

### 375. Phosphine Oxide Complexes. Part II.<sup>1</sup> Cations of the Type $[(\text{Ph}_3\text{PO})_4\text{M}]$ with $\text{M} = \text{Mn}(\text{II}), \text{Fe}(\text{III}), \text{Co}(\text{II}), \text{Cu}(\text{II}),$ and $\text{Zn}(\text{II})$ .

By E. BANNISTER and F. A. COTTON.

Complex cations of the type  $[(\text{Ph}_3\text{PO})_4\text{M}]^{n+}$  with  $\text{Mn}(\text{II}), \text{Fe}(\text{III}), \text{Co}(\text{II}), \text{Cu}(\text{II}),$  and  $\text{Zn}(\text{II})$  are easily obtained by reaction of triphenylphosphine oxide and the appropriate metal perchlorate in alcohol solution. Magnetic and spectral data leave little doubt that the  $\text{Co}(\text{II})$  complex is tetrahedral, and the  $\text{Zn}(\text{II})$  salt is isomorphous with it. The  $\text{Fe}(\text{III})$  complex seems likely to be tetrahedral. The  $\text{Cu}(\text{II})$  complex is almost certainly planar, and the  $\text{Mn}(\text{II})$  complex probably also planar. The planar configurations refer to the  $\text{MO}_4$  groupings and it is necessary to assume  $\text{M}-\text{O}-\text{P}$  angles of  $\leq \sim 160^\circ$  in these cases because of the steric requirements of the  $\text{PPh}_3$  groups.

THE existence of the type of compound described in this paper has been briefly reported recently,<sup>2</sup> and the nickel(II) compound, which has some curious properties, was discussed in the preceding Part.<sup>1</sup> We now discuss the properties of the  $\text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Cu}(\text{II}),$  and  $\text{Zn}(\text{II})$  compounds of the type  $[(\text{Ph}_3\text{PO})_4\text{M}](\text{ClO}_4)_2$ , of  $[(\text{Ph}_3\text{PO})_4\text{Fe}](\text{ClO}_4)_3$ , and of the  $\text{Co}(\text{II})$  compound with tris-(*p*-dimethylaminophenyl)phosphine oxide.

While there are minor differences, all of these compounds are rather easy to prepare by mixing alcoholic solutions of the metal perchlorates and the ligand in about 1:4:2 molar ratio. Their colours, analyses, magnetic moments, and absorption bands are listed in the Table and the reflection spectra are shown in Fig. 1.

#### Properties of the compounds $[(\text{Ph}_3\text{PO})_4\text{M}](\text{ClO}_4)_x$ ( $x = 2$ or $3$ ).

Compound (colour)	C (%)		H (%)		Magnetic moments (B.M.) (corrected susceptibilities)	Spectral peaks ( $m\mu$ )
	Req.	Found	Req.	Found		
$[(\text{Ph}_3\text{PO})_4\text{Mn}](\text{ClO}_4)_2$ (white) ...	63.3	62.6	4.4	4.4	5.97 ( $14,847 \times 10^{-6}$ at $298^\circ$ )	320
$[(\text{Ph}_3\text{PO})_4\text{Fe}](\text{ClO}_4)_3$ (yellow) ...	58.9	58.8	4.1	4.4	5.92 ( $14,647 \times 10^{-6}$ at $298^\circ$ )	345
$[(\text{Ph}_3\text{PO})_4\text{Co}](\text{ClO}_4)_2$ (blue) .....	63.1	63.4	4.4	4.3	4.72 <sup>a</sup>	640
$[(\text{Me}_2\text{N}\cdot\text{C}_6\text{H}_4)_3\text{PO}]_4\text{Co}(\text{ClO}_4)_2$ (blue) .....	61.1	61.0	6.4	6.6 <sup>c</sup>	4.76 <sup>a</sup>	No data
$[(\text{Ph}_3\text{PO})_4\text{Cu}](\text{ClO}_4)_2$ (pale blue)	62.9	62.6	4.4	4.7	1.90 <sup>b</sup>	335, 700
$[(\text{Ph}_3\text{PO})_4\text{Zn}](\text{ClO}_4)_2$ (white) ...	62.8	62.6	4.4	4.4	Diamagnetic	No data

<sup>a</sup> Measured over a temperature range by Dr. R. H. Holm; to be reported fully and discussed in a forthcoming general study of  $\text{Co}(\text{II})$  compounds. <sup>b</sup> Measured over a temperature range (see Experimental section); a slight dependence of moment on field strength was observed. <sup>c</sup> Found: N, 8.9. Req'd.: N, 8.9%.

It will be convenient to discuss the cobalt compounds first since, for these, magnetic and spectral data permit the conclusion that the cation is truly tetrahedral, in the sense that the ligand field experienced by the  $\text{Co}(\text{II})$  ion has  $T_d$  symmetry. These conclusions are based on theoretical and empirical generalizations about the dependence of spectral and magnetic properties of  $\text{Co}(\text{II})$  complexes on the symmetry and strength of the ligand field. It has been shown by Holm and Cotton<sup>3</sup> for the tetrahalogenocobaltate(II) ions,  $\text{CoCl}_4^{2-}$ ,  $\text{CoBr}_4^{2-}$ ,  $\text{CoI}_4^{2-}$ , and for  $\text{Co}(\text{SCN})_4^{2-}$  that the magnitude of the magnetic moment is determined by the strength of the tetrahedral ligand field, whereas for planar and octahedral complexes the ground state has intrinsic orbital degeneracy which results for such compounds in moments of the order of 4.95—5.2 B.M., not governed in any simple way, so far as is known, by the strength of the ligand field.<sup>4</sup> Thus, the moments of the two

<sup>1</sup> Part I, preceding paper.

<sup>2</sup> Cotton, Bannister, Barnes, and Holm, *Proc. Chem. Soc.*, 1959, 158.

<sup>3</sup> Holm and Cotton, *J. Chem. Phys.*, 1959, **31**, 788.

<sup>4</sup> Holm and Cotton, unpublished work.

Co(II) complexes are well below the range for planar complexes and are at the same time of about the magnitude to be expected for tetrahedral complexes on the basis of our previous work<sup>3</sup> and the position normally occupied by oxygen ligands in the spectrochemical series.<sup>5</sup> Thus the magnetic moments alone indicate a tetrahedral configuration. The spectrum of the  $[(\text{Ph}_3\text{PO})_4\text{Co}]^{2+}$  ion (Fig. 1b) provides even stronger evidence. While it does not show good resolution, which can seldom be obtained with the reflectance technique, it is clearly not at all the type of spectrum given by planar and octahedral spin-free Co(II) complexes,<sup>4</sup> whereas it resembles very closely the spectra of the tetrahedral halogenocobaltous ions.<sup>3</sup> Further, the energy of the band is about where it might be expected in view of the usual position of oxygen in the spectrochemical series. Whatever the structure of the  $[(\text{Ph}_3\text{PO})_4\text{Co}]^{2+}$  cation, the analogous Zn(II) cation must have the same structure,

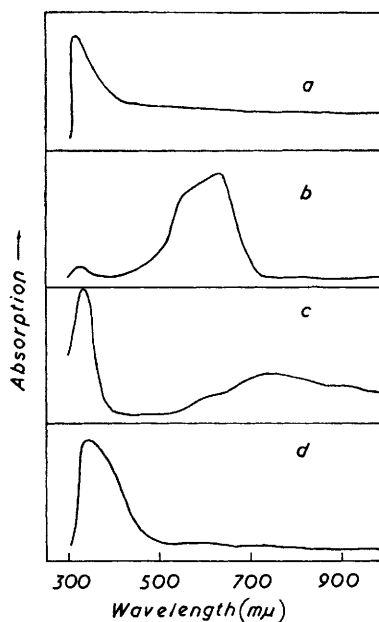


FIG. 1. Reflectance spectra of triphenylphosphine oxide complexes of some metal perchlorates,  $[(\text{Ph}_3\text{PO})_4\text{M}](\text{ClO}_4)_2$ .

a, Mn. b, Co. c, Cu. d, Fe.

since the two perchlorates are strictly isomorphous. This may be seen by comparison of the X-ray powder patterns of these two compounds in Fig. 2; they are exactly superposable. Thus, if the above evidence for the tetrahedral configuration of the Co(II) cation is accepted, the Zn(II) complex cation is also established as tetrahedral. That these two may be tetrahedral is not surprising since both the cobalt(II) and the zinc(II) ion are known to form other tetrahedral complexes.

Another of the complex cations which *may* be tetrahedral is  $[(\text{Ph}_3\text{PO})_4\text{Fe}]^{3+}$ , since for Fe(III), with a spherically symmetrical half-filled  $d$ -shell, there is no ligand-field stabilization energy to favour any other configuration. The magnetic moment of 5.92 B.M., which agrees quite well with that expected for a  $d^5(^6S)$  ion, *viz.*, 5.92 B.M., shows that the Fe(III) ion in this complex has indeed such a spherically symmetrical  $d$ -shell. Moreover, at least one other complex of Fe(III) is known<sup>6</sup> to be tetrahedral, namely,  $\text{FeCl}_4^-$ . However, it should be emphasized that we can offer no direct proof of the configuration and it may be other than tetrahedral.

It is appropriate to discuss next the Mn(II) complex. Here again the ion is in a  $d^5(^6S)$  state with a spherically symmetrical  $d$ -shell, as shown by its magnetic moment of 5.97 B.M. We believe that in this case the configuration is probably not tetrahedral {although there

<sup>5</sup> Orgel, *J. Chem. Phys.*, 1955, **23**, 1004, who discusses the concept of this spectrochemical series, originally developed empirically, in terms of ligand-field theory.

<sup>6</sup> Zaslav and Rundle, *J. Phys. Chem.*, 1957, **61**, 490.

are several established<sup>7</sup> examples of tetrahedral Mn(II) complexes, *viz.*,  $[\text{MnX}_4]^{2-}$ , because of the close resemblance of the powder patterns of  $[(\text{Ph}_3\text{PO})_4\text{Ni}](\text{ClO}_4)_2$  and  $[(\text{Ph}_3\text{PO})_4\text{Mn}](\text{ClO}_4)_2$ . While the patterns do not match exactly, so that isomorphism cannot be asserted with certainty, the resemblance is very close, and we feel that it is likely that the crystals are of nearly the same structure. This would mean then that the  $[(\text{Ph}_3\text{PO})_4\text{Mn}]^{2+}$  and the  $[(\text{Ph}_3\text{PO})_4\text{Ni}]^{2+}$  cation also have about the same structure. According to detailed arguments given in Part 1,<sup>2</sup> we believe that the complex nickel(II)

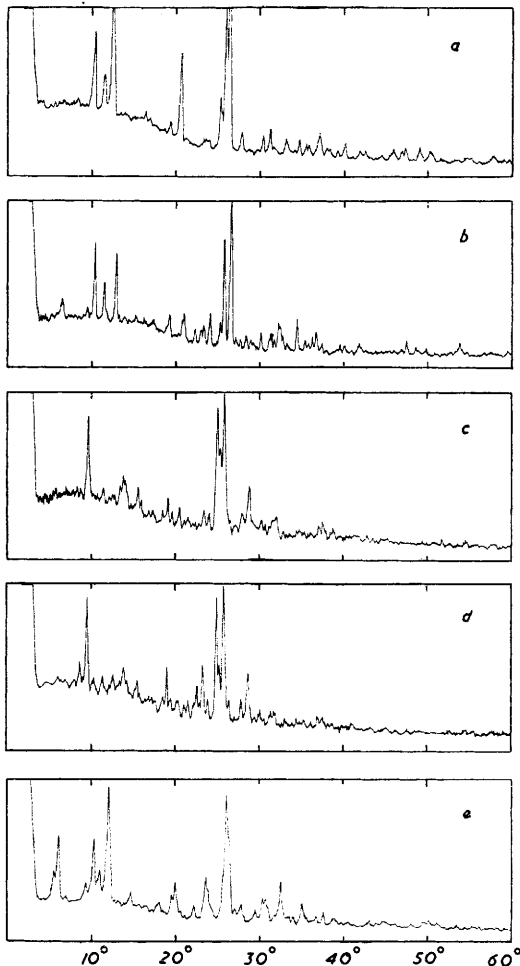


FIG. 2. X-Ray powder diffraction patterns of triphenylphosphine oxide complexes of some metal perchlorate salts,  $[(\text{Ph}_3\text{PO})_4\text{M}](\text{ClO}_4)_2$ .

a, Ni. b, Mn. c, Zn. d, Co. e, Cu.

cation has a nearly planar  $\text{NiO}_4$  grouping, with the steric requirements of the  $\text{PPh}_3$  residues met by  $\text{Ni-O-P}$  angles of  $\leq \sim 160^\circ$  with two *trans*- $\text{PPh}_3$  groups above and the other two below the median plane of the  $\text{NiO}_4$  grouping. A similar structure may thus be considered likely for  $[(\text{Ph}_3\text{PO})_4\text{Mn}]^{2+}$ .

Finally, the Cu(II) compound gives an X-ray powder pattern (Fig. 2) which differs from all of the others and so gives no positive evidence as to the structure of the complex cation. However, if the cation were tetrahedral, with linear  $\text{Cu-O-P}$  groups, it should be so similar in size and other properties to the tetrahedral cations of Co(II) and Zn(II) that isomorphism of  $[(\text{Ph}_3\text{PO})_4\text{Cu}](\text{ClO}_4)_2$  with the analogous Co(II) and Zn(II) compounds could be expected. In this sense, then, there is some negative evidence against a tetrahedral configuration for

<sup>7</sup> Gill and Nyholm, *J.*, 1959, 3997.

the complex cation of Cu(II). The magnetic moment, 1.90 B.M., might be thought to provide evidence against a tetrahedral configuration, but this is not so. It is true, as has been shown by Figgis<sup>8</sup> and Ito and Ito,<sup>9</sup> who applied Kotoni's theory, that tetrahedral Cu(II) should have a relatively large orbital contribution to its magnetic moment, giving a net value of  $\geq \sim 2.2$  B.M., at temperatures above about 200° K according to Figgis's calculations. However, a rigorously tetrahedral Cu(II) complex is not likely to exist since a Jahn-Teller distortion may be expected, splitting the otherwise degenerate ( ${}^2T_1$ ) ground state. In  $\text{Cs}_2\text{CuCl}_4$ , the distortion is a flattening of the tetrahedron,<sup>10</sup> which lowers the magnetic moment from the expected  $\sim 2.2$  to  $1.93 \pm 0.05$  B.M.<sup>11</sup> While a tetrahedral  $[(\text{Ph}_3\text{PO})_4\text{Cu}]^{2+}$  ion would be very crowded, there would probably be enough latitude in the O-Cu-O and Cu-O-P angles to permit a degree of distortion comparable to that of  $\text{Cs}_2\text{CuCl}_4$ , so that the magnetic moment could be as low as 1.90 B.M. despite an approximately tetrahedral confirmation. Thus the only safe conclusion appears to be that the observed magnetic moment is consistent with any ligand-field symmetry from distorted  $T_d$  through  $D_{2d}$  to  $D_{4h}$ .

However, the spectrum of  $[(\text{Ph}_3\text{PO})_4\text{Cu}]^{2+}$  does seem to provide good evidence against a tetrahedral configuration. The observed band is quite broad and its peak is at  $\sim 700$  m $\mu$ . Since the hexaquo-copper(II) ion has its peak maximum at  $\sim 800$  m $\mu$ ,<sup>12</sup> we should expect the  $[(\text{Ph}_3\text{PO})_4\text{Cu}]^{2+}$  ion to have a band at about four-ninths of this energy, *i.e.*,  $\sim 1700$  m $\mu$ , and certainly not at a slightly higher energy. Moreover, a rather narrow band would be expected in a tetrahedral complex since only a single transition would be involved. The broad band observed is what would be expected for a planar complex having two or three superposed absorptions and may be compared both in position and breadth with those observed in other planar Cu(II) complexes.<sup>13</sup> A final point in favour of a planar configuration for the Cu(II) cation is the well-known fact that planar rather than tetrahedral co-ordination is usual for Cu(II).

In view of the results presented here and in Part I,<sup>1</sup> the following conclusion can be drawn concerning the stereochemical requirements of  $\text{Ph}_3\text{PO}$  as a ligand. It is not required that the M-O-P group be linear. When the metal ion, M, normally forms tetrahedral complexes, it does so with  $\text{Ph}_3\text{PO}$ , and in those cases [Co(II) and Zn(II) being the two so far found] it is likely that the great size of the  $\text{PPh}_3$  groups will tend to keep the M-O-P group linear or nearly linear. However, for ions which rarely form tetrahedral complexes, the configuration of the  $\text{MO}_4$  grouping may be planar or nearly so because non-linearity of the M-O-P groupings permits the  $\text{PPh}_3$  groups to keep out of one another's way. This possibility was not considered at the time of our preliminary communication,<sup>2</sup> and the suggestion advanced there that all  $[(\text{Ph}_3\text{PO})_4\text{M}]$  ions must necessarily be tetrahedral or nearly so is now recognized to be incorrect.

#### EXPERIMENTAL

Triphenylphosphine oxide (m. p. 158°) was prepared by oxidation of triphenylphosphine with nitrogen dioxide.<sup>14</sup> Tris-(*p*-dimethylaminophenyl)phosphine oxide was prepared according to Bourneuf's directions.<sup>15</sup>

All complexes were obtained by evaporating methanol or ethanol solutions of the hexaquo-metal perchlorate (0.001 mole) and phosphine oxide (0.0042 mole). The ferric compound separated from ethanol as a yellow oil which became solid on treatment with ether or benzene.

*Magnetic Measurements.*—These were made by the Gouy method, Mohr's salt being used to

<sup>8</sup> Figgis, *Nature*, 1958, **182**, 1568.

<sup>9</sup> Ito and Ito, *Austral. J. Chem.*, 1958, **11**, 406.

<sup>10</sup> Helmholz and Kruk, *J. Amer. Chem. Soc.*, 1952, **74**, 1176.

<sup>11</sup> M. D. Meyers, Massachusetts Institute of Technology, unpublished observation.

<sup>12</sup> Bjerrum, Ballhausen, and Jorgensen, *Acta Chem. Scand.*, 1954, **8**, 1289.

<sup>13</sup> See, for example, Belford, Martell, and Calvin, *J. Inorg. Nuclear Chem.*, 1956, **2**, 11.

<sup>14</sup> Cox and Westheimer, *J. Amer. Chem. Soc.*, 1959, **80**, 5441.

<sup>15</sup> Bourneuf, *Bull. Soc. chim. France*, 1923, **33**, 1808.

calibrate the tubes <sup>16</sup> and diamagnetic corrections made by using the susceptibility ( $-801 \times 10^{-6}$  c.g.s. unit) of the zinc compound, the value of which is in good agreement with an estimate from Pascal's constants <sup>16</sup> [plus an additional correction for  $\text{ClO}_4^-$  in the  $\text{Fe(III)}$  compound]. The  $\text{Mn(II)}$ ,  $\text{Fe(III)}$ , and  $\text{Zn(II)}$  compounds were measured at only one temperature and the magnetic moment computed from the Curie equation. The  $\text{Cu(II)}$  compound was measured at three temperatures. The susceptibilities, in c.g.s. units per mole, corrected for diamagnetism are:  $1465 \times 10^{-6}$  at  $303^\circ$ ,  $2283 \times 10^{-6}$  at  $195^\circ$  and  $6255 \times 10^{-6}$  at  $73.7^\circ$ . Using the Curie-Weiss equation,  $\mu = 2.84\sqrt{[\chi(T - \theta)]}$ , we obtain  $\theta = 2^\circ$ ,  $\mu = 1.90$  B.M. The cobalt(II) compounds were measured at three temperatures by Dr. R. H. Holm; each had a Weiss constant of  $-5.5^\circ \pm 0.5^\circ$ . The moments are quoted in the Table.

*Spectra.*—The reflectance spectra in the visible and the ultraviolet region were measured with a Beckman DU spectrophotometer with a reflectance attachment and magnesium carbonate as the reference; since the spectra shown in Fig. 1 are reflectance spectra, the absorbancy scale is arbitrary and true extinction coefficients are unknown.

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DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
CAMBRIDGE 39, MASS., U.S.A.

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<sup>16</sup> See Selwood, "Magnetochemistry," 2nd edn., Interscience Publ. Inc., New York, 1956.

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