

## Hexakis(tris(hydroxymethyl)phosphine oxide)Metal(II) and (III) Perchlorates [1]

C. M. MIKULSKI\*, J. S. SKRYANTZ†, N. M. KARAYANNIS†, L. L. PYTLEWSKI and L. S. GELFAND

*Department of Chemistry, Drexel University, Philadelphia, Pa. 19104, U.S.A.*

Received July 7, 1977

*Complexes of tris(hydroxymethyl)phosphine oxide (thpo) with various metal perchlorates were prepared by interaction of ligand and salt in triethyl orthoformate. Characterization of the new complexes by means of spectral, magnetic and conductance studies led to their formulation as  $[M(thpo)_6](ClO_4)_n$  ( $M = Mg^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Nd^{3+}$ ;  $n = 2$  or  $3$ ), involving low symmetry hexacoordinated complex cations and exclusively ionic perchlorate. Thpo acts as a unidentate ligand, coordinating through the P=O oxygen. The tendency of thpo to form 6:1 cationic metal complexes, in contrast to other phosphine oxides, which yield 4:1 or 5:1 complexes with the same metal perchlorates, is attributed to its lower ligand-field strength. The metal–thpo bonds are weaker than the corresponding bonds in the complexes of other phosphine oxides. This leads to a less sterically crowded environment around the central metal ion, and allows the accommodation of six thpo molecules in the first coordination sphere.*

### Introduction

Metal complexes of triorganophosphine oxides have been the subject of numerous studies in recent years [2–12]. Bulky phosphine oxides (such as triphenyl and tri-*n*-butyl- (tppo and tbpo, respectively)) invariably form 4:1 complexes with 3d metal perchlorates [2–4, 7–11], while trimethylphosphine oxide (tmpo) was found to yield both 4:1 and 5:1 complexes with the same metal perchlorates [2, 6]. Quite recently, de Bolster *et al.*, reported that 5:1 complexes of tppo with 3d metal tetrafluoroborates can be isolated in certain cases [12]. An analogous bulky ligand, hexamethylphosphoramide (hmpa) also forms 4:1 complexes with most metal perchlorates [13]. In contrast to the above ligands, dimethyl

methylphosphonate (dmmp) and trimethyl phosphate (tmp) were found by these laboratories to produce many 5:1 and 6:1 complexes with various 3d and other metal perchlorates [14–16]. During comparisons of the stoichiometries of the latter metal complexes to those of tmpo, we attributed the higher ligand to metal ratios observed with phosphonate or phosphate methylesters to the fact that they are weaker ligands than tmpo. Weaker (longer) M–O bonds are, thus, formed during the coordination of these esters (relative to tmpo), and the accommodation of one additional ligand molecule in the first coordination sphere of the metal ion becomes possible [14, 15].

We were recently interested in studying the coordination complexes of a phosphine oxide ligand of intermediate strength between tmpo, on the one hand, and tmp and dmmp, on the other. Such a ligand is tris(hydroxymethyl)phosphine oxide (thpo;  $(HOCH_2)_3P=O$ ). This ligand has similar steric features to those of tmpo, dmmp and tmp, and its  $\Sigma\sigma_\phi$  value (sum of Kabachnik substituent constants for organophosphorous compounds [17, 18]) is  $-1.65$  vs.  $-2.88$  for tmpo,  $-1.20$  for dmmp and  $-0.36$  for tmp. Previous work by these laboratories has established the interdependence between  $\Sigma\sigma_\phi$  and ligand-field strength for various organophosphoryl ligands [19]. Accordingly, we have undertaken synthetic and characterization studies of metal perchlorate complexes with thpo. The results of this work are reported in the present paper. It should be mentioned at this point that, prior to this work, only one thpo complex (with  $CuCl_2$ ) had been reported in the literature [5].

### Experimental

#### Chemicals

Reagent grade hydrated metal perchlorates and organic chemicals were used throughout this work. The thpo sample (product of Oldbury Electrochemical Co.) was a viscous liquid. It was slowly crystallized from ethanol (m. p. of solid thpo 54–55 °C) [20].

\**Department of Chemistry & Physics, Beaver College, Glenside, Pa. 19038, U.S.A.*

†*Amoco Chemicals Corporation, Naperville, Ill. 60540, U.S.A.*

TABLE I. Analytical Data for  $M(\text{thpo})_6(\text{ClO}_4)_n$  Complexes.

$M^{n+}$	Color	%C		%H		%P		%Metal	
		Calc	Found	Calc	Found	Calc	Found	Calc	Found
$\text{Mg}^{2+}$	Colorless	20.33	20.62	5.12	5.52	17.47	18.01	2.06	2.23
$\text{Cr}^{3+}$	Dark green	18.16	18.84	4.57	4.86	15.61	15.57	4.37	3.91
$\text{Mn}^{2+}$	Pale yellow	19.76	20.29	4.97	5.40	16.98	16.73	5.02	4.90
$\text{Fe}^{2+}$	Deep yellow	19.74	20.59	4.97	5.53	16.97	17.17	5.10	4.83
$\text{Fe}^{3+}$	Yellow-brown	18.10	17.54	4.56	4.86	15.56	14.97	4.67	4.29
$\text{Co}^{2+}$	Brick red	19.68	20.38	4.96	5.31	16.92	16.26	5.37	4.84
$\text{Ni}^{2+}$	Deep yellow	19.69	20.25	4.96	5.26	16.92	16.37	5.35	4.94
$\text{Cu}^{2+}$	Green	19.60	20.07	4.94	4.76	16.85	16.25	5.76	5.33
$\text{Zn}^{2+}$	Colorless	19.57	20.15	4.93	5.34	16.82	16.58	5.92	5.75
$\text{Cd}^{2+}$	Colorless	18.77	18.61	4.73	4.96	16.14	15.77	9.76	10.12
$\text{Nd}^{3+}$	Pale blue-violet	16.85	17.31	4.24	3.82	14.48	14.09	11.23	11.75

### Synthetic Procedure

Ligand and hydrated metal salt were dissolved separately in the minimum necessary amount of triethyl orthoformate, a dehydrating agent [21], and the resulting solutions were treated under stirring, at *ca.* 60 °C, for 30 min–1 hr. Then, the two solutions were combined at a 6.2:1 ligand to metal molar ratio. The reaction mixture was treated for about 30 min at 60 °C, under stirring, and then, the solvent was allowed to evaporate slowly (30–40 °C). The residue was, in all cases examined, a very viscous liquid product. Treatment of these products with anhydrous diethyl ether or n-butanol, under stirring, increases their viscosity considerably. The final products of these treatments can be characterized either as extremely viscous liquids or as soft amorphous solids. The synthesis of each of the new complexes was repeated several times: occasionally, the ether or alcohol treatment led to the isolation of small amounts of very deliquescent, crystalline solids, but in most cases, the soft solids mentioned above were obtained. Analytical results (A. Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, W. Germany; Table I) for the crystalline and soft solid products of the same metal ion were virtually identical. Hence, the soft solid products, which were available in substantial amounts, were subjected to characterization studies.

After their preparation, the new complexes were washed with several portions of diethyl ether and stored in an evacuated desiccator over calcium chloride. The dry products are very hygroscopic: brief exposure to atmospheric moisture results in the appearance of the  $\delta_{\text{H-O-H}}$  water band at *ca.* 1630  $\text{cm}^{-1}$  [22] (the  $\nu_{\text{OH}}$  (water) band overlaps with the  $\nu_{\text{OH}}$  band of the hydroxymethyl group (*vide infra*)). Ir spectra of dry complex samples between IRTRAN 2(ZnS) windows (sampling in the dry-box, under dry  $\text{N}_2$  atmosphere) do not exhibit the  $\delta_{\text{H-O-H}}$  band at

1630  $\text{cm}^{-1}$ . It was also established that in Nujol mulls of the new complexes, the mineral oil protects these compounds from the atmospheric moisture. The new metal complexes are insoluble in ether, and sparingly soluble in alcohols. The  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Nd}^{3+}$  complexes are generally very sparingly soluble in organic media; whereas, the rest of the new complexes dissolve in some polar solvents, including nitromethane.

### Spectral, Magnetic and Conductance Measurements

Ir spectra (Table II) were obtained both on neat samples and hexachlorobutadiene and Nujol mulls of the metal complexes, between IRTRAN 2 (4000–750  $\text{cm}^{-1}$ ) and high density polyethylene (800–200  $\text{cm}^{-1}$ ) windows, by using a Perkin-Elmer 621 Spectrophotometer. Electronic spectra (Table III) were obtained on Nujol mulls of the new complexes, applied on filter or thin tissue paper [16], by using a Beckman DK-2A Spectrophotometer. Magnetic susceptibility (Table III) and conductance measurements were performed by methods described elsewhere [23]. Molar conductivities of  $10^{-3}$  M nitromethane solutions at 25 °C of the new complexes were as follows:  $\Lambda_{\text{M}}$ ,  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ :  $\text{Mg}^{2+}$ , 128;  $\text{Cr}^{3+}$ , 207;  $\text{Mn}^{2+}$ , 125;  $\text{Fe}^{3+}$ , 231;  $\text{Ni}^{2+}$ , 129;  $\text{Cu}^{2+}$ , 127;  $\text{Zn}^{2+}$ , 132. The rest of the complexes are not sufficiently soluble in organic media for conductance measurements, as already mentioned. All samples for the above measurements were prepared in the dry-box.

### Discussion

#### Infrared Spectra and Molar Conductivities

Analytical data suggest that the new metal complexes are of the general type  $M(\text{thpo})_6(\text{ClO}_4)_n$  (Table I). The  $\Lambda_{\text{M}}$  values for nitromethane solutions

TABLE II. Infrared Spectra (4000–600 cm<sup>-1</sup>) of M(thpo)<sub>6</sub>(ClO<sub>4</sub>)<sub>n</sub> Complexes (cm<sup>-1</sup>)<sup>a</sup>.

Compound	$\nu_{\text{OH}}$	$\nu_{\text{P=O}} + \nu_3(\text{ClO}_4)^{\text{b}}$	$\nu_4(\text{ClO}_4)$	Other Ligand Bands
thpo	3300vs, vb	1130vs	—	2889s, 2815s, sh, 2060w, 1418s, b, 1382s, sh, 1305w, 1188s, sh, 1038vs, 925s, sh, 890s, 865s, b
M <sup>n+</sup> = Mg <sup>2+</sup>	3400vs, vb	1102vs, sh, 1080vs, b	624s	2900s, 2825s, sh, 2060w, 1418m–s, 1310w, b, 1190s, sh, 1036vs, 922s, sh, 890s, b, 865s, sh
Cr <sup>3+</sup>	3440vs, vb	1111vs, sh, 1090vs, b	621s	2910s, 2840s, sh, 2058w, 1419s, 1390s, sh, 1307w, b, 1190s, sh, 1034vs, 925s, sh, 897s, b, 870s, b
Mn <sup>2+</sup>	3390vs, vb	1100vs, vb	619s	2899s, 2815s, 2055w, 1414s, 1385s, sh, 1300w, b, 1185s, sh, 1032vs, 919s, sh, 893s, b, 868s, sh
Fe <sup>2+</sup>	3410vs, vb	1116s, sh, 1088 vs, b	623s	2901s, 2840s, 2055w, 1417s, 1382s, sh, 1305w, b, 1187s, sh, 1037vs, 920s, sh, 886s, b, 866s, sh
Fe <sup>3+</sup>	3445vs, vb	1085vs, vb	617s	2905s, 2815s, sh, 2065w, 1412m, 1397m, sh, 1300w, b, 1185s, sh, 1033vs, 924m, sh, 882m–s, b, 860m–s, sh
Co <sup>2+</sup>	3410vs, vvb	1102vs, 1093vs	621s	2902s, 2841s, 2058w, 1418s, 1388s, sh, 1310w, b, 1182s, sh, 1040vs, 921s, sh, 895s, b, 871s, b
Ni <sup>2+</sup>	3395vs, b	1110vs, 1097vs, sh	623s	2905s, 2830s, b, 2060w, 1417s, 1385s, sh, 1310w, b, 1190s, sh, 1039s, 922s, sh, 885s, b, 867s, sh
Cu <sup>2+</sup>	3390vs, vb	1099vs, 1080vs, b	618s	2902s, 2840s, 2060w, 1414s, 1396s, sh, 1298w, b, 1195s, sh, 1032s, 919s, sh, 887s, b, 862s, sh
Zn <sup>2+</sup>	3425vs, b	1111vs, 1095vs, b	620s	2901s, 2825s, b, 2055w, b, 1421s, 1295s, sh, 1305w, b, 1184s, sh, 1036s, 925s, sh, 897s, b, 875s, sh
Cd <sup>2+</sup>	3395vs, b	1103vs, 1092vs	617s	2899s, 2835s, sh, 2050w, b, 1417s, 1387s, sh, 1312w, 1190s, sh, 1038s, 926s, sh, 898s, b, 868s, sh
Nd <sup>3+</sup>	3400vs, vb	1119vs, 1100vs, b	626s	2904s, 2818s, 2045w, b, 1415s, 1380s, b, 1300w, vb, 1192s, sh, 1037s, 923s, sh, 898s, b, 859s, sh

<sup>a</sup>Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder. <sup>b</sup> $\nu_{\text{P=O}}$  and  $\nu_3(\text{ClO}_4)$  overlap in the spectra of the metal complexes (see text). In the case involving two maxima in this region, the higher frequency band is most probably due to  $\nu_{\text{P=O}}$  [4, 5] and the lower frequency band due to  $\nu_3(\text{ClO}_4)$  [26].

TABLE III. Electronic Spectra (Nujol mull) and Magnetic Moments (300 °K) of M(thpo)<sub>6</sub>(ClO<sub>4</sub>)<sub>n</sub> Complexes<sup>a</sup>.

M <sup>n+</sup>	$\lambda_{\text{max}}$ , nm	$10^6 \chi_{\text{M}}^{\text{cor}}$ , cgsu	$\mu_{\text{eff}}$ , BM
Cr <sup>3+</sup>	<300vvs, 425s, b, 575s, sh, 612s	6,021	3.82
Mn <sup>2+</sup>	<300vvs, 530w	15,291	6.08
Fe <sup>2+</sup>	<300vvs, 780m, 1015m, 1300m–s, b	11,728	5.33
Fe <sup>3+</sup>	<300vvs	14,301	5.86
Co <sup>2+</sup>	<300vvs, 490s, sh, 508s, 740w, sh, 1350m–s, b	9,646	4.96
Ni <sup>2+</sup>	<450vvs, 745m, 1010m, sh, 1280m, b	4,802	3.41
Cu <sup>2+</sup>	<400vvs, 845s, b	1,830	2.10
Nd <sup>3+</sup>	<300vvs, 515m, b, 575m, b, 615w, b	5,162	3.53

<sup>a</sup>Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder.

of the new complexes suggest that the trivalent metal ion complexes behave as 1:3 electrolytes, and those of the divalent metal ions as 1:2 electrolytes [24]. These values are, in most cases, on the low side of the ranges of values reported for 1:3 or 1:2 electrolytes [24]. As far as the neat new complexes are concerned, the  $\Lambda_{\text{M}}$  values, in combination with the ir evidence, which establishes the complete absence of

coordinated perchlorato groups (*vide infra*), demonstrate that these compounds involve exclusively ionic ClO<sub>4</sub>, and are of the general type [M(thpo)<sub>6</sub>](ClO<sub>4</sub>)<sub>n</sub>. The relatively low  $\Lambda_{\text{M}}$  values in nitromethane might be due to some exchange between thpo and perchlorato ligands in solution [25].

The ir spectrum of the ligand sample (crystallized from ethanol) is almost identical to that reported by

Anteunis *et al.* [20], viz. ( $\text{cm}^{-1}$ ): 3300vs, vb ( $\nu_{\text{OH}}$ ), 2889s and 2815s, sh ( $\nu_{\text{CH}_2}$ ), 2060w, 1418vs, b ( $\delta_{\text{CH}_2}$ ), 1305w, 1188s, sh, 1130vs ( $\nu_{\text{P=O}}$ ), 1038vs ( $\delta_{\text{C-O}}$ ), 925s, sh, 890s, 865s, b. Metal complex formation leads to positive frequency shifts of the  $\nu_{\text{OH}}$  band and negative frequency shifts of the  $\nu_{\text{P=O}}$  absorption (Table II). The latter band overlaps in the spectra of the metal complexes with the  $\nu_3$  mode of ionic ( $\text{T}_d$ ) perchlorate [26], which occurs at 1100–1070  $\text{cm}^{-1}$ . The rest of the ligand bands from 4000–800  $\text{cm}^{-1}$  remained practically unchanged in the spectra of the metal complexes and there is no evidence suggesting the presence of coordinated  $\text{ClO}_4$  [27]. Thus, no intensification of the absorption at 925  $\text{cm}^{-1}$  (region of the  $\nu_1$  mode of  $\text{ClO}_4$ , ir-inactive in compounds involving exclusively ionic perchlorate), or splittings of the  $\nu_3(\text{ClO}_4)$  mode are observed [27]. The lower frequency ir spectra of the complexes show generally poor resolution, and identification of the metal-sensitive bands was not possible. The  $\nu_4$  mode of ionic perchlorate appears as a medium-to-strong, sharp band at *ca.* 620  $\text{cm}^{-1}$  in the spectra of all the new complexes.

The negative frequency shifts of  $\nu_{\text{P=O}}$  clearly demonstrate the coordination of thpo through the phosphoryl oxygen [2, 28]. A similar frequency shift was reported for  $\text{CuCl}_2 \cdot 4(\text{thpo})$  ( $\nu_{\text{P=O}}$  at 1106  $\text{cm}^{-1}$ ) [5]. The ligand could also, conceivably, form bonds to the metal ion through one or more hydroxymethyl oxygens [29]. The fact that  $\nu_{\text{OH}}$  in the metal complexes occurs in the same region (3500–3400  $\text{cm}^{-1}$ ) as the  $\nu_{\text{OH}}$  mode in compounds characterized by the  $-\text{CH}_2\text{OH}$  group (*e.g.*, alcohols) [30], rules out this possibility. This is also supported by the positive frequency shifts of the  $\nu_{\text{OH}}$  mode of the free ligand upon metal complex formation. The occurrence of this vibrational mode at lower frequency in the free ligand is presumably due to intra- or intermolecular H-bonding [20, 31, 32]. The association of the P=O oxygen with hydrogen in free thpo is shown by the relatively low frequency of the  $\nu_{\text{P=O}}$  mode (1130  $\text{cm}^{-1}$ ). In fact, if no H-bonding was occurring, thpo should exhibit the  $\nu_{\text{P=O}}$  mode at a frequency intermediate between those of trialkyl- (*e.g.*, tbp:  $\nu_{\text{P=O}}$  at 1157  $\text{cm}^{-1}$  [8]) and triphenyl- ( $\nu_{\text{P=O}}$  at 1195  $\text{cm}^{-1}$  [9]) phosphine oxides, on the basis of the  $\Sigma\sigma_\phi$  substituent values [17, 18, 33].

#### Electronic Spectra and Magnetic Moments

The magnetic moments of the new metal complexes are within the range of values corresponding to high-spin hexacoordinated compounds of these metal ions [34]. Only the Ni(II) complex has a somewhat higher  $\mu_{\text{eff}}$  value than expected for a pure  $\text{O}_h$  symmetry. However, the overall symmetry influencing the central metal ions in the complexes is definitely lower than  $\text{O}_h$ , in view of the non-linearity of the M–O–P groupings [4, 35] and the arrangement

of the six bulky thpo ligands in space [36, 37]. Several low symmetry hexacoordinated Ni(II) complexes exhibiting  $\mu_{\text{eff}}$  values of *ca.* 3.40 BM have been reported [36–39].

The electronic spectra of the new complexes are generally typical of low symmetry hexacoordinated compounds of these metal ions (Table III). Thus, the Cr(III) complex exhibits a split  ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$  transition (575, 612 nm), while the  ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$  (425 nm) band is broad [36]. An approximate Dq calculation towards octahedral Cr(III) (by assuming pure  $\text{O}_h$  symmetry) gives a value of 1683  $\text{cm}^{-1}$ . Thus, thpo appears to be as strong a ligand as 2,6-lutidine N-oxide [23]; dmmp and tmp are considerably weaker ligands (Dq values toward  $\text{O}_h$   $\text{Cr}^{3+}$  in the 1450–1500  $\text{cm}^{-1}$  region [14–16]). The Cu(II) complex exhibits a very broad, strong band at 845 nm, attributable to the  ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$  transition (Dq = 1183  $\text{cm}^{-1}$ ). A similar spectrum was observed for  $\text{CuCl}_2 \cdot 4\text{thpo}$  ((d–d) band at 845 nm), which was characterized as tetragonally distorted octahedral [5]. For the Co(II) complex, the following (d–d) band assignments are made:  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ , 1350;  $\rightarrow {}^4\text{A}_{2g}(\text{F})$ , 508;  ${}^4\text{T}_{1g}(\text{P})$ , 490 nm (Dq = 960  $\text{cm}^{-1}$ ;  $\beta = 0.78$ ). In the case of the Ni(II) complex, the  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$  transition is masked by a strong charge-transfer absorption; the rest of the (d–d) bands are assigned as follows:  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ , 1280;  $\rightarrow {}^1\text{E}_g(\text{D})$ , 1010 [38];  ${}^3\text{T}_{1g}(\text{F})$ , 745 nm (Dq = 784  $\text{cm}^{-1}$ ). The ferrous complex shows a split  ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$  band (780, 1015, 1300 nm), as is quite common in distorted octahedral Fe(II) compounds [40]. The spectrum of the Nd(III) complex did not exhibit satisfactory resolution, as to exhibit the usual splittings in the hypersensitive transition regions ( ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{7/2}$ ,  ${}^2\text{G}_{5/2}$ ) [41]. The maxima of the relatively broad bands are, however, in the same wavelength regions as in the corresponding spectra of hexacoordinated  $\text{Nd}(\text{ClO}_4)_3$  complexes with phenyl-, benzyl- and n-butyl-substituted phosphine oxides [42]. Finally, the (d–d) transitions in the Mn(II) and Fe(III) complexes are masked by charge-transfer bands. It is, nevertheless, noteworthy that neither the Mn(II) complex exhibits a band at *ca.* 320 nm, nor the Fe(III) complex one at *ca.* 350 nm. Bands in these regions were observed in the spectra of pentacoordinated Mn(II) and Fe(III) perchlorate complexes with tppo [4] and diisopropyl methylphosphonate [43]. Hence, the electronic spectral evidence favors coordination number six in these cases, too [14–16].

In conclusion, during the preparation of a series of thpo complexes with metal perchlorates, it was established that this ligand invariably forms 6:1 cationic complexes with di- and tri-valent metal ions. As mentioned in the introduction to this paper, we have previously attributed [14–16] the increasing number of coordinated organophosphoryl ligands with about the same steric features ( $\text{CH}_3$ - or  $\text{CH}_3\text{O}$ -substituted)

with decreasing ligand-field strength, to the weakening of the metal-oxygen bond. This makes the immediate environment of the central metal ion less crowded and thus allows the accommodation of additional ligand molecules in the first coordination sphere [14-16]. The  $\Sigma\sigma_\phi$  constant of thpo (-1.65) is relatively close to that of dmmp (-1.20), and considerably lower than that of tmpo (-2.88) [17, 18]. Thus, the formation of 6:1 cationic complexes between thpo and di- or tri-valent metal ions appears to confirm our previous interpretation [14-16]. It is also worth noting that thpo is the first example of a triorganophosphine oxide invariably forming 6:1 complexes with metal perchlorates. The only other 6:1 complexes with a phosphine oxide-type ligand (i.e.,  $RR'R''P=O$ , where all R substituents are bonded through carbon to phosphorous) reported, involve hmpa complexes with the larger lanthanide(III) ions [44, 45].

## References

- C. M. Mikulski, J. S. Skryantz, N. M. Karayannis, L. L. Pytlewski and L. S. Gelfand, *Abstracts, the 168th National Meeting, Amer. Chem. Soc., Atlantic City, N. J., September 8-13 (1974) No. INOR 105.*
- N. M. Karayannis, C. M. Mikulski and L. L. Pytlewski, *Inorg. Chim. Acta Rev.*, **5**, 69 (1971).
- K. Issleib and B. Mitscherling, *Z. anorg. allg. Chem.*, **304**, 73 (1960).
- F. A. Cotton and E. Bannister, *J. Chem. Soc.*, 1873 (1960); E. Bannister and F. A. Cotton, *ibid.*, 1878 (1960).
- D. M. L. Goodgame and F. A. Cotton, *ibid.*, 2298, 3735 (1961).
- 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).
- N. M. Karayannis, C. M. Mikulski, L. L. Pytlewski and M. M. Labes, *Inorg. Chem.*, **9**, 582 (1970).
- N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nucl. Chem.*, **32**, 2629 (1970).
- Idem, ibid.*, **33**, 2691 (1971).
- F. Mani, *Inorg. Nucl. Chem. Lett.*, **7**, 447 (1971).
- M. W. G. de Bolster, I. E. Kortram and W. L. Groeneveld, *J. Inorg. Nucl. Chem.*, **34**, 575 (1972).
- J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **1**, 866 (1962); **2**, 1158 (1963).
- N. M. Karayannis, C. Owens, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nucl. Chem.*, **31**, 2767 (1969).
- N. M. Karayannis, E. E. Bradshaw, L. L. Pytlewski and M. M. Labes, *ibid.*, **32**, 1079 (1970).
- N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta*, **8**, 91 (1974).
- M. I. Kabachnik, *Dokl. Akad. Nauk, SSSR*, **110**, 393 (1956); *Z. Chem.*, **1**, 289 (1961).
- T. A. Mastryukova and M. I. Kabachnik, *J. Org. Chem.*, **36**, 1201 (1971).
- C. M. Mikulski, N. M. Karayannis and L. L. Pytlewski, *J. Inorg. Nucl. Chem.*, **36**, 971 (1974).
- M. Anteunis, M. Verzele and G. Dacremont, *Bull. Soc. Chim. Belg.*, **74**, 622 (1965).
- P. W. N. M. van Leeuwen and W. L. Groeneveld, *Inorg. Nucl. Chem. Lett.*, **3**, 145 (1967).
- I. Gamo, *Bull. Chem. Soc. Japan*, **34**, 760 (1961).
- N. M. Karayannis, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta*, **3**, 415 (1969).
- W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
- J. H. Nelson and R. O. Ragsdale, *Inorg. Chim. Acta*, **2**, 439 (1968); N. M. Karayannis, S. D. Sonsino, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *ibid.*, **4**, 141 (1970).
- B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).
- A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, **4**, 404 (1965); S. F. Pavkovic and D. W. Meek, *ibid.*, **4**, 1091 (1965); M. E. Farago, J. M. James and V. C. G. Trew, *J. Chem. Soc. A*, 820 (1967).
- F. A. Cotton, R. D. Barnes and E. Bannister, *ibid.*, 2199 (1960).
- O. A. Osipov, V. I. Gaivoronskii and A. A. Shvets, *Zh. Neorg. Khim.*, **8**, 2190 (1963).
- V. Imhoff and R. S. Drago, *Inorg. Chem.*, **4**, 427 (1965); P. W. N. M. van Leeuwen, *Rec. Trav. Chim. Pays-Bas*, **86**, 247 (1967).
- N. Filipescu, L. M. Kindley, H. E. Podall and F. A. Serafin, *Can. J. Chem.*, **41**, 821 (1963).
- J. Chatt, R. G. Guy, L. A. Duncanson and D. T. Thompson, *J. Chem. Soc.*, 5170 (1963).
- S. Nomura and R. Hara, *Anal. Chim. Acta*, **25**, 212 (1961).
- B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, **6**, 37 (1964).
- F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **85**, 2402 (1963).
- W. Byers, A. B. P. Lever and R. V. Parish, *Inorg. Chem.*, **7**, 1835 (1968); A. D. van Ingen Schenau, J. C. Verschoor and C. Romers, *Acta Crystallogr.*, **30B**, 1686 (1974).
- W. F. Currier and J. H. Weber, *Inorg. Chem.*, **6**, 1539 (1967); C. V. Berney and J. H. Weber, *ibid.*, **7**, 283 (1968).
- R. Whyman, W. E. Hatfield and J. S. Paschal, *Inorg. Chim. Acta*, **1**, 113 (1967); K. M. Nykerk, D. P. Eyman and R. L. Smith, *Inorg. Chem.*, **6**, 2262 (1967).
- A. N. Specca, N. M. Karayannis, L. L. Pytlewski, L. J. Winters and D. Kandasamy, *ibid.*, **12**, 1221 (1973); A. N. Specca, L. L. Pytlewski and N. M. Karayannis, *J. Inorg. Nucl. Chem.*, **35**, 4029 (1973).
- A. B. P. Lever, *Coord. Chem. Rev.*, **3**, 119 (1968).
- P. Krumholz, *Spectrochim. Acta*, **10**, 277 (1958).
- O. A. Serra, M. L. R. Gibran and A. M. B. Galindo, *Inorg. Nucl. Chem. Lett.*, **8**, 673 (1972).
- N. M. Karayannis, C. Owens, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nucl. Chem.*, **31**, 2059 (1969).
- J. T. Donoghue, E. Fernandez, J. A. McMillan and D. A. Peters, *ibid.*, **31**, 1431 (1969).
- E. Giesbrecht and L. Barbieri-Zinner, *Inorg. Nucl. Chem. Lett.*, **5**, 575 (1969).