sh, 455 s	440 vs	315 s	580 sh, 555 w, 500 sh, 475 sh, 407 s, 380 s, b, 350 sh
$[Co(TBPO)_4](ClO_4)_2$	1118 s	−39	1080 vs	620 vs		480 s		580 sh, 551 m, 499 sh, 470 sh, 402 m, 383 s, 345 sh, 307 w
$[Ni(TBPO)_4](ClO_4)_2$	1126 s	−31	1092 vs	618 vs		464 s		580 sh, 550 sh, 505 sh, 475 sh, 402 sh, 380 s, 345 sh, 306 w
$[Cu(TBPO)_4](ClO_4)_2$	1108 s, sh	−49	1080 s, b	623 vs		470 vs[b]		585 sh, 559 m, 503 sh, 470 vs,[b] 404 sh, 389 s, 348 sh, 301 sh
$[Zn(TBPO)_4](ClO_4)_2$	1113 vs	−43	1085 vs	621 vs		462 s		582 sh, 554 w, 506 sh, 470 sh, 402 sh, 384 s, 345 sh, 306 w
$[Ce(TBPO)_4(OClO_3)_2](ClO_4)$	1105 s	−52	1076 s	632 vs	1160 vs, b, 1030 s, b, 930 s, 638 s, 620 s, 605 sh, 482 vs	390 s	333 s	580 sh, 555 w, 504 sh, 470 sh, 400 sh, 380 sh, 300 sh

[a] C_{3v} $OClO_3$ vibrations were assigned as follows in $[Cu(H_2O)_2(OClO_3)_2]$ (cm^{-1}):[13] ν_4 1158, ν_1 1030, ν_2 920, ν_3 648, ν_5 620, 605, ν_6 480, 460. Similar assignments are made for the bands observed in the Cr(III), Fe(II), Fe(III), and Ce(III) complexes. [b] Overlapping bands. [c] A shoulder occurring at 1090 cm^{-1} is assigned to a ligand vibration at this position (see text). [d] Abbreviations: s, strong; m, medium; w, weak; b, broad; sh, shoulder; v, very.

Discussion

Complexes Involving Coordinated Perchlorate.—The experimental data given in Tables II–IV and Figures 1–3 allow the characterization of most of the complexes reported. Coordination to the metal through the phosphoryl oxygen of the ligand in all cases examined is demonstrated by the negative ν_{P-O} shifts (Table II).[11] The free ligand exhibits the following ir absorptions in the 1250–900-cm^{-1} region: 1230 (s), 1157 (vs) (ν_{P-O}), 1090 (s), 1048 (m), 1000 (m), 966 (m), 900 (s). This spectrum is in good agreement with that reported for TBPO.[12] The far-ir spectrum of TBPO (600–300 cm^{-1}) is given in Table II. The ir spectra of the Cr(III), Fe(II), Fe(III), and Ce(III) complexes provide definitive evidence for the presence of coordinated perchlorate groups (Table II).[13] In fact, bands attributable to vibrational modes of C_{3v} $OClO_3$[13] were

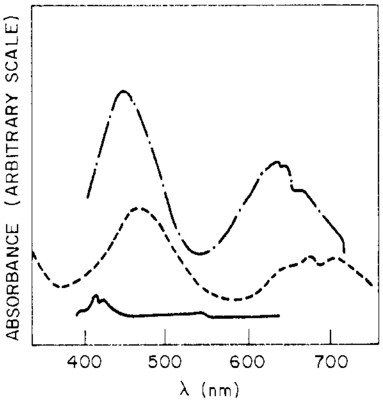

Figure 2.—Electronic spectra (350–750 nm) of $[Mn(TBPO)_4](ClO_4)_2$ in nitromethane (——) and of $[Cr(TBPO)_4(OClO_3)_2](ClO_4)$ in Nujol mull (– – – –) and in nitromethane (—·—).

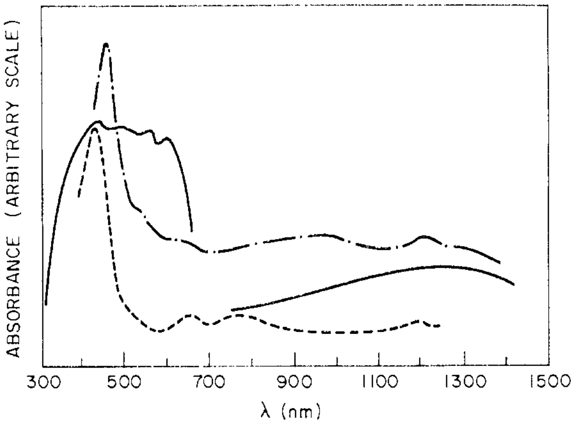

Figure 3.—Electronic spectra (300–1500 nm) of $[Ni(TBPO)_4](ClO_4)_2$ in Nujol mull (——), in nitromethane (– – – –), and in nitromethane in the presence of excess TBPO (—·—).

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

(12) L. L. Burger, *J. Phys. Chem.*, **62**, 590 (1958).

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Table III

Electronic Spectra of Tri-*n*-butylphosphine Oxide–Metal Complexes[a]

Complex	Medium	λ_{max}, nm (ϵ_{max})
$[Cr(TBPO)_4(OClO_3)_2](ClO_4)$	Nujol mull	466 s, b, 647 sh, 671 s, 706 s
	5×10^{-3} *M* in CH_3NO_2	456 (45), 629 (37), 646 (36), 669 (31), 709 sh
$[Mn(TBPO)_4](ClO_4)_2$	Nujol mull	304 s, b, 415–500 w, b
	38×10^{-3} *M* in CH_3NO_2	415 (0.8), 427 (0.6), 561 sh
$Fe(TBPO)_4(OClO_3)_2$	Nujol mull	312 s, 473 sh, 735 sh, 1000–1500 m, vb (max at *ca.* 1350)
	7.8×10^{-3} *M* in CH_3NO_2	<380 (>300), 1453 b (17)
$[Fe(TBPO)_4(OClO_3)_2](ClO_4)$	Nujol mull	343 s
	In CH_3NO_2	<380 (>2000)
$[Co(TBPO)_4](ClO_4)_2$	Nujol mull	500 sh, 560 s, 586 s, 608 s, sh, 633 vs, 1382 s, 1573 s, b, 1735 s
	1.4×10^{-3} *M* in CH_3NO_2	500 sh, 562 (233), 581 (307), 607 (328), 635 (376), 1370 (64), 1600 (71), 1805 (65)
	1.4×10^{-3} *M* in 0.1 *M* solution of TBPO in CH_3NO_2	500 sh, 558 (269), 584 (354), 606 (385), 630 (431), 1390 (78), 1595 (82), 1780 (79)
$[Ni(TBPO)_4](ClO_4)_2$	Nujol mull	440 s, 510 sh, 555 s, 595 s, 1200–1350 w, b
	8×10^{-3} *M* in CH_3NO_2	425 (26), 650 (6), 770 (6), 1190 (5.5)
	4×10^{-3} *M* in 0.1 *M* solution of TBPO in CH_3NO_2	428 sh, 442 (54), 452 sh, 470 sh, 500 sh, 694 (18), 960 (18), 1212 (18)
$[Cu(TBPO)_4](ClO_4)_2$	Nujol mull	845 s, b
	1.8×10^{-2} *M* in CH_3NO_2	812 (44)
$[Ce(TBPO)_4(OClO_3)_2](ClO_4)$	Nujol mull	282 vs, 379 m
	In CH_3NO_2	<380 (>160)

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

observed in the above compounds, and only the assignments made for the ν_6 mode are tentative, owing to overlaps with ligand and ν_{M-O} vibrations. Tentative assignments of ν_{M-O} (ligand) vibrations are given for all the complexes in Table II. These bands are in the same region as the ν_{M-O} vibrations reported for TMPO metal complexes.[14] The four complexes discussed exhibit additional strong bands in the 340–290-cm^{-1} region, which are absent in the rest of the complexes reported. This is the region in which M–O stretching modes occur in metal compounds involving coordinated XO_3 or XO_4 anions (X = N, P, Cl, S, etc.).[15] Moreover, Hezel and Ross stress the point that the only reliable criterion for the detection of coordination in MXO_4 compounds is the discovery of an M–O frequency.[16] These bands are, therefore, assigned as ν_{M-O} (perchlorate) (Table II).

The electronic spectrum of the Cr(III) complex exhibits splittings of the (d–d) bands (Table III, Figure 2), and is characteristic of Cr(III) in a tetragonally distorted octahedral ligand field.[17,18] The common coordination number for Cr(III) is 6, and only a few examples of tri-, tetra-, and pentacoordinated Cr(III) compounds have been reported.[19] The accommodation of more than four TBPO molecules in the first coordination sphere of Cr(III) is obviously sterically hindered, and the metal ion is stabilized in its preferred hexacoordinated configuration by coordination of two monodentate perchlorate groups. In nitromethane this complex is dissociated and behaves as a 3:1 electrolyte (Table IV). A similar behavior has been reported for $M(TMPO)_4(OClO_3)^+$ complexes (M = 3d metal ion).[5] The electronic spectrum of the Cr(III) complex in nitromethane is substantially different from the solid state spectrum of this compound (Table III, Figure 2) and may be attributed to a solvation product of the type $[Cr(TBPO)_4(CH_3NO_2)_2]^{3+}$. The Fe(II) and Fe(III) complexes are also dissociated in nitromethane (Table IV). The X-ray powder diffraction patterns of the Cr(III), Fe(II), and Fe(III) complexes are almost identical (Figure 1) and these compounds are isomorphous. The solid-state electronic spectrum of the Fe(II) complex is typical of a tetragonal compound of the type FeL_4X_2.[18,20] The very broad band (Table III) which covers the region between 1000 and 1500 nm is interpreted in terms of overlap of the $^5A_{1g} \leftarrow {}^5B_{2g}$ and $^5B_{1g} \leftarrow {}^5B_{2g}$ transitions, if a $^5B_{2g}$ ground state is assumed.[18,20] The formulation of the complexes discussed as $[M(TBPO)_4(OClO_3)_2](ClO_4)$ [M = Cr(III), Fe(III)] and $Fe(TBPO)_4(OClO_3)_2$ is justified from the evidence presented above.

Table IV

Magnetic Moments (297°K) and Molar Conductivities of 10^{-3} *M* Nitromethane Solutions (25°) of TBPO–Metal Complexes

Complex	$10^6\chi_M^{cor}$	μ_{eff}, BM	Λ_M, ohm^{-1} cm^2 mol^{-1}	Type of conductor
$[Mg(TBPO)_4](ClO_4)_2$	Diamagnetic		185	2:1
$[Cr(TBPO)_4(OClO_3)_2](ClO_4)$	6,430	3.91	237	3:1
$[Mn(TBPO)_4](ClO_4)_2$	14,279	5.83	175	2:1
$Fe(TBPO)_4(OClO_3)_2$	11,265	5.18	188	2:1
$[Fe(TBPO)_4(OClO_3)_2](ClO_4)$	14,492	5.89	252	3:1
$[Co(TBPO)_4](ClO_4)_2$	9,690	4.79	185	2:1
$[Ni(TBPO)_4](ClO_4)_2$	5,682	3.68	164	2:1
$[Cu(TBPO)_4](ClO_4)_2$	1,581	1.94	175	2:1
$[Zn(TBPO)_4](ClO_4)_2$	Diamagnetic		190	2:1
$[Ce(TBPO)_4(OClO_3)_2](ClO_4)$	3,043	2.69	117	1:1

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(19) D. J. Machin, D. F. C. Morris, and E. L. Short, *J. Chem. Soc.*, 4658 (1964); G. W. A. Fowles, P. T. Greene, and J. S. Wood, *Chem. Commun.*, 971 (1967); E. C. Alyea, J. S. Basi, D. C. Bradley, and M. H. Chisholm, *ibid.*, 495 (1968).

(20) N. S. Gill, *J. Chem. Soc.*, 3512 (1961).

The X-ray pattern of the Ce(III) complex differs from those of the isomorphous complexes discussed (Figure 1). The larger size of the cerous ion allows, presumably, the assumption of a configuration closer to pure octahedral than in the cases of the 3d metal ions. The Ce(III) complex is almost negligibly dissociated in nitromethane, as indicated by its conductance (Table IV), which is slightly higher than that observed in 1:1 electrolytes.[21] Complexes of Ce(III) with organophosphoryl compounds, involving coordinated perchlorate groups (*e.g.*, $\mathrm{[Ce(DMMP)_6(OClO_3)](ClO_4)_2}$; DMMP = dimethyl methylphosphonate) do not dissociate when dissolved in nitromethane.[22] Coordination numbers higher than 6 are not uncommon in Ln(III) compounds.[22,23] However, the Ce(III) complex does not exhibit bands attributable to bidentate perchlorato groups (*e.g.*, the ν_8 mode at 1220–1200 $\mathrm{cm^{-1}}$)[13] and is, thus, formulated as $\mathrm{[Ce(TBPO)_4(OClO_3)_2](ClO_4)}$.

Complexes of the Type $\mathrm{[M(TBPO)_4]^{2+}}$.—Essentially tetrahedral ligand field symmetries may be assigned to the Ni(II),[6] Mn(II), Co(II), and Zn(II) complexes, on the basis of the spectral, magnetic, conductance, and X-ray evidence (Tables II–IV). The Co(II) and Zn(II) complexes are isomorphous, as demonstrated by the fact that their X-ray patterns are identical (Figure 1). The electronic spectrum and magnetic moment of the Co(II) complex (Tables III, IV) are very similar to those reported for the TPPO[2] and TMPO[4] analogs. A $\mathrm{T_d}$ symmetry is thus assigned to the metal ions in these two complexes, which are formulated as $\mathrm{[M(TBPO)_4](ClO_4)_2}$. Addition of excess TBPO in nitromethane solutions of the Co(II) complex does not lead to the formation of higher coordinated species (Table III). The electronic spectrum of the Co(II) complex allows the calculation of the spectrochemical parameters[7,8,24] for TBPO toward tetrahedral Co(II): ν_2 is assigned at 6650 $\mathrm{cm^{-1}}$ and ν_3 at 16,370 $\mathrm{cm^{-1}}$ (Table III). These assignments yield the following values: $\Delta = 3800 \pm 100\ \mathrm{cm^{-1}}$, $B' = 761\ \mathrm{cm^{-1}}$, $\beta = (B'/967) = 0.79$, $\lambda' = 219 \pm 20\ \mathrm{cm^{-1}}$. Thus, TBPO has the following position in the spectrochemical series toward tetrahedral Co(II): TMNO (4780 ± 20)[7] > azide (3920)[24] > TMPO,[4] TBPO (3800 ± 100) > TPPO (3680)[25] > HMPA (3440 ± 90)[7] > chloride (3100).[25]

The X-ray patterns of the Ni(II) and Mn(II) complexes exhibit great similarity (Figure 1) and these two compounds have about the same structure. The Ni(II) complex was characterized elsewhere and assigned a distorted tetrahedral effective symmetry.[6] As is the case with the TMNO analog,[7] the red rose Ni(II) complex yields yellow-green solutions in organic solvents (nitromethane, acetone, etc.) (Table III, Figure 3), due to formation of hexacoordinated solvation products.[6] Changes in the electronic spectrum are observed upon addition of excess ligand to nitromethane solutions of the Ni(II) complex (Table III, Figure 3). The positions and intensities of the bands in the spectrum of this complex in the presence of excess TBPO are suggestive of the presence of a pentacoordinated species, *i.e.*, $\mathrm{Ni(TBPO)_5^{2+}}$.[5] An exactly similar behavior was reported for the HMPA analog in the presence of excess ligand,[8] presumably due to formation of $\mathrm{Ni(HMPA)_5^{2+}}$ under these conditions. The Mn(II) complex shows an electronic spectrum (Table III, Figure 2) very similar to that reported for the tetrahedral $\mathrm{Mn(HMPA)_4^{2+}}$.[26] The band intensities in the spectrum of nitromethane solutions of $\mathrm{Mn(TBPO)_4^{2+}}$ are suggestive of an essentially $\mathrm{T_d}$ symmetry.[26] Thus, both the Ni(II) and Mn(II) complexes are assigned an essentially tetrahedral configuration and are formulated as $\mathrm{M(TBPO)_4^{2+}}$.

An interesting feature of the Mn(II) and Ni(II) complexes is that they have an intermediate ligand field symmetry between those assigned to their HMPA[8,26] and TPPO[2] analogs. $\mathrm{M(HMPA)_4^{2+}}$ complexes (M = Mn, Fe, Co, Ni, Zn) have identical X-ray patterns and are tetrahedral.[8,26] TPPO yields $\mathrm{T_d}$ cationic complexes with Co(II) and Zn(II), but the Mn(II) and Ni(II) analogs are of $\mathrm{D_{2d}}$ symmetry, which is intermediate between $\mathrm{T_d}$ and $\mathrm{D_{4h}}$ (planar), owing to considerable bending of the M–O–P groupings.[2] The Mn(II) and Ni(II) complexes reported here have electronic spectra resembling those of the HMPA analogs[8,26] and quite different from those of $\mathrm{M(TPPO)_4^{2+}}$ (M = Mn, Ni).[2] However, a pure $\mathrm{T_d}$ symmetry cannot be assigned to these complexes, since their X-ray patterns differ from those of the $\mathrm{T_d}$ Co(II) and Zn(II) complexes of TBPO (Figure 1). A pure $\mathrm{T_d}$ symmetry is, thus, assigned to the $\mathrm{NiO_4}$ and $\mathrm{MnO_4}$ moieties, but the effective symmetry influencing the metal ions is obviously lower. Lower symmetry components are, presumably, introduced to the ligand field, due to some bending of the M–O–P groupings[2,27] and the steric requirements for accommodation of four bulky TBPO molecules around the metal ion.[27] Further, the magnetic moment of the Ni(II) complex (3.68 BM) is rather low for a pure tetrahedral Ni(II) compound.[7,8] This moment may be attributed to some loss in orbital degeneracy of the $\mathrm{^3T_1(F)}$ ground state, caused by introduction of lower symmetry components.[27]

The X-ray patterns of the Cu(II) and Mg(II) complexes differ from each other and from those of the other complexes reported (Figure 1). Conductance measurements (Table IV) are in favor of the formulation of these compounds as $\mathrm{M(TBPO)_4^{2+}}$. The position of the (d–d) band in the electronic spectrum of the Cu(II) complex[28] may be interpreted in terms of either a symmetry intermediate between distorted $\mathrm{T_d}$

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and D_{4h}[2,29] or a polymeric hexacoordinated tetragonal structure, involving both terminal and bridging ligand molecules.[27] This complex is, therefore, formulated as $[Cu(TBPO)_4]_n(ClO_4)_{2n}$ ($n = 1, 2, \ldots$). No structural assignment can be made for $Mg(TBPO)_4^{2+}$ on the basis of the available data. Finally, the fact that Fe(II) yields $Fe(TBPO)_4(OClO_3)_2$ instead of a tetrahedral cationic complex (as is the case with HMPA[26]) is interpreted in terms of the crystal field stabilization energy favoring a hexacoordinated configuration.[20]

Conclusion

The novel features introduced by the present study are the syntheses of essentially tetrahedral Ni(II) and Mn(II) cationic complexes and a number of cationic and neutral complexes of the type $ML_4(OClO_3)_2^{n+}$ (M = Cr(III), Fe(II), Fe(III), Ce(III); n = 0, 1) with a phosphine oxide (TBPO). In contrast to HMPA, which forms many complexes of the type $M(HMPA)_6^{3+}$ (M = Cr, Fe,[26] Sc, Y, Ln[30]), only four TBPO molecules coordinate to Cr(III), Fe(III), and Ce(III), owing to the bulkiness of the ligand.

The bulkiness of the ligand has, undoubtedly, a decisive effect on the stereochemistry of tetracoordinated cationic Ni(II)[9] and Mn(II) complexes. Thus, the only tetrahedral complexes of the type NiL_4^{2+} reported are those of the very bulky ligands TMNO,[7] HMPA,[8] and TBPO.[6] The fact that TEPO yields a yellow cationic Ni(II) complex,[3] having presumably a D_{2d} symmetry,[2] may be attributed to the smaller size of this ligand. TPPO is, however, a very bulky ligand, and the D_{2d} symmetry of its cationic Mn(II) and Ni(II) complexes[2] may be interpreted in terms of the less severe steric requirement of trigonal than tetrahedral carbon.[5] This is supported by the fact that complexes of the type ML_5^{2+} (M = Fe, Co, Ni, Zn; L = diphenyl methylphosphine oxide) can be isolated.[5] Further, at least two of the three aromatic rings are not coplanar with the plane of symmetry of the electron cloud of the P=O π bond,[31] and the arrangement of the phenyl groups around the metal ion may introduce lower symmetry components to the ligand field. On the other hand, the combination of inductive with the steric effects may influence the stereochemistry imposed to the metal ion by the ligand. In fact, the relative stabilities of metal complexes of a number of dialkyl and diaryl sulfoxides have been interpreted in terms of a combination of steric and inductive effects.[32] For NiL_6^{2+} complexes with 4-substituted pyridine N-oxides, a decrease in the extent of metal to ligand back-bonding with increasing electron-releasing properties of the substituent has been proposed, on the basis of far-ir evidence.[33] Increasing π character of the metal-to-oxygen bond will favor a square-planar rather than tetrahedral configuration.[9] In addition, the extent of back-bonding will affect the lengths of the M–O and O–P bonds and the M–O–P angle[34] and influence, thus, the stereochemistry of the complex.[2] TBPO is a stronger donor toward phenol than TPPO,[35] and the stereochemistries of their Mn(II) and Ni(II) complexes may be interpreted in terms of a combination of inductive (extent of $d\pi-p\pi$ back-bonding) and steric effects. Support to this argument is provided by the fact that with neutral phosphonate esters (DIMP), which are weaker donors than phosphine oxides due to the electron-sink property of the alkoxy oxygen,[12,22,36] not only Ni(II) and Mn(II) but also Co(II) yields a distorted tetrahedral complex of the type $Co(DIMP)_4^{2+}$.[10] A study of the steric and inductive effects influencing the properties of transition and nontransition metal complexes of triorganophosphine oxides and neutral phosphonate and phosphate esters is in progress at this laboratory.

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