

374. *Phosphine Oxide Complexes. Part I. Preparation and Properties of the Cation $[(\text{Ph}_3\text{PO})_4\text{Ni}]^{2+}$.*

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The preparation and properties of $[(\text{Ph}_3\text{PO})_4\text{Ni}](\text{ClO}_4)_2$ are reported. Four lines of evidence, *viz.*, visible spectrum, magnetic moment, X-ray powder patterns, and steric requirements of the ligands, are discussed with regard to the configuration of the cation. It is concluded that a regular tetrahedral ligand field about the Ni(II) ion can be ruled out although the magnetic moment (3.51 B.M.) appears unusually high for a strictly planar field. The possibility of an intermediate configuration giving D_{2d} symmetry in the NiO_4 group is considered.

In a preliminary note¹ we reported that triphenylphosphine oxide forms complexes with many transition-metal salts containing non-complex-forming anions. The complexes obtained so far* have the general formulæ $[(\text{Ph}_3\text{PO})_4\text{M}]^{n+}\text{X}^-_n$, where M^{n+} is the n -valent metal ion and X^- is the non-complex-forming anion, assumed here to be a univalent one such as ClO_4^- . This is the first of several papers describing in detail the spectral, magnetic, infrared, and structural characteristics of such complexes.

Tetrakis(triphenylphosphine oxide)nickel(II) perchlorate, $[(\text{Ph}_3\text{PO})_4\text{Ni}](\text{ClO}_4)_2$, is a pale yellow substance prepared by direct combination of nickel perchlorate and triphenylphosphine oxide in approximately stoichiometric proportion in alcohol and evaporation of the solution. It is insoluble in water and benzene but somewhat soluble, apparently without decomposition, in nitromethane. It also dissolves in alcohol but here it apparently decomposes since the solution is green, and not yellow as is the solid.

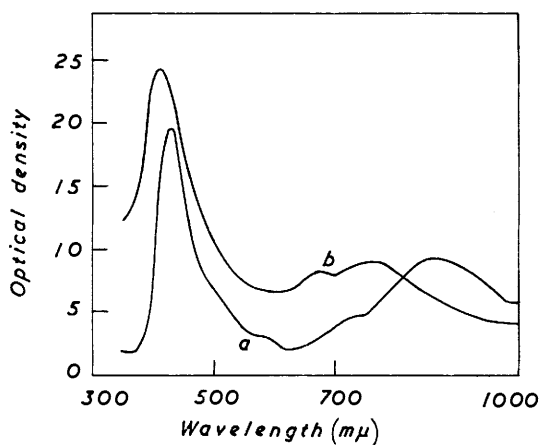
The most important problem with respect to $[(\text{Ph}_3\text{PO})_4\text{Ni}]^{2+}$ seems to concern its structure. We suggested earlier,¹ on the basis of certain data, that it appeared to be

* Owing to an oversight a compound $[(\text{Ph}_3\text{PO})_4\text{Cu}](\text{NO}_3)_2$ was mentioned in reference 1. This should have been the perchlorate. Actually, no such nitrate has been prepared, addition of triphenylphosphine oxide to cupric nitrate giving $(\text{Ph}_3\text{PO})_2\text{Cu}(\text{NO}_3)_2$, a compound to be described along with its Ni(II) and Co(II) analogues in Part III.

¹ Cotton, Bannister, Barnes, and Holm, *Proc. Chem. Soc.*, 1959, 158.

tetrahedral. We now re-examine that conclusion in the light of all the available evidence. Whether tetrahedral complexes of nickel(II) exist has been a moot point for a long time. Before the recent acceptance of the ligand-field theory by co-ordination chemists, there was no criterion, short of X-ray structure determination, by which the tetrahedral configuration of a nickel(II) complex could be unequivocally established. The two important criteria provided by ligand-field theory are: (1) the type of spectrum due to parity-forbidden $3d-3d$ transitions which would be expected, and (2) the magnitude of the orbital contribution to the magnetic moment of the ground state. In the present work we shall also utilize two additional, but generally less conclusive criteria, namely, (3) X-ray powder patterns, and (4) consideration of the steric requirements of the ligands.

(1) *The Visible Absorption Spectrum.*—It was stated earlier¹ that the spectrum is in accord with what we should expect from theory for T_d symmetry of the ligand field, taking D_q to be about 400 cm^{-1} . This statement was based on a calculation in which the Slater integrals measuring interelectronic repulsion were assumed to be the same for the complexed Ni(II) ion as for the free ion (meaning in effect that the ${}^3F-{}^3P$ separation was taken



Ultraviolet absorption of $[(\text{Ph}_3\text{PO})_4\text{Ni}](\text{ClO}_4)_2$,
(a) of solid and (b) in nitromethane solution.

as that for the free ion²) and the effects of spin-orbit coupling were ignored. Thus the two principal absorptions of the solid compound (Figure *a* and Table 1) were assigned to the ${}^3T_1(F) \rightarrow {}^3A_2$ and ${}^3T_1(F) \rightarrow {}^3T_1(P)$ transitions. Shortly after this, however, Liehr and Ballhausen³ published detailed and "exact" calculations of the energy levels of Ni^{2+} in both tetrahedral and octahedral fields. On the basis of these more accurate theoretical results it appears necessary to alter our previous conclusion from the spectral data. In the following discussion we shall be referring to Fig. 1 of reference 3, an energy

TABLE 1. Visible spectral data for $[(\text{Ph}_3\text{PO})_4\text{Ni}](\text{ClO}_4)_2$.

Sample	Positions of absorption bands (10^{-3} cm^{-1}) (extinction coefficients; $\text{cm}^2 \text{ mmole}^{-1}$)		
Solid	23.0 ^a	13.8 ^a shoulder	11.4 ^a
Solution	24.3 (~24)	14.8 (~8)	13.1 (~9)

^a ϵ not measured.

level diagram for Ni(II) in a tetrahedral ligand field where energies and spin multiplicities are shown as a function of D_q (here signifying one-tenth of the separation between the one-electron orbitals of e and t_2 symmetry).

Because, according to Liehr and Ballhausen, there is an appreciable diminution of the

² Moore, "Atomic Energy Levels," U.S. Nat. Bur. Standards Circular 467, Vol. II, Washington, D.C., 1952.

³ Liehr and Ballhausen, *Ann. Phys.*, 1959, **6**, 134.

${}^3F-{}^3P$ separation due to the ligand field, the previously proposed assignment of the absorption at $\sim 23,000$ cm^{-1} to the ${}^3T_1(F)-{}^3T_1(P)$ transition with a D_q value of 400–500 cm^{-1} is not possible. Indeed the diagram shows that the only possible assignment of the experimental data would be: $h\nu = 23,000$ cm^{-1} as the ${}^3\Gamma_1({}^3T_1) \rightarrow {}^3\Gamma_{1,3,4,5}({}^3T_1)$ transition and $h\nu = \sim 11,000-14,000$ cm^{-1} as the ${}^3\Gamma_1({}^3T_1) \rightarrow {}^3\Gamma_{2,3,4,5}({}^3T_2)$ transition with D_q equal to about 1700 cm^{-1} . There seems little doubt that a D_q of 1700 cm^{-1} is unacceptable. Hexaquo-nickel(II) ion has a D_q of ~ 850 cm^{-1} , so that, according to the well-known relation, derivable on the assumption of electrostatic ligand-metal interaction, in a tetrahedral complex also containing oxygen ligands D_q should be about 400 cm^{-1} . That D_q in the tetrahedral case could vastly exceed that in the octahedral case seems impossible.

Since publication of our note¹ we have obtained the spectrum of $[(\text{Ph}_3\text{PO})_4\text{Ni}](\text{ClO}_4)_2$ in nitromethane solution (Figure: *b*), thus permitting an evaluation of the molar extinction coefficients of the bands, which are in the range 6–25. This is the range characteristic for Ni(II) in centrosymmetric, *i.e.*, octahedral and planar, environments, attributable solely to vibronic coupling. In the only published absorption spectrum of a truly tetrahedral complex of Ni(II), namely, that given by Gruen and McBeth⁴ for NiCl_4^{2-} , the extinction coefficients are ~ 180 , as might be expected as a result of $g-u$ mixing in the tetrahedral field and also as a result of possible covalency in the metal-ligand bonds. Thus it would appear that the intensities of the bands in $[(\text{Ph}_3\text{PO})_4\text{Ni}]^{2+}$ also argue against its being tetrahedral.

To conclude the discussion of the spectrum we must consider whether the spectrum appears consistent with a square configuration. While the quality of the spectra we have been able to obtain for $[(\text{Ph}_3\text{PO})_4\text{Ni}]^{2+}$ does not justify an attempt to make a detailed analysis using Maki's results and equations,⁵ it certainly appears that the data are compatible with expectation for a planar complex. Comparison of our spectra with several reported by Maki for similar complexes, *e.g.*, bis(salicylaldehyde)nickel(II), makes this obvious. Thus, the spectral data provide evidence, not only against a tetrahedral configuration, but for a planar one.

(2) *Magnetic Data.*—The magnetic moment of the nickel ion in $[(\text{Ph}_3\text{PO})_4\text{Ni}]^{2+}$ is 3.51 ± 0.05 B.M. evaluated from data at 74°, 195°, and 300° K. The Curie-Weiss equation is followed with a relatively small Weiss constant of only -9° . This datum figured strongly in our earlier conclusion that the complex ion was tetrahedral. For octahedral complexes of Ni(II) the ground state is an orbital singlet, and theory predicts that the mixing in of orbital momentum from excited states *via* spin-orbit coupling should lead to moments of the order of 3.1–3.3 B.M. Experimental data,⁶ with a few exceptions which may be spurious, lie in this range. There does not seem to be any reason why a planar compound should have a higher orbital contribution; in fact, the reverse might be expected. On the other hand it has been estimated by Figgis⁷ that moments of tetrahedral complexes should run between 3.6 and 4.2 B.M., depending upon how much configuration interaction is permitted by the magnitude of the ligand field. Moreover, while data for truly tetrahedral complexes are meagre, those given by Gill, Nyholm, and P. Pauling⁸ for tetrahalogeno-anions vary from ~ 3.5 to ~ 3.9 B.M., in good accord with theory. Thus the moment of 3.51 B.M. for $[(\text{Ph}_3\text{PO})_4\text{Ni}]^{2+}$ appeared by itself to suggest a tetrahedral ligand field. However, in view of the incompatibility of the spectra with the assumption of a ligand field of T_d symmetry, we must abandon this conclusion. Actually, 3.5 B.M. is about the lowest possible value for a tetrahedral field and is only 0.15–0.20 B.M. above the higher previously observed values for centrosymmetric fields. We shall discuss later a way in which an intermediate value could perhaps arise.

⁴ Gruen and McBeth, *J. Phys. Chem.*, 1959, **63**, 393.

⁵ Maki, *J. Chem. Phys.*, 1958, **28**, 651; 1958, **29**, 162.

⁶ Foex, "Constantes Selectionées Diamagnetisme et Paramagnetisme," Masson et Cie., Paris, 1957.

⁷ Figgis, quoted in ref. 8.

⁸ Gill, Nyholm, and Pauling, *Nature*, 1958, **182**, 168.

(3) *X-Ray Evidence*.—The compounds of the general formula $[(\text{Ph}_3\text{PO})_4\text{M}](\text{ClO}_4)_2$ which we have isolated and characterised are those with $\text{M} = \text{Mn}, \text{Ni}, \text{Co}, \text{Cu},$ and Zn . These other than the nickel compound are described in the following paper, but we shall anticipate in order to make comparisons. The spectral and magnetic properties of the cobalt compound indicate unequivocally that the $[(\text{Ph}_3\text{PO})_4\text{Co}]^{2+}$ ion is tetrahedral. It has been found that the *X-ray* powder patterns for the cobalt and zinc compounds are indistinguishable, indicating without doubt strict isomorphism. Thus the two ions, Co(II) and Zn(II) , which exhibit tetrahedral co-ordination fairly commonly, both form tetrahedral $[(\text{Ph}_3\text{PO})_4\text{M}]^{2+}$ ions. The powder pattern for the copper compound differs from those of all the others. The patterns of the manganese and nickel compounds are very similar though not indistinguishable, suggesting, but not conclusively proving, isomorphism of these two. However, they both differ from the cobalt and zinc patterns to such an extent that isomorphism of the nickel compound with these two is rather unlikely. Thus, the *X-ray* results are in accord with the idea that the nickel compound does not contain a tetrahedral cation, as do the cobalt and zinc compounds.

(4) *Stereochemical Considerations*.—Another line of reasoning used earlier¹ to support the suggestion that the $[(\text{Ph}_3\text{PO})_4\text{Ni}]^{2+}$ cation was tetrahedral was based upon steric considerations. Inspection of an accurate scale model of $[(\text{Ph}_3\text{PO})_4\text{Ni}]^{2+}$ indicates with little doubt that the four ligands cannot be coplanar at any reasonable Ni–O bond distance, but only if we insist upon linearity of the Ni–O–P chain. We assumed this linearity at that time, but now realise that it cannot be justified. In fact, it has been shown that in $\text{SbCl}_5 \cdot \text{O} \cdot \text{PCl}_3$ the Sb–O–P angle is 146.5° .⁹ If we consider the possibility of non-linearity of the Ni–O–P groups, it is apparent from models that a planar disposition of oxygen atoms with an Ni–O distance of $\sim 2 \text{ \AA}$ is possible for an Ni–O–P angle of $\leq \sim 160^\circ$ if two *trans*-ligands are bent upwards and the other two downwards. Thus, when properly considered, steric requirements permit planarity in the NiO_4 group.

(5) *Conclusion*.—Steric requirements and the available *X-ray* data can be satisfied by either a tetrahedral configuration with linear Ni–O–P chains or a planar configuration with Ni–O–P angles $\leq \sim 160^\circ$.

The electronic spectra appear irreconcilable with a tetrahedral ligand field but not incompatible with a square one. However, the magnetic moment, while low for a tetrahedral field, is higher than any previously recorded for a square field. We suggest the possibility of a configuration intermediate between tetrahedral and square as an explanation of the slight, but troublesome, inconsistency between the spectral and the magnetic data. Such a configuration would be that of a squashed tetrahedron, with some bending of the Ni–O–P groups, and would give the NiO_4 system D_{2d} symmetry. The high moments of tetrahedral complexes are attributable to the fact that the ground state is an orbital triplet (although slightly split by spin–orbit coupling and probably also by a Jahn–Teller distortion). When the tetrahedron is squashed this triplet will split into an A_2 and an E level (in D_{2d}) which in the square (D_{4h}) limit become A_{2g} and E_g states with the A_{2g} lying the lower. It appears reasonable to suppose that there is an intermediate configuration in which the separation of the ground state from the uppermost excited states is such as to give a spectrum similar to spectra of planar and octahedral complexes, while preserving sufficient orbital degeneracy or near-degeneracy to supply an orbital contribution to the magnetic moment which is less than expected for tetrahedral but higher than usual for strictly planar complexes.

That a somewhat uncommon configuration may exist in this complex is not greatly surprising if one considers that it may be determined by the opposing factors of the relative rarity of tetrahedral co-ordination of nickel(II) and the steric requirements of the bulky ligands. The suggestion is, however, speculative and can only be tested by detailed computations or, better, by an *X-ray* determination of the structure of $[(\text{Ph}_3\text{PO})_4\text{Ni}]^{2+}$.

⁹ Agerman, Andersson, Lindqvist, and Zackrisson, *Acta Chem. Scand.*, 1958, **12**, 477.

EXPERIMENTAL

Preparation.—Hexa-aquonickel(II) perchlorate (0.37 g., 0.001 mole) in ethanol (5 ml.) was added to triphenylphosphine oxide (1.17 g., 0.0042 mole) in ethanol (5 ml.), giving a pale green solution which was then taken to dryness on a steam-bath, affording a pale yellow, solid *complex*. This was then boiled with benzene to remove excess of phosphine oxide, filtered off, and dried in a vacuum (Found: Ni, 4.19; C, 61.6; H, 4.8. $C_{72}H_{80}Cl_2O_{12}NiP_4$ requires Ni, 4.28; C, 63.1; H, 4.4%).

TABLE 2. *Magnetic data for $(Ph_3PO)_4Ni(ClO_4)_2$.*

Temp. (K)	73.8°	195.4°	299.4°
$10^{-6} \chi$ (per g.)	12.912	4.884	3.041
$10^6 \chi_{corr.}^{mol.}$ ^a	18,499	7495	4969

^a Diamagnetic correction of -801×10^{-6} c.g.s. unit used.

Magnetic Measurements.—Bulk susceptibilities were measured at three temperatures, by using a Gouy balance of standard design equipped with a Dewar vessel which was filled with liquid nitrogen or acetone–solid carbon dioxide to maintain the lower temperatures. Two or three packings of the tube were used for duplicate measurements at each temperature. The measured diamagnetic susceptibility of the compound $(Ph_3PO)_4Zn(ClO_4)_2$ was used as the correction for diamagnetism. The measured value is -801×10^{-6} c.g.s. units compared with -787×10^{-6} computed from Pascal's constants.¹⁰ The experimental data are recorded in Table 2. The Curie–Weiss law, $\mu = 2.84\sqrt{[\chi_{corr.}^{mol.}(T - \theta)]}$, is followed with $\mu = 3.51 \pm 0.05$ B.M. and $\theta = -9^\circ$.

Spectral Measurements.—Part of the infrared spectrum has been reported and discussed elsewhere.¹¹ It may be noted here that the infrared spectrum affords evidence against the presence of water, co-ordinated or otherwise, in the compound, since there are no absorptions in either the O–H stretching or the H–O–H bending region. The visible spectrum was measured for both the solid and solutions in nitromethane. The reflectance spectrum of the solid was measured with a Beckman DU spectrophotometer with the standard Beckman reflectance accessory and magnesium carbonate as the control material. Solution spectra were also measured with a Beckman DU instrument. The visible spectra are shown in the Figure. Separate examination of the spectra of triphenylphosphine oxide and ClO_4^- [as $Zn(ClO_4)_2$] showed that neither of these has absorption bands in the region 350–800 m μ .

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¹⁰ See P. W. Selwood, "Magnetochemistry," Interscience Publ. Inc., New York, 1956, 2nd edn., p. 78.

¹¹ Cotton, Barnes, and Bannister, *J.*, in the press.