456. *Phosphine Oxide Complexes. Part III.*[1] *Bis(triphenylphosphine Oxide)dinitrato-complexes of Cobalt*(II), *Nickel*(II), *Copper*(II), *and Zinc*(II).

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The nitrates of cobalt(II), nickel(II), copper(II), and zinc(II) co-ordinate with two mols. of triphenylphosphine oxide. The compounds $(Ph_3PO)_2M(NO_3)_2$ are non-electrolytes of very high thermal stability. The cobalt compound appears to be tetrahedral in the solid; for solutions in 1,2-dichloroethane the configuration is uncertain but the infrared spectra indicate co-ordination of NO_3^- *via* one oxygen atom and are in general accord with the findings of Gatehouse, Livingston, and Nyholm for other, generally less stable, nitrate complexes.

IN earlier publications [1-3] we described triphenylphosphine oxide complexes $[(Ph_3PO)_4M]^{n+}$ where M is Mn(II), Fe(III), Co(II), Ni(II), Cu(II), or Zn(II). These are prepared by treatment of the metal perchlorates with the phosphine oxide and presumably, since perchlorate ion has negligible donor properties, the metals satisfy co-ordination number 4 by co-ordinating four molecules of the phosphine oxide. The nitrate ion is generally considered to have weak, though not entirely negligible, donor properties and this study was undertaken to

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[1] Part II, Bannister and Cotton, *J.*, 1960, 1878.
[2] Cotton, Bannister, Barnes, and Holm, *Proc. Chem. Soc.*, 1959, 158.
[3] Cotton and Bannister, *J.*, 1960, 1873.

determine whether the nitrate ion too would be excluded from co-ordination by triphenylphosphine oxide; we find that it is not. The nitrate ions enter into the co-ordination shell so that the compounds obtained are of the type [$M(Ph_3PO)_2(NO_3)_2$]. They are listed in Table 1 along with their colours, melting points, and analytical data.

TABLE 1. *Colours, melting points, and analyses of the complexes.*

Compound	M. p.	Colour	Found (%) C	Found (%) H	Required (%) C	Required (%) H
$Co(Ph_3PO)_2(NO_3)_2$	246°	Blue-purple (solid)	58·0	4·2	58·5	4·1
$Ni(Ph_3PO)_2(NO_3)_2$	266	Yellow	58·4	4·1	58·5	4·1
$Cu(Ph_3PO)_2(NO_3)_2$	209	Pale blue	57·7	4·1	58·1	4·1
$Zn(Ph_3PO)_2(NO_3)_2$ [a]	226	White	57·1	4·15	58·0	4·05

[a] Found: N, 3·7. Reqd.: N, 3·8%.

Nitrato-co-ordination compounds are far from abundant and the nitrate ion is commonly considered a poor ligand. In the measurement of stability constants of complex ions in aqueous solution, ammonium and alkali-metal nitrates have often been used to maintain constant ionic strength on the assumption that competition of nitrate ions for places in the co-ordination sphere would be slight. In view of the paucity of well-characterised nitrato-complexes (see Gatehouse *et al.*[4] for a list of most of them) and the presumed poor ligand properties of the nitrate ion, the compounds we have isolated show remarkable thermal stability and resistance to dissociation in polar solvents. The melting points (Table 1) are all quite high. In fact all of the compounds can be heated as much as 30° above their melting points, and, after cooling, the original sharp melting behaviour can be repeated. Lack of dissociation in nitrobenzene and nitromethane has been demonstrated by the low conductivities in these solvents. According to various authors[5] the molar conductivities expected for uni-univalent electrolytes at concentrations of $\sim 10^{-4}$M are about 25 Ω^{-1} in nitrobenzene and about 80 Ω^{-1} in nitromethane. The values reported in Table 2 are negligibly small in comparison. Also, the molecular weight of $Cu(Ph_3PO)_2(NO_3)_2$ was measured cryoscopically in nitrobenzene and found to be 772 ± 30, the theoretical value for no dissociation being 744.

TABLE 2. *Physical properties of the* $(Ph_3PO)_2M(NO_3)_2$ *compounds.*

Metal	Magnetic moment (B.M.)	Molar conductivity (Ω^{-1})				Absorption bands, visible and ultraviolet (mμ)	
		in $Me{\cdot}NO_2$	in $Ph{\cdot}NO_2$	Molarity (10^{-3})	Temp.	Reflectance	Solution ($\varepsilon_{max.}$ in parentheses)
Co	4·69 (solid) [b]	7·4	—	1·0	30°	565, 320	557 (128) [f]
	4·52 (soln.) [b]	—	2·3	0·4	30		560 (143) [g]
Ni	3·45 (solid) [c]	7·7	—	1·24	25	800, 720(sh), 440	—
Cu [a]	1·97 (solid) [d]	7·6	—	0·9	28	920, 350	915 (55) [h]
			1·7	20·4	28		
			2·1	0·8	25		
Zn	Diamagnetic	15·5 [e]	—	1·1	30	—	—
			2·6	1·0	30		

[a] Shown to be monomeric in $Ph{\cdot}NO_2$ by cryoscopy. [b] Measurements by Dr. R. H. Holm on solid over a temperature range and on solution in CH_2Cl_2 at room temperature. Solid obeys Curie–Weiss law with $\theta = -8°$. Details to be published shortly. [c] Corrected (-406×10^{-6}) susceptibilities $\times 10^6$: 17,280 (73·7°), 7110 (194·7°), 4790 (299·0°). Curie–Weiss law followed with $\theta = -12°$. [d] Corrected (-406×10^{-6}) susceptibility at 298·3°: 1601 $\times 10^{-6}$. [e] It appears, visually, that the Zn compound decomposes slowly in nitromethane. [f] CH_2Cl_2 solution. [g] $Me{\cdot}NO_2$ solution. [h] $Ph{\cdot}NO_2$ solution.

The molecular-weight and conductivity data indicate that in solution the

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[4] Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.

[5] Morris and Nyholm, *J.*, 1956, 4375; Fergusson and Nyholm, *Nature*, 1959, **183**, 1039; Foss and Gibson, *J.*, 1949, 3063; Malatesta and Sacco, *Z. anorg. Chem.*, 1953, **273**, 248; Parish, Thesis, University of London, 1958.

$M(Ph_3PO)_2(NO_3)_2$ complexes contain four co-ordinate metal ions. This conclusion receives strong support from the infrared spectra (Table 3) of the compounds both as solids and in solution in dichloromethane. For all four compounds bands characteristic of co-ordinated nitrate ions, *i.e.*, of the grouping $M–O–NO_2$ are found. The assignments are based upon the correlations developed by Gatehouse, Livingstone, and Nyholm.[4] Conversely, we believe that the excellent agreement of our results with the assignments proposed by these authors provides evidence of the general correctness and usefulness of their correlations.

TABLE 3. *Infrared bands of co-ordinated nitrate.*

Compound	Phase [b]	Frequencies [a] (cm.$^{-1}$)			
$Co(Ph_3PO)_2(NO_3)_2$	Solid	1497(s, b)	1290(s, shp)	1024(m, shp)	812(w, shp)
	Soln.	1512(sh)	1258(sh)	1031(sh)	812(w, shp)
		1499(s, shp)	1261(s, b)	1025(m, shp)	
$Ni(Ph_3PO)_2(NO_3)_2$ [c] ...	Solid	1492(s, b)	1282(s, shp)	1022(m, shp)	806(w, shp)
	Soln.	1521(sh)	1285(sh)	1033(sh)	812(w, shp)
		1501(s, shp)	1263(s, b)	1025(m, shp)	
$Cu(Ph_3PO)_2(NO_3)_2$	Solid	1495(s, b)	1283(s, shp)	1012(m, shp)	806(w, shp)
	Soln.	1512(sh)	1283(sh)	1028(w, shp)	807(w, shp)
		1498(s, shp)	1260(s, shp)	1011(m, shp)	
$Zn(Ph_3PO)_2(NO_3)_2$	Solid	1492(s, b)	1301(s, shp)	1026(m, shp)	819(m, shp)
Assignment [d]	—	Asym NO_2 str.	Sym NO_2 str.	NO str.	non-plane def.
Range [d]	—	1531— 1481	1290— 1253	1034— 970	800— 781

[a] s, strong; m, medium; w, weak; shp, sharp; b, broad; sh, shoulder. [b] Solid means spectrum was taken on mulls in mineral oil and hexachlorobutadiene; solutions were in CH_2Cl_2. [c] Also, 1385(w, b) and 1342(sh) found in hexachlorobutadiene only. [d] According to Gatehouse *et al.*[4]

A few details of the infrared spectra merit comment. It will be noted that the band assigned by Gatehouse *et al.* as the out-of-plane deformation of co-ordinated $O{\cdot}NO_2$ occurs in all our compounds slightly above the range they proposed. It therefore seems that the range limits for this band should be given as 820—780 instead of 800—780 cm.$^{-1}$. For the three $M(Ph_3PO)_2(NO_3)_2$ compounds examined in solution the three NO stretching bands always appear doubled, usually with one of the two components appearing only as a shoulder. This may be due to the fact that somewhat better resolution of the solution spectra permits observation of a coupling *via* the metal atom between corresponding vibrations in the two ligands. This might then suggest a lack of an inversion centre in the complexes either because they are tetrahedral or *cis*-planar, or because the steric requirements of the very bulky triphenylphosphine oxide groups distort an essentially *trans*-planar configuration. We conclude by considering what conclusions may be drawn about the configuration of the $[M(Ph_3PO)_2(NO_3)_2]$ compounds from the magnetic and the spectral data given in Table 3. Such data provide no evidence in the case of the zinc(II) compound.

For $Cu(Ph_3PO)_2(NO_3)_2$ the magnetic moment of 1·97 B.M. is in accord with either a planar or a " tetrahedral " configuration, since for the latter the true ligand field symmetry would be only C_{2v} and the higher moment expected for a ligand field of true T_d symmetry would not be observed (for a discussion of this point with references to the literature see ref. 1). However, just as with the $[Cu(Ph_3PO)_4]^{2+}$ cation,[1] the appearance of a broad absorption band at 915—920 mμ indicates a planar configuration.

The reflectance spectrum of the nickel(II) complex has been measured and found to be very similar to that of $[Ni(Ph_3PO)_4]^{2+}$ reported previously.[3] For reasons then discussed,[3] we believe that this spectrum by itself suggests a planar rather than a tetrahedral configuration. The magnetic moment of $Ni(Ph_3PO)_2(NO_3)_2$ is 3·45 B.M. from a Curie–Weiss plot fitted to data at three temperatures. Again as with $[Ni(Ph_3PO)_4]^{2+}$ ($\mu = 3{\cdot}51$ B.M.) this moment is higher than any previously reported for planar or octahedral complexes of nickel(II), and might, by itself, suggest a tetrahedral configuration, but the spectrum does not appear to us to bear this out. Again, the tentative hypothesis [3] is suggested that, because of crowding due to the very bulky phosphine oxide groups, the NiO_4 configuration may not be completely planar, but rather wrinkled to a configuration of D_{2d} symmetry. We have only recently noticed that Furlani [6] published some theoretical conclusions as to the effect upon the spectrum of a planar nickel(II) complex of pushing two *trans*-ligands up and the other two down from the plane by an angle of 17° (which is the magnitude of angle considered likely when the suggestion of a D_{2d} configuration of the NO_4 grouping in $[Ni(OPPh_3)_4]^{2+}$ was made.[3] He shows that the expected spectrum in this D_{2d} ligand field differs only a little from the spectrum in a D_{4h} field (same ligands and bond distances assumed, of course), while, like the D_{4h} spectrum, the D_{2d} spectrum is qualitatively different from the spectrum in a T_d field. Thus Furlani's results provide excellent support, from the spectral side, for our proposal. It is fair to note, however, that there is still no further evidence concerning the validity of our assumption that a D_{2d} field causes the nickel(II) ion to have a magnetic moment (3·4—3·5 B.M.) intermediate between those for D_{4h} (3·0—3·2 B.M.) and T_d (~3·5—4·2 B.M.) fields.

It seems quite likely that the solid complex $(Ph_3PO)_2Co(NO_3)_2$ contains tetrahedrally co-ordinated cobalt(II). According to rather extensive correlations recently developed in this laboratory [7] between the magnitude of the orbital contribution to the magnetic moment and the position of the ligands (or average position when several different ones are present) in the spectrochemical series, cobalt(II) co-ordinated tetrahedrally by two Ph_3PO and two NO_3^- groups might be expected to have a magnetic moment of 4·6—4·7 B.M. The strong absorption peak at 565 mμ has the appearance typical of those for other [7] tetrahedral cobalt(II) complexes. It is, however, at a somewhat higher energy than might have been expected. In methylene chloride and nitromethane solutions, the compound also has a peak at about the same position. Curiously, the intensity is considerably less than the intensity in the $CoCl_4^{2-}$ ion [8] ($\varepsilon_{max.}$ ~600). There is also a change in the magnetic moment on dissolution in methylene chloride which is large enough (~0·17 B.M.) to merit consideration. It appears possible that there is some difference between the configurations in the solid and in solution, but we think it unlikely that it becomes planar in solution. For a planar species we should expect [9] a moment of around 5·0 B.M. and a much richer visible spectrum.

EXPERIMENTAL

Preparative Methods.—Triphenylphosphine oxide was prepared by the method of Cox and Westheimer [10] and melted 156—157°.

The complexes (Table 1) were all prepared by mixing alcoholic solutions of the metal nitrate (usually hydrated) and an excess of the phosphine oxide. The solutions were then taken to dryness on a steam-bath and the solid residues boiled with benzene which removed traces of water and excess of phosphine oxide. The complexes were then filtered off, washed with sodium-dried benzene and dried *in vacuo*.

Physical Measurements.—Electronic absorption spectra in the range 300—1200 mμ were measured for the solid compounds by using a Beckman DU spectrophotometer equipped with a reflectance attachment and with magnesium carbonate as the reference. Solution measurements to 800 mμ were made on a Cary recording spectrophotometer and from 800 to 1200 mμ on the Beckman DU instrument.

Magnetic susceptibilities were measured with a sensitive Gouy balance. The cobalt(II) compound was measured by Dr. R. H. Holm and details will be published shortly in a general correlation of magnetic properties of spin-free cobalt(II) complexes. The solid nickel(II) complex was measured over a temperature range and the results fit the Curie–Weiss equation $\mu = 2{\cdot}84[\chi(T - \theta)]^{\frac{1}{2}}$.

[6] Furlani, *Gazzetta*, 1958, **88**, 279.
[7] Holm and Cotton, *J. Chem. Phys.*, 1959, **31**, 877; *ibid.*, in the press.
[8] Ballhausen and Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 397.
[9] Holm and Cotton, unpublished work.
[10] Cox and Westheimer, *J. Amer. Chem. Soc.*, 1958, **80**, 5441.

Conductivities were measured with a Serfass conductivity bridge and a cell calibrated with aqueous potassium nitrate.

Infrared spectra were recorded on a Perkin–Elmer Model 21 double-beam spectrometer equipped with a rock-salt prism.

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