

Continued investigations of the decompositions of diazidoquinones and related compounds as well as a study of the chemistry of cyanoketenes are in progress.

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Spectra and Structure of a Tetrahedrally Distorted Low-Spin Nickel(II) Complex with P_2I_2 as the Donor Set

Sir:

Several complexes with NiP_2X_2 chromophore ($X =$ halogen) are known, and some of their structures have been determined by X-ray analysis. Among the complexes with monodentate phosphines, those with triphenylphosphine and $X = Cl^1$ or Br^2 have been found to have a distorted tetrahedral geometry, whereas the triethylphosphine derivative with $X = Br^3$ and the chloro complex with tricyclohexylphosphine⁴ have been found to be rigorously planar.

Among the complexes of NiX_2 with the ditertiary diphenyldiphosphines $Ph_2P(CH_2)_nPPH_2$, those with $n = 1, 2,$ and 3 are low-spin with a square-planar geometry and those with $n = 4$ or 5 are high-spin with a distorted tetrahedral geometry, both indicated by spectroscopic data.^{5,6} The introduction of an oxygen atom in the place of the central methylene group in the diphenyldiphosphine complex with NiX_2 and $n = 5$ gives rise again to high-spin tetrahedral complexes. In this case the oxygen atom is not bonded to the metal, as showed by the X-ray analysis of the complex $[Ph_2P(CH_2)_2O(CH_2)_2PPh_2]NiCl_2$ (chromophore NiP_2Cl_2).⁷

Also the complexes of NiX_2 with the diphosphine $Ph_2P(CH_2)_3PPh_2$ are high-spin distorted tetrahedral.⁸ Now if two methylene groups (positions 3 and 6) are substituted by two oxygen atoms, the ligand 1,8-bis(diphenylphosphino)-3,6-dioxaoctane (POOP), $Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$, is obtained, which reacts with NiI_2 to form a monomeric diamagnetic complex. The allowable stereochemistries for this complex are therefore the four- or five-coordinate, depending on whether the ligand is bi- or tridentate.

The reflectance spectrum of this complex shows bands at 12.5 (sh), 13.7, 21.2, and 27.5 kK (Figure 1). The d-d band in the absorption spectrum in benzene (Figure 1) falls at 14.8 kK and shows a remarkable red shift with respect to the corresponding band found for some square-planar NiP_2X_2 complexes (Table I).⁹

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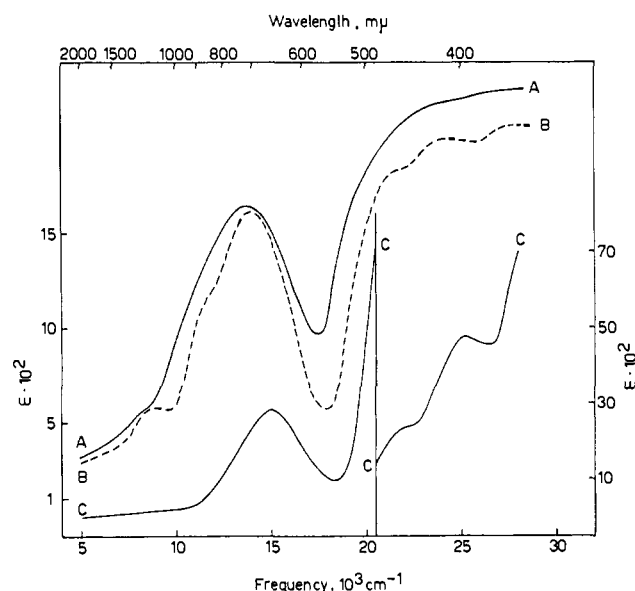


Figure 1. Solid-state spectra (arbitrary scale) of $Ni(POOP)I_2$ at 19° (A) and at -160° (B). Absorption spectrum in benzene of $Ni(POOP)I_2$ (C).

Because of the bathochromic contribution of the iodine atoms, the greatest shift is found for the $(Et_3P)_2NiBr_2$ complex, for which the structure has been established by X-ray analysis.³ On the other hand, the spectra of $Ni(POOP)I_2$ differ from those of low-spin nickel(II) complexes with trigonal-bipyramidal¹⁰ or square-pyramidal¹¹ geometries. Therefore, it is not possible to assign unequivocally either a square-planar, or a five-coordinate structure.

Table I

Compound	Absorption maxima in benzene, kK (log ϵ)		
$(Et_3P)_2NiBr_2$	25.0 (3.79)	21.8 (3.46)	18.5 (2.55)
$(Et_3P)_2NiI_2$	26.8 (3.67)	21.8 (3.46)	16.4 (2.69)
$(Bu_3PhP)_2NiI_2$	27.0 (3.61)	21.6 (3.44)	16.6 (2.69)
$Ni(POOP)I_2$	25.1 (3.68)	21.7 (3.39)	14.8 (2.76)

To give a definitive answer on this problem, an X-ray analysis on the $Ni(POOP)I_2$ complex was undertaken. The crystal data are: space group $P2_1/c$, $a = 11.564 \pm 0.011$, $b = 18.316 \pm 0.027$, $c = 14.878 \pm 0.035$ Å, $\beta = 118^\circ 28' \pm 12'$, $Z = 4$, $D_c = 1.80$, $D_m = 1.79$ g cm⁻³.

The 1564 independent reflections observed were measured on integrated Weissenberg films, using $Cu K\alpha$ radiation. The structural determination was carried out with one Patterson and two three-dimensional Fourier syntheses. These were refined by a full-matrix least-squares treatment with anisotropic temperature factors for iodine, nickel, and phosphorus atoms and isotropic factors for the other atoms, to an R factor of 0.091.

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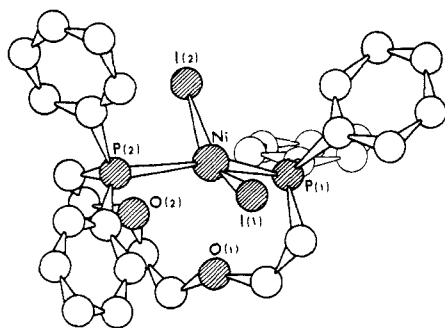


Figure 2. A perspective view of the Ni(POOP)I₂ molecule.

The structure consists of discrete molecules of Ni(POOP)I₂ (Figure 2). The nickel atom is tetracoordinated and linked to the two phosphorus atoms and the two iodine atoms. Each oxygen atom occupies statistically two positions differing for orientation about the C···C axis in the C–O–C moiety. Occupancy factors are close to 50% for the two positions as evidenced by a ΔF Fourier synthesis and by the subsequent refinement. Temperature factors for O(1) and O(2) dropped from 9.60 and 10.70 Å², respectively, to 4.75 and 5.17 Å² [O(1) and O(1)'] and to 3.83 and 5.11 Å² [O(2) and O(2)'] after disordering was considered.

The shortest distance of each oxygen atom from the metal atom is equal to 3.2 Å. The coordination geometry about the nickel atom can be described as intermediate between square planar and tetrahedral. In fact, the angles about the nickel are: I(1)–Ni–I(2), 143.5; I(1)–Ni–P(1), 89.2; I(1)–Ni–P(2), 94.3; I(2)–Ni–P(1), 97.6; I(2)–Ni–P(2), 90.0; and P(1)–Ni–P(2), 162.1° (average σ 0.2°). The distances of the ligand atoms from the metal atom are the following: Ni–I(1), 2.51; Ni–I(2), 2.49; Ni–P(1), 2.24; and Ni–P(2), 2.24 Å (average σ 0.007 Å). Considering the least-squares plane calculated by the positions of the nickel, the two iodine, and the two phosphorus atoms, the following displacements from this plane were found: Ni, –0.17; I(1), +0.61; I(2), +0.60; P(1), –0.52; and P(2) –0.52 Å. The angle between the plane containing Ni, I(1), and I(2), and the plane containing Ni, P(1), and P(2) is 86°.

Until now, X-ray structural determinations have shown all low-spin tetracoordinated nickel(II) complexes to be either perfectly planar or only very slightly distorted, with the greatest tetrahedral distortion being 173°, as found in the biacetylbis(mercaptoethylimine)-nickel(II) complex.¹² The complex Ni(POOP)I₂, therefore, shows the largest distortion toward a tetrahedron of all the low-spin tetracoordinated nickel(II) complexes analyzed by X-rays so far. The closeness of this geometry to the tetrahedral one is again more evident if the I–Ni–I angle (143.5°) is compared not with the theoretical value of 109° 28', but with those found in the distorted tetrahedral (Ph₃P)₂NiX₂ complexes, e.g., Br–Ni–Br (126°) and Cl–Ni–Cl (123°) taking into account, furthermore, that a greater value for I–Ni–I angle would be expected.

Since the chain between the two phosphorus atoms in the POOP ligand has nearly the same length as the –(CH₂)₈– chain in Ph₂P(CH₂)₈PPh₂ (C–C = 1.54, C–O = 1.43 Å), which forms high-spin tetrahedral

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complexes, the distortion in the Ni(POOP)I₂ complex may be attributed to a different disposition of the chain. This different disposition is probably due to an electrostatic interaction of the oxygen atoms with the metal atom. In fact, of all the atoms in the chain, the oxygen atoms are the nearest to the metal (3.2 Å).

This distortion from planarity can account for the low-energy shift observed in the crystal-field band in the Ni(POOP)I₂. In effect the distortion of the coordination polyhedron toward a tetrahedral geometry causes less destabilization of the $d_{x^2-y^2}$ orbital (with respect to planar complexes), with consequent reduction in frequency of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition, to which the observed band is assigned.¹³

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A New Route to Tropones Based on the 1,3-Dipolar Reactivity of Heteroaromatic Betaines

Sir:

We wish to report (a) that anhydro-3-hydroxy-1-methylpyridinium hydroxide (**1**) reacts with N-phenylmaleimide, acrylonitrile, and methyl acrylate to yield the adducts **2**, **3a**, and **3b**, respectively, and (b) a new synthesis of tropones and tropolones from the methiodides of these adducts.

The reactions of type a are the first examples of the C(6)–N–C(2) unit of a simple pyridine ring acting as the 1,3-dipole in a dipolar addition. Indeed electrocyclic reactions in pyridine chemistry are rare; thus pyridine adds 2 mol of dimethyl acetylenedicarboxylate across the –C=N– bond via a two-step addition–cyclization mechanism.¹ However, the conversions **1** → **2**, **3** were sought as mesoionic compounds such as sydnone have long been known to behave as 1,3 dipoles,² and it has recently been shown^{3,4} that corresponding derivatives with six-membered rings react analogously (certain pyrimidinium betaines dimerize by an alternative path⁵). One of us pointed out many years ago⁶ that "mesoionic" structures were mesomeric betaines with aromatic character. Hence mesomeric betaines of type **1** should also show 1,3-dipolar character. Ullman⁷ has found such reactivity for benzpyrylium oxides and aziridines can ring-open to dipolar azomethine ylides.⁸

The adducts (**2**, **3**) bear an obvious resemblance to tropane alkaloids, which have been converted by successive Hofmann eliminations into cycloheptane derivatives.⁹ In the present case Hofmann elimination

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