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Infrared Studies of Five-Coordinate $[M(II)L_4X]^+$ Complexes of Diphenylmethyl-Phosphine and -Arsine Oxides and their Triphenyl Analogues

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Received May 27, 1969

Infrared data are reported for five-coordinate complexes of diphenylmethylarsine oxide and diphenylmethylphosphine oxide complexes of composition $[M(II)L_4(ClO_4)]ClO_4$, *M = Mn, Fe, Co, Ni Cu, and Zn; L = Ph₂MePO, Ph₂MeAsO.* *These results indicate stronger metal-ligand bonding and a concomitant weaker metal-anion bonding for* $M = Cu^{II}$ *compared with that for complexes of the other ions. A similar effect is observed for related metal complexes of triphenylphosphine oxide and triphenylarsine oxide for which the same basic structure is postulated. There is some evidence that the arsine oxide complexes of iron(II) exhibit a distortion similar to that found for copper(II).*

Introduction

Diphenylmethylarsine oxide has been shown[1,2] to form isomorphous five-coordinate square-pyramidal complexes $[M(II)(Ph_2MeAsO)_4(ClO_4)](ClO_4)$, for M = Mn, Fe, Co, Ni, Cu and Zn. Details of the molecular structure, determined from an X-ray analysis[2] of the cobalt complex, are given in Figure 1. An infrared study has now been made of these complexes and also the related compounds obtained with the corresponding phosphine oxide, diphenylmethylphosphine oxide and the triphenyl analogues, triphenylarsine oxide and triphenylphosphine oxide $(M(II)L_4(ClO_4)_2$, (L = Ph_2MePO, Ph_3AsO, Ph_3PO: M = Mn, Fe, Co, Ni, Cu and Zn). Evidence is presented for a close structural similarity between these complexes.

Results and Discussion

X-ray powder photographs show that the five-coordinate square-pyramidal structure (Figure 1) is adopted by all diphenylmethylarsine oxide and diphenylphosphine oxide complexes of the same composition, *i.e.* $[M(Ph_2MeXO)_4(ClO_4)]ClO_4$ M = Mn, Fe, Co, Ni, Cu, and Zn for both X = P and As (Table I). With triphenylphosphine oxide and triphenylarsine oxide isomorphous complexes of composition $M(Ph_3XO)_4(ClO_4)_2$ can be isolated for M = Mn, Fe, Co, and Ni, with X = P and M = Mn, Co, and Ni for X = As (Table I). The close similarity of the electronic spectra of the cobalt and nickel complexes with those of the diphenylmethyl series (Table II) suggests that the triphenylphosphine oxide and triphenylarsine oxide perchlorate complexes also have a basically square-pyramidal structure, although it was believed earlier that they were four coordinate.[3,4,5] However the cobalt(II) complexes which are members of the isomorphous series (b, Table I) are green whereas those reported by Bannister and Cotton[4] and Tyree and Phillips[3] are blue and undoubtedly tetrahedral. The formation and interconversion of the blue and green forms are discussed in the Experimental Section. While the copper(II) complexes, $Cu(Ph_3XO)_4(ClO_4)_2$, X = P and As, and $Fe(Ph_3AsO)_4(ClO_4)_2$

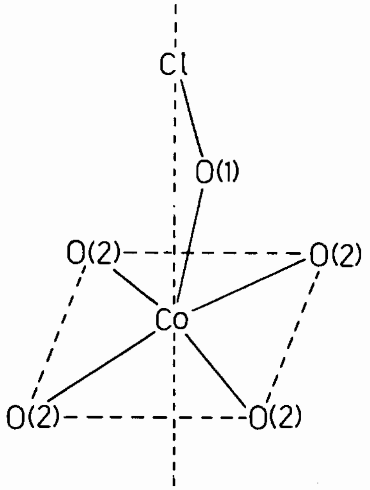

Figure 1. Structure of $[Co(Ph_2MeAsO)_4ClO_4]^+$. The chlorine and cobalt atoms lie on a four-fold crystallographic axis. The coordinated perchlorate oxygen (1) which is disordered is 0.72 Å from this axis and 2.14 (6) Å from the cobalt atom. The cobalt-oxygen (2) (arsine oxide) distance is 2.02 (2) Å and the cobalt atom is 0.32 Å above the plane of the four O (2) atoms.

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(1) J. Lewis, R. S. Nyholm, and G. A. Rodley., *Nature*, *207*, 72 (1965).

(2) P. Pauling, G. B. Robertson, and G. A. Rodley, *Nature*, *207*, 73 (1965).

(3) S. Y. Tyree and D. J. Phillips, *J. Am. Chem. Soc.*, *83*, 1806 (1961).

(4) E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 1878 (1960).

(5) F. A. Cotton, and E. Bannister, *J. Chem. Soc.*, 1873 (1960).

Table I. Complexes of composition $ML_4(anion)_2$

Ligand	Mn^{II}	Fe^{II}	Co^{II}	Ni^{II}	Cu^{II}	Zn^{II}
Ph_2MePO	[a]	[a]	[a]	[a]	[a]	[a]
Ph_2MeAsO	[a]	[a]	[a]	[a]	[a]	[a]
Ph_3PO	[b][1]	[[b]]	[b], [c][2], [d]	[b][1], [d]	[[b]], [d]	[c][3]
Ph_3AsO	[b][1]	[[b]]	[b], [c][2], [d]	[b][1], [d]	[[b]], [d]	[c][3]

[a] Isomorphous five-coordinate, $[M(II)(Ph_2MeXO)_4(ClO_4)]ClO_4$ complexes (X = P and As). [b] Isomorphous five-coordinate, $[M(II)(Ph_3XO)_4(ClO_4)]ClO_4$ complexes (X = P and As). [[b]] Complexes with powder photographs similar to, but not identical with, those of [b]. [c] Isomorphous tetrahedral $[M(II)(Ph_3XO)_4](ClO_4)_2$ complexes (X=P and As). [d] Isomorphous five-coordinate $[M(II)(Ph_3XO)_4(ReO_4)]ReO_4$ complexes (X = P and As). [1] Previously considered to be four-coordinate. (Refs 3, 4 and 5). [2] The complexes of composition $Co(II)L_4(ClO_4)_2$ which were isolated by previous workers (Refs 3 and 5). [3] Five-coordinate complexes not isolable.

Table II. Band Maxima (kK) for Diffuse Reflectance Spectra

$[Co(Ph_2MePO)_4(ClO_4)]ClO_4$	21.9, 19.1, 16.7, 11.1, 6.45 br.
$[Co(Ph_2MeAsO)_4(ClO_4]ClO_4$	22.2, 16.8, 11.3, 6.6 br.
$[Co(Ph_3PO)_4(ClO_4)]ClO_4$	21.7, 19.5, 16.8, 11.8, 7.0 br.
$[Co(Ph_3PO)_4(ReO_4)]ReO_4$	21.2, 20.1 sh, 19.2, 16.6, 10.9, 6.5 br.
$[Co(Ph_3AsO)_4(ClO_4)]ClO_4$	22.0, 16.8, 12.25, 7.1 br.
$[Co(Ph_3AsO)_4(ReO_4)]ReO_4$	21.4, 18.3, 16.5, 11.4, 6.9 br.
$[Ni(Ph_2MePO)_4(ClO_4)]ClO_4$	22.8, 18.9, 16.8, 14.0, 11.05, 10.4 br.
$[Ni(Ph_2MeAsO)_4(ClO_4)]ClO_4$	23.0, 18.7, 16.5, 13.8, 11.7, 7.4 br.
$[Ni(Ph_3PO)_4(ClO_4)]ClO_4$	23.2, 20.0 (sh), 17.1, 14.1, 11.7, 8.0 br.
$[Ni(Ph_3PO)_4(ReO_4)]ReO_4$	22.4, 19.2 (sh), 16.95, 14.1, 10.95, 7.4 br.
$[Ni(Ph_3AsO)_4(ClO_4]ClO_4$	23.6, 19.8, 16.8, 13.9, 12.3, 9.4 br.
$[Ni(Ph_3AsO)_4(RcO_4)]ReO_4$	22.8, 18.8, 16.3, 13.8 (sh), 11.5, 8.1 br.
$[Cu(Ph_2MePO)_4(ClO_4)]ClO_4$	12.4 br.
$[Cu(Ph_2MeAsO)_4(ClO_4)]ClO_4$	16.4 (sh), 14.2 br.
$[Cu(Ph_3PO)_4(ClO_4)]ClO_4$	11.2 (sh), 13.25 br.
$[Cu(Ph_3PO)_4(ReO_4)]ReO_4$	12.0 br.
$[Cu(Ph_3AsO)_4(ClO_4)]ClO_4$	14.5, 17.5 (sh).
$[Cu(Ph_3AsO)_4(ReO_4)]ReO_4$	13.4 br.

Table III. Infrared Spectra (cm^{-1})

Compound	ν(Cl—O), ν(Re—O) [a]	ν(P—O), ν(As—O)	ν(M—O) or metal-sensitive bands [b]
Ph_2MePO		1171 s	—
$[Mn(Ph_2MePO)_4(ClO_4)]ClO_4$	1143 s, 1089 s, 1037 m	1145 s	417 m, 324 m
$[Fe(Ph_2MePO)_4(ClO_4)]ClO_4$	1144 s, 1087 s, 1034 m	1144 s	416 m, 324 mw
$[Co(Ph_2MePO)_4(ClO_4)]ClO_4$	1142 s, 1090 s, 1038 m	1142 s	419 m, 331 mw
$[Ni(Ph_2MePO)_4(ClO_4)]ClO_4$	1139 s, 1088 s, 1035 m	1139 s	419 m, 339 mw
$[Cu(Ph_2MePO)_4(ClO_4)]ClO_4$	1088 s	1137 s	427 m, 352 mw
$[Zn(Ph_2MePO)_4(ClO_4)]ClO_4$	1146 s, 1091 s, 1037 m	1138 s	418 m, 329 mw
Ph_2MeAsO		875 s	—
$[Mn(Ph_2MeAsO)_4(ClO_4)]ClO_4$	1136 s, 1092 s, 1046 s	871 s	383 m
$[Fe(Ph_2MeAsO)_4(ClO_4)]ClO_4$	1091 s	842 s	425 m
$[Co(Ph_2MeAsO)_4(ClO_4)]ClO_4$	1132 s, 1094 s 1048 s	858 s	406 m
$[Ni(Ph_2MeAsO)_4(ClO_4)]ClO_4$	1137 s, 1092 s, 1045 m	854 s	417 m
$[Cu(Ph_2MeAsO)_4(ClO_4)]ClO_4$	1087 s	850 s	436 mw
$[Zn(Ph_2MeAsO)_4(ClO_4)]ClO_4$	1134 s, 1091 s, 1047 s	861 s	397 m
Ph_3PO		1195 s	
$[Mn(Ph_3PO)_4(ClO_4)]ClO_4$	1090 s, br	1152 s	410 mw, 333mw
$[Fe(Ph_3PO)_4(ClO_4)]ClO_4$	1090 s, br	1147 s	414 mw, 336 mw
$[Co(Ph_3PO)_4(ClO_4)]ClO_4$	1090 s, br	1146 s	412 mw, 345 mw
$[Ni(Ph_3PO)_4(ClO_4)]ClO_4$	1090 s, br	1143 s	410 mw, 357 mw
$[Cu(Ph_3PO)_4(ClO_4)]ClO_4$	1090 s, br	1131 s	425 mw, 375 mw
$[Co(Ph_3PO)_4(ReO_4)]ReO_4$	931 s, 921 sh, 908 s, 897 sh	1143 s	414 mw, 341 mw
$[Ni(Ph_3PO)_4(ReO_4)]ReO_4$	931 s, 921 sh, 906 s	1142 s	414 mw, 349 mw
$[Cu(Ph_3PO)_4(ReO_4)]ReO_4$	927 sh, 922 s, 910 s, 888 s	1135 s	420 mw, 366 mw
Ph_3AsO		880 s	—
$[Mn(Ph_3AsO)_4(ClO_4)]ClO_4$	1090 s, br	873 s	386 m
$[Fe(Ph_3AsO)_4(ClO_4)]ClO_4$	1090 s, br	862 s	423 m
$[Co(Ph_3AsO)_4(ClO_4)]ClO_4$	1090 s, br	860 s	403 m
$[Ni(Ph_3AsO)_4(ClO_4)]ClO_4$	1090 s, br	863 s	417 m
$[Cu(Ph_3AsO)_4(ClO_4)]ClO_4$	1090 s, br	844 s	442 mw
$[Co(Ph_3AsO)_4(ReO_4)]ReO_4$	929 s, 916 sh, 907 s	866 s	402 m
$[Ni(Ph_3AsO)_4(ReO_4)]ReO_4$	931 s, 916 sh, 908 s	864 s	409 m
$[Cu(Ph_3AsO)_4(ReO_4)]ReO_4$	921 sh, 916 sh, 906 s	852 s	437 mw

[a] For the perchlorate complexes the first and third bands listed are considered to be associated with coordinated ClO_4, and the second band with ionic ClO_4. [b] The bands listed for Ph_2MeAsO and Ph_3AsO complexes are assigned as ν(M—O). The absorptions for the complexes of Ph_2MePO and Ph_3PO are those which are metal-sensitive.

have similar powder photographs to those of their congeners (Table I), they may have structures more closely square planar than five-coordinate, as indicated below.

In view of the evidence for five coordination for the triphenyl complexes they may be formulated as $[M(Ph_3XO)_4(ClO_4)]ClO_4$. However, infrared evidence for anion coordination is not as conclusive as for the diphenylmethyl series where marked splittings of ~ 100 cm^{-1} for the ν(Cl–O) band occur (Table III). An attempt was made to establish anion coordination for the triphenyl compounds by preparing $[ML_4(ClO_4)]BPh_4$ derivatives in an analogous manner to that used for related trimethylphosphine oxide and trimethylarsine oxide complexes.[6] However, only tetrahedral complexes were isolated.

$$[ML_4](ClO_4)(BPh_4),\quad M = \text{Mn and Co};\quad L = Ph_3PO \text{ and } Ph_3AsO \qquad (1)$$

and

$$[ML_4](BPh_4)_2,\quad M = \text{Co and Ni};\quad L = Ph_3AsO \qquad (2)$$

On the other hand the infrared spectra of some analogous perrhenate complexes indicate anion coordination. Whereas $[Co(HMPA)_4](ReO_4)_2$, containing only ionic perrhenate, has a single ν(Re–O) absorption at 905 cm^{-1} all the complexes prepared with Ph_3PO and Ph_3AsO give multiple ν(Re–O) absorptions (Table III).

The structural information outlined above must be considered in the interpretation of infrared data. The isomorphism of the diphenylmethyl complexes means that differences in infrared absorptions (which are quite marked for iron(II) and copper(II)) can be taken as a reliable indication of changes in metal-ligand binding. For the triphenyl series the situation is somewhat complicated by the lack of isomorphism.

In general the diphenylmethyl perchlorate complexes show a marked splitting of ν(Cl–O) bands, (Table III) enabling the assignment of two bands (at approximately 1040 and 1140 cm^{-1}) to coordinated perchlorate and a third at 1090 cm^{-1} to ionic perchlorate. The marked splitting is consistent with the relatively short M–O bond length of about 2.15 Å for the bound perchlorate.[2] However, for the copper complexes and $[Fe(Ph_2MeAsO)_4(ClO_4)]ClO_4$ no splitting is observed, indicating a weaker M–O (perchlorate) bonding in these compounds.

Infrared data also indicate that in these iron and copper complexes the metal-oxygen (oxide) bonding is stronger than that for other members of the isomorphous series. Metal sensitive bands in the range, 380-440 cm^{-1}, may be assigned as ν(M–O) for diphenylmethylarsine oxide complexes,[7] and in the $[M(Ph_2MeAsO)_4(ClO_4)]ClO_4$ series these have higher values for iron and copper than for manganese, cobalt, nickel and zinc (Table III). For the corresponding diphenylmethylphosphine oxide series, $[M(Ph_2MePO)_4(ClO_4)]ClO_4$, it is more difficult to assign ν(M–O) modes as two bands at 416-427 cm^{-1} and 324-352 cm^{-1} are metal sensitive. However, both have their highest values for M = Cu and while the exact nature of the modes giving rise to these absorptions is unknown, high values probably indicate stronger metal-ligand bonding. The infrared data for the diphenylmethyl complexes therefore indicate that weakening of bonding in the axial position and strengthening in the equatorial plane are concomitant effects. This may be considered to be a distortion of the square pyramidal structure towards a square planar arrangement.

A similar effect is probably operative in the related triphenylphosphine oxide and triphenylarsine oxide perchlorate complexes although differences in anion bonding can not be detected because in no case is the ν(Cl–O) band split, (Table III), the perchlorate bonding apparently being weaker for the triphenyl ligands.

Some splitting of ν(Re–O) does occur for the related perrhenate complexes, $[M(Ph_3XO)_4(ReO_4)]ReO_4$, M = Co, Ni and Cu for X = P and As, but it is not significantly less for copper than for cobalt and nickel. However, differences in M–O bonding appear to follow the same pattern as that observed for the corresponding diphenylmethyl series in that the iron and copper triphenylarsine oxide perchlorate complexes have the highest ν(M–O) values, and $[Cu(Ph_3PO)_4(ClO_4)]ClO_4$ has the highest metal sensitive bands (Table III). The related perrhenate complexes show the same trends (Table III). (Single bands in the 370-440 cm^{-1} range can be assigned as ν(M–O) for triphenylarsine oxide complexes[7] but triphenylphosphine oxide complexes have two metal-sensitive bands in similar positions to those found for diphenylmethylphosphine oxide complexes. There is some uncertainty about the assignment of ν(M–O) for triphenylphosphine oxide complexes[8]).

Although all of the perrhenate complexes studied were isomorphous, in the case of the perchlorates those triphenyl complexes which appear to have stronger M–O (oxide) bonding, $[M(Ph_3AsO)_4(ClO_4)]ClO_4$, M = Fe and Cu, and $[Cu(Ph_3PO)_4(ClO_4)]ClO_4$, are not strictly isomorphous with their congeners. The slight differences in powder photographs are possibly related to the distortions proposed for these complexes.

Trimethylphosphine oxide and trimethylarsine oxide also give complexes of the type $[ML_4(ClO_4)]ClO_4$[6] where M = Fe and Cu for L = Me_3PO and M = Mn, Fe, Ni, and Cu for L = Ph_3AsO. While the highest ν(M–O) values were again observed for the copper complexes no evidence was obtained for differences in perchlorate bonding as only single ν(Cl–O) absorptions were found.

In none of the phosphine oxide or arsine oxide complexes studied were absorptions observed in the 500-200 cm^{-1} range which could be assigned as ν(M–O) modes arising from metal-perchlorate bonding. Metal-oxygen bond lengths for $[Co(Ph_2MeAsO)_4(ClO_4)]ClO_4$[2] indicate that these bands would

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(6) A. M. Brodie, S. H. Hunter, G. A. Rodley, and C. J. Wilkins, *Inorg. Chim. Acta.*, *2*, 195 (1968).
(7) G. A. Rodley, D. M. L. Goodgame, and F. A. Cotton, *J. Chem. Soc.*, 1499 (1965).
(8) G. B. Deacon and J. H. S. Green, *Spectrochim. Acta.*, *25A*, 335 (1969).

Table IV. Analyses

Compound	Found % C	Found % H	Calculated % C	Calculated % H
$[Mn(Ph_2MePO)_4(ClO_4)]ClO_4$	55.8	4.5	55.8	4.7
$[Fe(Ph_2MePO)_4(ClO_4)]ClO_4$	54.1	4.85 [a]	55.7	4.6
$[Co(Ph_2MePO)_4(ClO_4)]ClO_4$	55.0	4.9	55.5	4.6
$[Ni(Ph_2MePO)_4(ClO_3)]ClO_4$	55.0	4.8	55.5	4.6
$[Cu(Ph_2MePO)_4(ClO_4)]ClO_4$	55.8	5.0	55.5	4.6
$[Zn(Ph_2MePO)_4(ClO_4)]ClO_4$	55.3	4.65	55.2	4.6
$[Mn(Ph_2MeAsO)_4(ClO_4)]ClO_4$	48.6	4.0	48.2	4.0
$[Fe(Ph_2MeAsO)_4(ClO_4)]ClO_4$	47.4	4.1 [a]	48.2	4.0
$[Co(Ph_2MeAsO)_4(ClO_4)]ClO_4$	48.15	4.5	48.1	4.0
$[Ni(Ph_2MeAsO)_4(ClO_4)]ClO_4$	48.0	4.4	48.1	4.0
$[Cu(Ph_2MeAsO)_4(ClO_4)]ClO_4$	47.7	4.7	47.9	4.0
$[Zn(Ph_2MeAsO)_4(ClO_4)]ClO_4$	47.6	4.7	47.8	4.0
$[Co(Ph_3PO))_4(ClO_4)]ClO_4$ (green)	62.2	4.5	63.0	4.4
$[Co(Ph_3PO)_4(ReO_4)]ReO_4$	51.7	3.6	51.7	3.6
$[Ni(Ph_3PO)_4(ReO_4)]ReO_4$	51.5	3.65	51.7	3.6
$[Cu(Rh_3PO)_4(ReO_4)]ReO_4$	51.5	3.65	51.7	3.6
$[Cu(Ph_3PO)_4(ReO_4)]ReO_4$	50.9	3.6	51.5	3.6
$[Co(Ph_3AsO)_4(ClO_4)]ClO_4$ (green)	55.4	4.0	55.7	4.0
$[Co(Ph_3AsO)_4(ReO_4)]ReO_4$	47.15	3.4	46.8	3.25
$[Ni(Ph_3AsO)_4(ReO_4)]ReO_4$	46.2	3.3	46.8	3.25
$[Cu(Ph_3AsO)_4(ReO_4)]ReO_4$	46.8	3.35	46.6	3.2

[a] See Experimental Section.

be at lower values than ν(M–O) oxide bands and they may be obscured by ligand absorptions.

Experimental Section

The $[ML_4(ClO_4)]ClO_4$ complexes (L = Ph_2MePO, Ph_2MeAsO) were obtained from reaction of a slight excess of the ligand with the metal salt in acetone or ethanol, containing ethylorthoformate as a dehydrating agent. The product was washed with solvent and ether and dried under high vacuum. The Ph_2MePO complexes, which are sensitive to moisture, were handled in a dry box. Pure samples of $[Fe(Ph_2MeXO)_4(ClO_4)](ClO_4)$, X = P and As, were difficult to obtain. Also $[FeL_5]^{2+}$ species appear to form preferentially, particularly in the case of the phosphine oxide.

The Ph_3AsO and Ph_3PO complexes were prepared from acetone and ethanol solutions of the appropriate metal salt and ligand. Under these conditions only the blue tetrahedral $[CoL_4](ClO_4)_2$ complexes can be isolated. However, these are slowly converted on standing to the blue-green $[CoL_4(ClO_4)]ClO_4$ complexes. This conversion is assisted by suspending the complex in water and is reversed by heating to 120°C indicating that the five coordinate structure may be stabilised by the presence of water in the lattice. Analyses are given in Table IV.

Physical Measurements. Electronic spectra were run over the range 5-30 kK using a Beckman DK2A spectrophotometer with standard reflectance attachment for solid samples. Infrared spectra were obtained from Nujol mulls using Perkin-Elmer 337 (to 400 cm^{-1}) and Grubb-Parsons DM4 (500-200 cm^{-1}) spectrophotometers. Calibrations were made with polystyrene and water vapour respectively.