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The preparation of 2,6,7-trioxa-1, 4-diphosphabicyclo [222] octane and the study of some transition metal complexes of trimethyl phosphite

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THE PREPARATION OF 2,6,7-TRIOXA-1,4-DIPHOSPHABICYCLO[2.2.2]OCTANE AND THE STUDY OF SOME TRANSITION METAL COMPLEXES OF TRIMETHYL PHOSPHITE

by

Kenneth James Coskran

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DOCTOR OF PHILOSOPHY

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Dean of Graduate College

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Ames, Iowa

1967

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PART I.

PART II.

PART I. THE PREPARATION OF 2,6,7-TRIOXA-1,4-DIPHOSPHABICYCLO[2.2.2]OCTANE (VIII) AND DERIVATIVES

INTRODUCTION

Relatively few bicyclic phosphorus compounds are known which have phosphorus atoms at the bridgehead. The most common examples of this type of compound are bicyclic phosphites which contain three alkoxy groups attached to the phosphorus. The known examples of such compounds are 2,8,9-trioxa-1-phospha-adamantane (I) reported by Stetter and Steinacker in 1952 (1), 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (II) prepared by Verkade and Reynolds in 1960 (2), and 2,6,7-trioxa-1-phosphabicyclo[2.2.1]heptane (III) prepared by Denney and Varga in 1966 (3). The bicyclic compounds to be discussed are represented schematically in Figure 1. In 1959 Mann (4) described the synthesis of a bicyclic trialkyldiphosphine, 1,4-diphosphabicyclo[2.2.2]octane (IV) and recently, Boros (5) reported the compound, 4-methyl-3,5,8-trioxa-1-phosphabicyclo-[2.2.2]octane (V). Closely related to these compounds are bicyclic aminophosphines of which two examples of the bicyclio[2.2.2]octane structure type are known: 2,3,5,6,7,8-hexamethyl-2,3,5,6,7,8-hexaaza-1,4-diphosphabicyclo[2.2.2]octane (VI) prepared by Payne, et al. (6), and 2,6,7-trimethyl-4-methyl-2,6,7-triaza-1-phosphabicyclo[2.2.2]octane (VII), recently prepared by Laube, et al. (7). Also, Holmes and Forstner (8) have reported the adamantane type aminophosphine, phosphorus tri-N-methylimide.

Although considerable work has been done on the coordination chemistry of the bicyclic phosphite compounds I and II (9-14), there is a notable absence of coordination chemistry of bicyclic phosphines. In view of this and the general differences in the nature of complexes

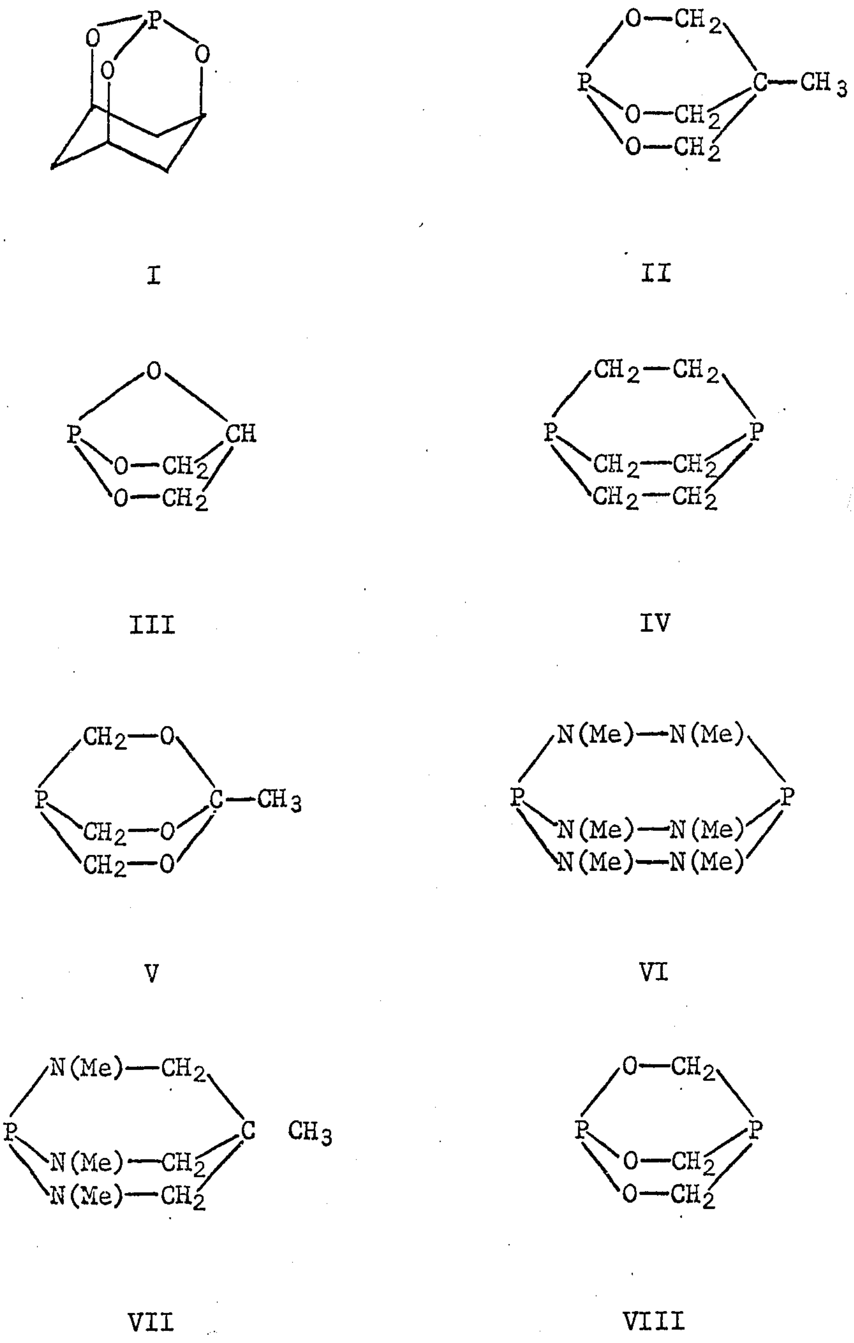


Figure 1. Schematic representations of the bicyclic phosphorus compounds I-VIII.

formed between trialkyl phosphites and trialkylphosphines (15-17), it became of interest to synthesize a bicyclic compound that was both a phosphite and a phosphine, in order that their relative coordinating abilities could be compared. For this purpose, the di-phosphorus compound, 2,6,7-trioxa-1,4-diphosphabicyclo[2.2.2]octane (VIII) was prepared. The 1,4-dioxo (VIIIa), the 1-sulfo (VIIIb), and the 1-sulfo-4-oxo (VIIIc) derivatives were also characterized.

EXPERIMENTAL

Analytical Methods

Elemental analyses

Carbon, hydrogen, phosphorus, and sulfur analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tenn.

Instrumentation

Infrared spectra

Infrared spectra were obtained in KBr pellets and CCl_4 solutions and recorded on a Perkin-Elmer Model 21 double-beam spectrometer using sodium chloride optics.

Nuclear magnetic resonance spectra

Proton n.m.r. spectra were obtained on approximately 15% solutions on Varian Associates Models HR-60 and A-60 spectrometers. Tier's salt was used as an internal standard for aqueous solutions and tetramethylsilane for all other solutions. P^{31} n.m.r. spectra were obtained on approximately 30% dimethyl sulfoxide solutions with 85% aqueous phosphoric acid as an external standard.

Melting points

Melting points were taken in capillaries and are uncorrected.

Materials

Tetrakis(hydroxymethyl)phosphonium chloride

Research quantities of tetrakis(hydroxymethyl) phosphonium cloride were obtained as a gift from Hooker Chemical Corp., Niagara Falls, N.Y., and recrystallized from 1-propanol.

Trimethyl phosphite

Trimethyl phosphite was purchased from Eastman Kodak Co., Rochester, N.Y., and was used without further purification.

2,2-Dimethoxypropane (DMP)

2,2-Dimethoxypropane (DMP) was purchased from Eastman Kodak Co., Niagara Falls, N.Y., and used without further purification.

VIII and Derivatives

Tris(hydroxymethyl)phosphine

This triol was prepared according to the method of Grayson (18), wherein a solution of 4.0 g. (0.10 mole) of sodium hydroxide dissolved in 100 ml. of absolute ethanol was added all at once to a stirred solution of 19 g. (0.10 mole) of tetrakis(hydroxymethyl)phosphonium chloride, dissolved in 175 ml. of absolute ethanol at room temperature. The solution was allowed to stir for 15 min. after which it was filtered and the ethanol removed under vacuum to give quantitative yields of the product in the form of a colorless sirup.

Anal. Calcd. for $C_3H_9O_3P$: C, 29.03; H, 7.25. Found: C, 29.04; H, 6.97.

2,6,7-Trioxa-1,4-diphosphabicyclo[2.2.2]octane (VIII)

The 0.10 mole of tris(hydroxymethyl)phosphine prepared in the previous reaction was slowly heated to approximately 65° with stirring after which 25 ml. of sodium-dried tetrahydrofuran was added and the solution stirred vigorously. (The triol is fairly soluble in tetrahydrofuran under these conditions, yet there is always present a small amount of an insoluble sirup adhering to the sides of the flask.) To this stirred solution, 12.4 g. (0.100 mole) of trimethyl phosphite was added dropwise and the resulting mixture was refluxed at 80° for 2 hr. The cloudy solution was decanted from the sirupy material adhering to the sides of the flask and the tetrahydrofuran was removed under vacuum to give a white solid from which 5.32 g. (35% yield) of clear colorless crystals, melting at 75-76° were obtained upon sublimation at approximately 0.1 mm. and 50°.

Anal. Calcd. for $C_3H_6O_3P_2$: C, 23.67; H, 3.95. Found: C, 23.62; H, 4.02.

When the reaction was carried out without the presence of a solvent, an uncontrollable exothermic reaction took place. No product could be recovered from this reaction mixture.

1,4-Dioxo-2,6,7-trioxa-1,4-diphosphabicyclo[2.2.2]octane (VIIIa)

To 0.3262 g. (2.200 mmoles) of VIII dissolved in 5 ml. of absolute ethanol, 0.354 ml. (4.40 mmoles) of 30% hyrogen peroxide was added dropwise with stirring. The reaction mixture, which became quite warm, was cooled producing 0.3100 g. (95% yield) of needle-like crystals melting at 210-213°.

Anal. Calcd. for $C_3H_6O_5P_2$: C, 19.58; H, 3.27. Found: C, 19.49; H, 3.28.

1-Sulfo-2,6,7-trioxa-1,4-diphosphabicyclo[2.2.2]octane (VIIIb)

An intimate mixture of 0.9016 g. (5.900 mmoles) of VIII and 0.1898 g. (5.900 mg-atoms) of sulfur was placed in a sealed tube and heated to 110°. After 20 min. at this temperature the yellow color of the sulfur disappeared and the resulting white solid was taken up in acetone from which 0.8147 g. (75% yield) of colorless, needle-like crystals were obtained on cooling, having a melting point of 235-237°.

Anal. Calcd. for $C_3H_6O_3P_2S$: C, 19.57; H, 3.27; S, 17.39. Found: C, 19.57; H, 3.30; S, 17.44.

1-Sulfo-4-oxo-2,6,7-trioxa-1,4-diphosphabicyclo[2.2.2]octane (VIIIc)

To a stirred solution of 0.4837 g. (2.630 mmoles) of VIIIb in 150 ml. of absolute ethanol was slowly added 2.1 ml. (26 mmoles) of 30% hydrogen peroxide. The solution was boiled for 5 min. after which it was cooled to 0° overnight. The white powder which formed was filtered and dissolved in boiling acetonitrile. Cooling the solution to 0° produced 0.4317 g. (82% yield based on $P(CH_2O)_3PS$) of small colorless crystals which decomposed at about 210°.

Anal. Calcd. for $C_3H_6O_4P_2S$: C, 18.00; H, 3.00; S, 16.00. Found: C, 17.55; H, 3.24; S, 15.63.

1-α-Oxo-1-β-triphenylmethyl-4-chloromethyl-1,4-diphospha-2,6-dioxacyclohexane

To 3.0 g. (0.020 mole) of VIII dissolved in 25 ml. of acetonitrile was added 5.6 g. (0.020 mole) of triphenylmethyl chloride. The solution was stirred magnetically and the solvent slowly evaporated by means of a dry stream of nitrogen. Within minutes a colorless crystalline salt formed in nearly quantitative yields.

Anal. Calcd. for $C_{22}H_{21}O_3P_2Cl$: C, 61.39; H, 4.88. Found: C, 61.07; H, 4.96.

1,4-Bis(triphenylmethyl)-2,6,7-trioxa-1,4-diphosphabicyclo[2.2.2]octane tetrafluoroborate

To a stirred solution of 1.4 g. (5.0 mmoles) of triphenylmethyl tetrafluoroborate in 10 ml. of acetonitrile, 1.52 g. (10.0 mmoles) of VIII was slowly added. As solid VIII reacted, a powdery solid was formed which dissolved initially, but which precipitated from solution on further addition of VIII. The n.m.r. spectrum of this compound reported in Table 1 was consistent with its formulation as $[P(CH_2O)_3P\cdot 2Ph_3C]^{2+}2BF_4^-$.

Uncharacterized Complexes of VIII

$Ni(ClO_4)_2\cdot 6DMSO$ + VIII

$Ni(ClO_4)_2\cdot 6DMSO$ was prepared according to the method of Selbin, et al., (19). To 0.38 g. (0.50 mmole) of the above, dissolved in 20 ml. of acetone, 0.76 g. (5.0 mmoles) of VIII dissolved in 5 ml. of acetone was added all at once to give a yellow solution with a yellow solid.

After filtration, the solid was scraped from the fritted funnel whereupon it exploded quite violently igniting the entire solid.

$Ni(NO_3)_2 \cdot 6H_2O$ + VIII

To 0.14 g. (0.50 mmole) of $Ni(NO_3)_2 \cdot 6H_2O$ dissolved in an acetone-DMP solution, 0.76 g. (5.0 mmoles) of VIII dissolved in 10 ml. of acetone was added all at once to give a yellow solid which was soluble in methanol. When this solid was allowed to dry in a vacuum desiccator or on the vacuum line for an extended period of time, it became more orange in color and showed only partial solubility in methanol. Elemental analyses were inconsistent with a variety of formulations.

$Cu(NO_3)_2 \cdot 3H_2O$ + VIII

To 0.11 g. (0.50 mmole) of $Cu(NO_3)_2 \cdot 3H_2O$ dissolved in an acetone-DMP solution, 0.76 g. (5.0 mmoles) of VIII dissolved in 10 ml. of acetone was added all at once. The blue color of the copper (II) solution changed to blue-green. After stirring several min. a very light blue-green solid precipitated which showed only partial solubility in boiling methanol. Various formulations could not be made to fit the elemental analyses.

$Co(NO_3)_2 \cdot 6H_2O$ + VIII

To 0.29 g. (1.0 mmole) of $Co(NO_3)_2 \cdot 6H_2O$ dissolved in an acetone-DMP solution, 1.52 g. (10.0 mmoles) of VIII dissolved in 10 ml. of acetone was added all at once. A brown-yellow solid formed immediately which could be extracted with boiling methanol to give a yellow solution and a tan colored solid. Treating the yellow extractant with ether only gave more tan solid.

$AgNO_3$+ VIII

To 0.17 g. (1.0 mmole) of $AgNO_3$ dissolved in 10 ml. of absolute ethanol, 0.91 g. (6.0 mmoles) of VIII dissolved in 10 ml. of absolute ethanol was added all at once to give a white solid. The solid turned black while drying on the vacuum line.

$CoCl_2 \cdot 6H_2O$ + VIII

To 0.24 g. (1.0 mmole) of $CoCl_2 \cdot 6H_2O$ dissolved in an acetone-DMP solution, 1.52 g. (10.0 mmoles) of VIII dissolved in 10 ml. of acetone was added all at once to give dark green solid. This solid was partially soluble in boiling methanol producing a yellow-orange solution from which the green solid could be re-obtained by adding a large volume of ether. Various formulations did not fit the elemental data.

$CuCl_2 \cdot 6H_2O$ + VIII

To 0.12 g. (0.50 mmole) of $CuCl_2 \cdot 6H_2O$ dissolved in an acetone-DMP solution, 0.76 g. (5.0 mmoles) of VIII dissolved in 10 ml. of acetone was added all at once to give a white solid. This solid was found to be very insoluble in most organic solvents and various formulations cound not be made to fit the analytical data.

$NiCl_2$ + VIII

Anhydrous $NiCl_2$ was obtained by heating the hydrated salt in a casserole over a flame. The $NiCl_2$ was separated from the NiO formed in heating by extraction into methanol. To 0.065 g. (0.50 mmole) of

$NiCl_2$ dissolved in a minimum amount of hot ethanol, 0.76 g. (5.0 mmoles) of VIII dissolved in 10 ml. of ethanol was added all at once producing a dark red colored solution. This solution was then poured into 200 ml. of ether producing a red-brown solid. The solid was insoluble in acetone, but dissolved in ethanol, methanol and N,N-dimethylformamide to give yellow solutions and in acetonitrile to give a green solution from which the brown solid could be recovered by adding a large volume of ether. No elemental formulations could be made which were consistent with the analytical data.

If the initial reaction mixture was allowed to stir in the ethanol solution for up to one hour, the original red color was replaced by a yellow color. No solid could be obtained from this solution.

NiI_2 + VIII

Anhydrous NiI_2 was prepared by the metathetical reaction of $NiCl_2$ and NaI in absolute ethanol. To 0.643 g. (2.06 mmoles) of NiI_2 dissolved in 10 ml. of absolute ethanol, 0.626 g. (4.12 mmoles) of VIII dissolved in 10 ml. of absolute ethanol was added all at once to give a dark purple solid. The solution was allowed to stir for one hr. without appreciable loss of color. The compound was partially soluble in acetone and methylene chloride although no crystals could be obtained from these solvents.

$Ni(BF_4)_2$ + VIII

To 0.19 g. (0.57 mmole) of $Ni(BF_4)_2 \cdot 6H_2O$ dissolved in 5 ml. of absolute ethanol, 0.86 g. (5.7 mmoles) of VIII dissolved in 10 ml.

of absolute ethanol was added all at once to give stable yellow solid. The compound was quite insoluble in most organic solvents.

DISCUSSION

VIII and Derivatives

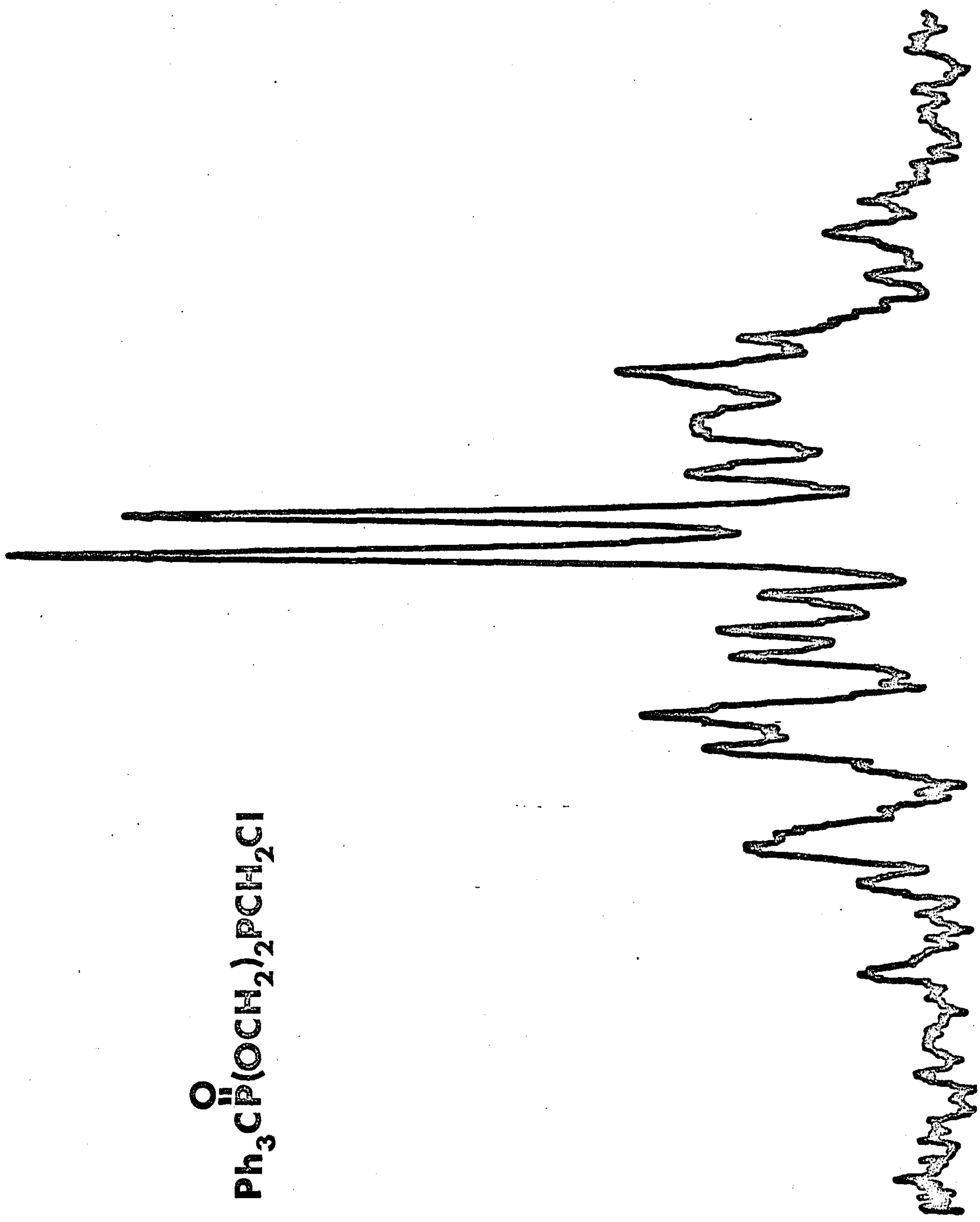
The preparation of VIII is accomplished by a simple transesterification of trimethyl phosphite by the phosphine triol, tris (hydroxymethyl)phosphine. The yields for this reaction are relatively poor due to probable extensive polymerization. When the reaction was carried out in the absence of a solvent with slow addition of trimethyl phosphite, a very exothermic reaction took place at the interface of the two immiscible reactants which caused ignition of the mixture. This problem was overcome by partially dissolving the triol in tetrahydrofuran, thus diluting one of the reactants. The product is stable to air oxidation and can be stored indefinitely under vacuum.

The oxo and sulfo compounds represent normal derivatives of trivalent phosphorus compounds, but it is worthy of note that four derivatives are missing from the list, namely, the 1-oxo, 4-oxo, 4-sulfo, and 1,4-disulfo. It is not surprising that the 1,4-dioxo compound is formed rather easily, but various attempts to prepare the monooxo compounds always yielded VIIIa. Similarly, only a di-phosphonium salt could be prepared even when VIII was in 100% excess of triphenylmethyl tetrafluoroborate. This suggests that both phosphorus nuclei are easily oxidized. In contrast, open-chain trialkylphosphines are very easily oxidized and are spontaneously flammable in air, while open-chain trialkyl phosphites are stable to dry air for long periods of time. It is possible that the reduced reactivity of the phosphine phosphorus in VIII toward oxidation is due to either a hybridization change around this atom because of the constrained structure of VIII and/or the presence of electron-withdrawing oxygens on the alkyl substituents. Although the latter explanation may seem the more plausible, it does not apply to the parent triol ($P(CH_2OH)_3$) which was readily oxidized in air (18).

The formation of the 1-sulfo compound and the absence of the 1,4-disulfo compound is indeed surprising in view of the apparent ease with which trialkylphosphine sulfides are produced under fusion conditions (20). Attempts to prepare the 1,4-disulfo compound using large excesses of sulfur only yielded the 1-sulfo derivative along with coprecipitated sulfur. It is interesting, however, that the 1-sulfo derivative could be further oxidized by forming an oxide at the phosphine phosphorus. This indicates that the phosphine phosphorus is sufficiently reactive to be attacked by the more electronegative oxygen which would be better able to polarize the phosphorus lone-pair electrons.

The Michaelis-Arbuzov reaction of VIII with triphenylmethyl chloride gave the expected product which was analogous to that obtained from a similar reaction of I and II (21). The proton n.m.r. spectrum and its integration shown in Figure 2 is consistent with the formulation of the compound shown schematically in the same figure. No attempt was made to analyse the complex $A_2B_2X_2$ pattern of the ring methylene hydrogens. At present there is insufficient evidence to postulate the conformation of this system. A P^{31} n.m.r. spectrum could not be obtained because of insufficient solubility of the compound.

Figure 2. Proton n.m.r. spectrum of Michaelis-Arbuzov product of VIII with triphenylmethyl chloride. (The phenyl proton absorptions are not shown.)



$\mathrm{Ph_3C\overset{O}{\overset{\|}{P}}(OCH_2)_2PCH_2Cl}$

H^1 n.m.r. spectra of VIII and derivatives

Evidence for the formulation of VIII, VIIIa, VIIIb, and VIIIc as the bicyclic structure stems primarily from the proton n.m.r. data which are summarized in Table 1. The spectra are reproduced in Figures 3-6.

The downfield proton chemical shift observed upon oxidation of VIII to VIIIa, VIIIb, and VIIIc parallels that found previously for II and its 1-oxo (IIa) and 1-sulfo (IIb) derivatives. It is also indicative of the electron withdrawal from the bicyclic molecule by the electronegative chalcogens.

The assignment of J_{PCH} = 9.3 Hz. in VIII is based on the very similar value of J_{PCH} = 8.3 Hz. observed for V (22). Similarly, the assignment of J_{POCH} = 2.7 Hz. is consistent with the value of J_{POCH}= 1.8 Hz. for II (21). Like the H^1 n.m.r. spectrum of VIII, the spectrum of VIIIa consists of two doublets (Figure 4) of separation 7.8 and 8.7 Hz. From the value of J_{PCH} = 7.4 Hz. for the oxide derivative of V (22), it is concluded that J_{PCH} = 7.8 Hz. and that J_{POCH}= 8.7 Hz.

The spectrum of the 1-sulfo compound represents a unique case, for it consists of an apparent 1:2:1 triplet (Figure 5) which does not resolve into any more peaks upon expansion. Very likely the "triplet" is composed of two overlapping doublets of equal separation. Thus both J_{PCH} and J_{POCH} = 7.8 Hz. In view of the increase of J_{POCH} upon oxidation of VIII to VIIIa, the value of 7.8 Hz. for J_{POCH} is not unexpected for VIIIb. It is surprising, however, that J_{PCH} should decrease from 9.3 to 7.8 Hz. when a sulfur atom has been attached only to the phosphite phosphorus. This long-range effect on J_{PCH} might be ascribed to significant bond angle changes in the entire molecule. The spectrum of VIIIc

Table 1. Proton chemical shifts of VIII and derivatives

Compound	H^{1a}	J_{PCH} Hz.	J_{POCH} Hz.	Solvent
$P(CH_2O)_3P$ (VIII)	4.45	9.3	2.7	CCl_4
$OP(CH_2O)_3PO$ (VIIIa)	5.28	7.8	8.7	D_2O^b
$P(CH_2O)_3PS$ (VIIIb)	5.20	7.8	7.8	DMSO[c]
$OP(CH_2O)_3PS$ (VIIIc)	5.15	8.3	8.9	DMSO[c]
$[Ph_3CP(CH_2O)_3PCPh_3][BF_4]_2$	5.54	6.3	8.5	CH_3CN

[a] Chemical shifts in p.p.m. with respect to $Si(CH_3)_4$ as internal standard.

[b] Tier's salt used as internal standard.

[c] Dimethylsulfoxide.

Figure 3. Proton n.m.r. spectrum of $P(CH_2O)_3P$ (VIII) with $\delta CH_2 = 4.54$ p.p.m., $J_{PCH} = 9.3$ Hz., and $J_{POCH} = 2.7$ Hz.

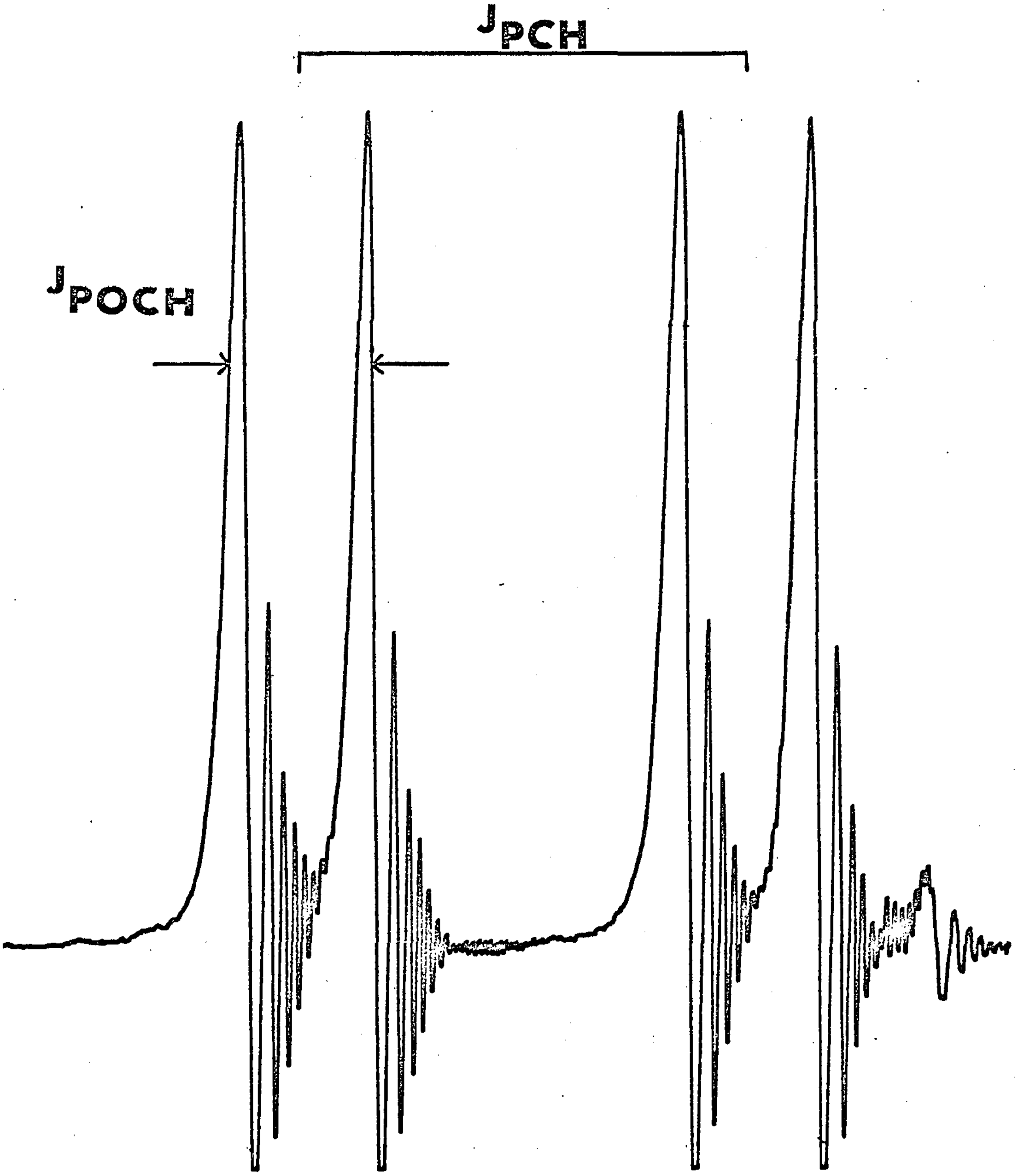

J_{PCH}
J_{POCH}

Figure 4. Proton n.m.r. spectrum of $OP(CH_2O)_3PO$ (VIIIa) with δCH_2 = 5.28 p.p.m., J_{PCH} = 7.8 Hz., and J_{POCH} = 8.7 Hz.

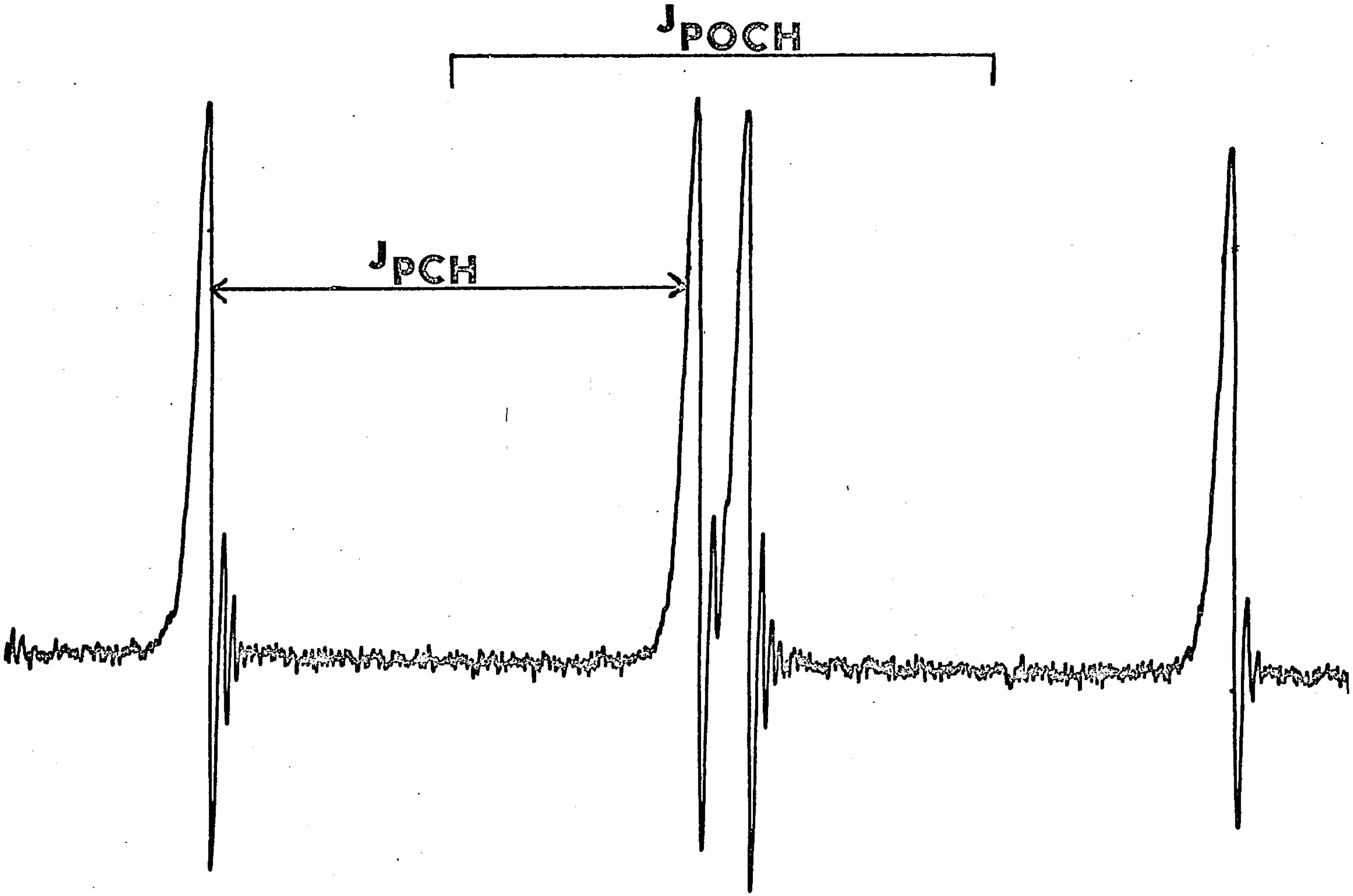
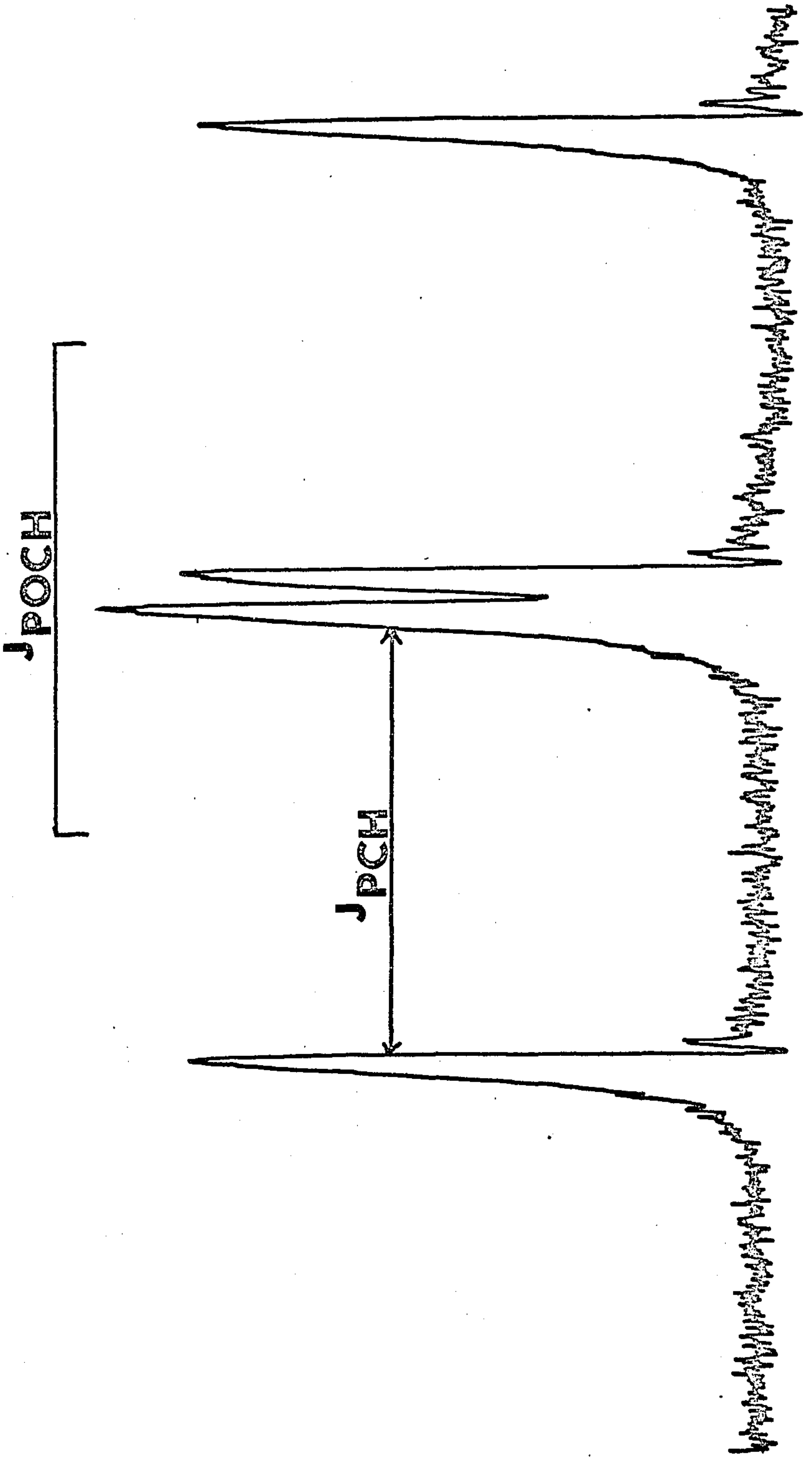

J_{POCH}
J_{PCH}

Figure 5. Proton n.m.r. spectrum of $P(CH_2O)_3PS$ (VIIIb) with δCH_2 = 5.15 p.p.m., J_{PCH} = 7.8 Hz., and J_{POCH} = 7.8 Hz.


J_{PCH}
J_{POCH}

Figure 6. Proton n.m.r. spectrum of $OP(CH_2O)_3PS$ (VIIIc) with δCH_2 = 5.15 p.p.m., J_{PCH} = 8.3 Hz., and J_{POCH} = 8.9 Hz.


J_{POCH}
J_{PCH}

also consists of two doublets (Figure 6) with coupling constants of 8.3 and 8.9 Hz. The larger value has been tentatively assigned to J_{POCH} and the smaller value to J_{PCH} to be consistent with the values observed for VIIIa and VIIIb.

Several interesting observations can be made about the proton-phosphorus couplings in VIII and its derivatives. Rather large values of J_{PCH} have previously been observed only for trialkylphosphine oxides (23) or in similar compounds where strongly electron-withdrawing groups are substituted for an alkyl group (24). For example, J_{PCH} for trimethylphosphine is 2.7 Hz. and 13.4 Hz. for its oxide, whereas for VIII a value of 9.7 Hz. is observed. Moreover, upon oxidation J_{PCH} decreases in contrast to increases observed for trialkylphosphines, whereas J_{POCH} increases from VIII to VIIIa, VIIIb, and VIIIc as observed earlier for polycyclic phosphites (21).

An explanation of these changes has been given (25) wherein hybridization arguments were invoked. It was presumed that the C-P-C bond angles were close to tetrahedral because of the constraints in the bicyclic system. Therefore, the per cent s character in the P-C bond would be higher than in trimethylphosphine, wherein the C-P-C bond angle is 98.9° (26), and thus J_{PCH} would be expected to be larger than in trimethylphosphine (23, 27).

Recently, however, other evidence has been obtained which detracts considerably form the hybridization arguments. The J_{PCH} values for V and its oxide derivative (Va) (8.0 and 7.3 Hz. (22), respectively) are similar to those of VIII and VIIIa. Boros (28) has shown that coordination of V in $[Ni(CO)_3V]$ and $[Mo(CO)_5V]$ yields J_{PCH} values of 2.1 and 1.8

Hz., respectively, which represent a greater decrease in the coupling constant than that observed for Va. Such a decrease contrasts with what has been observed for phosphorus-hydrogen coupling constants when the ligand is I or II (11, 14, 29). The most attractive explanation of these phenomena involves a change in the relative signs of the coupling constants. For when J_{PCH} in V is considered to be -8.0 and J_{PCH} for Va +7.3 Hz., then the expected large increase in J_{PCH} upon oxidation is accounted for with positive J_{PCH} values. Also, regardless of the sign of J_{PCH} for the nickel and molybdenum carbonyl complexes, the observed values still represent an increase. Therefore, in view of the similarity between V and VIII, the same arguments are applied to VIII in explaining the decrease in the absolute value of J_{PCH} upon oxidation.

P^{31} n.m.r. spectra of VIII and derivatives

The P^{31} n.m.r. data for tris-(hydroxymethyl)phosphine (THP), VIII, and derivatives of VIII in Table 2 along with the data on II, IIa, and IIb lend further support to the formulations of these compounds as shown. The spectrum of VIII shown in Figure 7 constitutes unequivocal support for the previous assignment of the coupling constants from the proton n.m.r. spectra. The P^{31} chemical shifts for phosphites and phosphines are usually separated by more than 100 p.p.m. (30, 31) making assignments of these resonances facile. Therefore, using known chemical shift values for the phosphite II (Table 2) and a trialkyl phosphine such as trimethylphosphine (+62 p.p.m. (30)) the two multiplets in the spectrum of VIII were assigned and the proton-phosphorus coupling constants calculated.

Table 2. P^{31} chemical shifts in DMSO

Compound	P^{31a} $[P(CH_2)_3]$	P^{31a} $[P(O)_3]$	J_{PCH}	J_{POCH}	J_{PP}
$P(CH_2OH)_3$ (THP)	+25.6		2.3		
$P(CH_2O)_3P$ (VIII)	+67.0	-90.0	8.9	2.6	37.7
$OP(CH_2O)_3PO$ (VIIIa)	- 6.4	+18.1	--[b]	--[b]	139.2
$P(CH_2O)_3PS$ (VIIIb)	+70.6	-51.8	Not Observed		56.1
$OP(CH_2O)_3PS$ (VIIIc)[c]					
$CH_3(CH_2O)_3P$ (II)		-91.5[d]		2[d]	
$CH_3(CH_2O)_3PO$ (IIa)		+ 7.9[d]		7[d]	
$CH_3(CH_2O)_3PS$ (IIb)		-57.4[d]		6[d]	

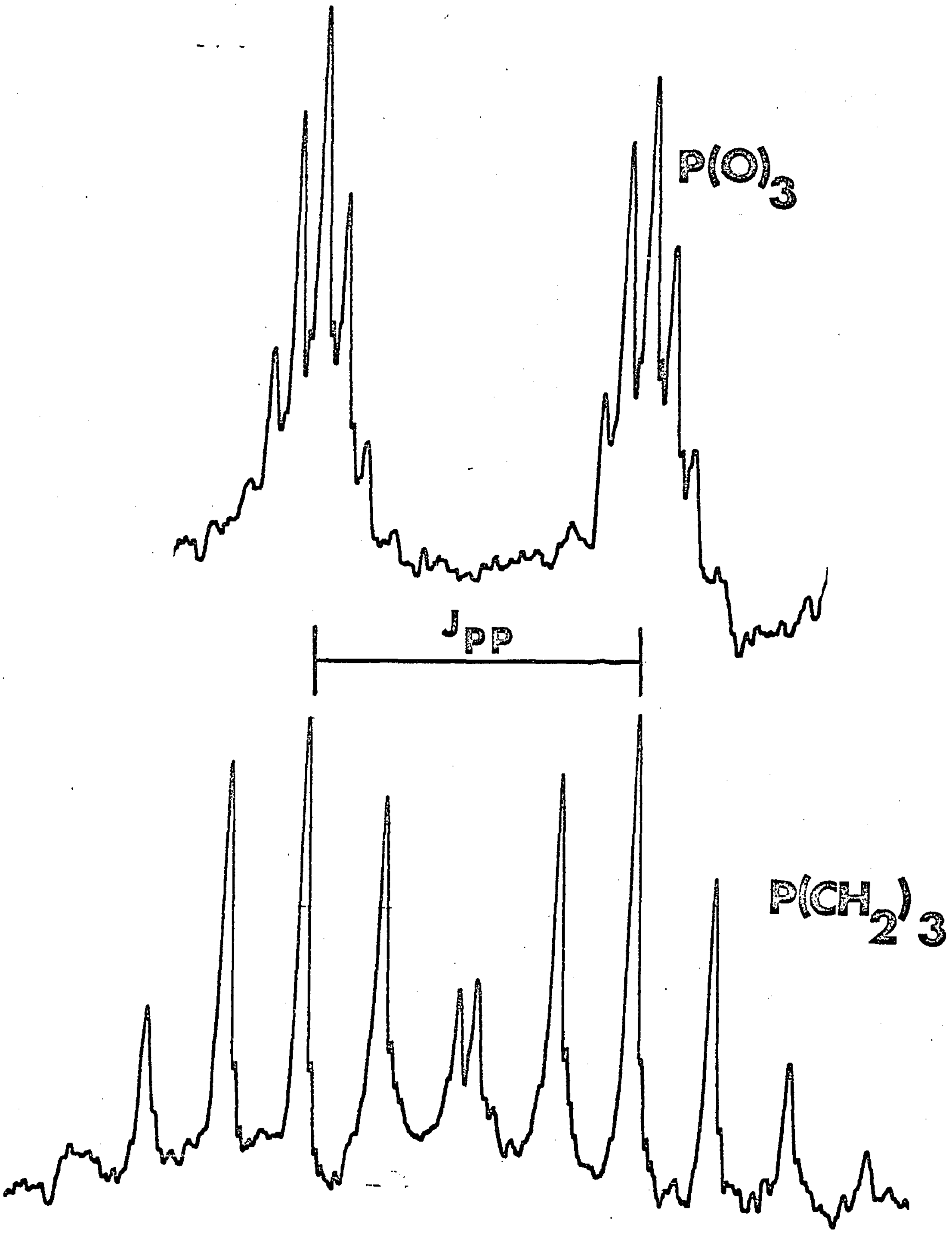
[a] P.p.m. vs. 85% aqueous H_3PO_4.

[b] Values are indistinguishable within experimental error.

[c] Insufficient solubility.

[d] See reference 29.

Figure 7. P^{31} n.m.r. spectrum of $P(CH_2O)_3P$ (VIII) with $\delta P(O)_3$ = −91 p.p.m., $\delta P(CH_2)_3$ = + 62 p.p.m. and J_{pp} = 35 Hz.


P(O)$_3$
J_{PP}
P(CH$_2$)$_3$

The downfield shift of THP relative to trimethylphosphine, might be interpreted in terms of a deshielding of the phosphorus by the electronegative oxygens.

Through utilization of characteristic P^{31} chemical shifts it was also possible to determine which phosphorus possessed the sulfur atom in VIIIb. If the sulfur were attached to the phosphine phosphorus, a negative chemical shift such as that observed for trimethylphosphine sulfide (-59.1 p.p.m.) (31) would be expected, while the phosphite phosphorus would be expected at -90 p.p.m. As seen from Table 2 the P^{31} absorptions are quite consistent with that of II and its derivatives.

Finally, the P^{31} chemical shifts for VIII were used in a calculation of the bond angles about phosphorus. Following the equations formulated by Parks (32) and Muller, et al. (33), relating the electron imbalance in the p electrons to the chemical shift of the phosphorus, representative X-P-X bond angles were calculated for VIII. These equations are:

$$|\varepsilon| = 0.16\ |X_A - X_B| + 0.035\ |X_A - X_B|^2$$

$$\delta = -230 + (29.0 \times 10^3\ e^{-46.0D'})$$

$$D' = (3/4 - \beta^2)\ \beta^2\ (1 - \varepsilon)$$

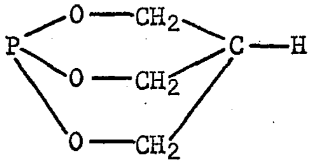
$$\beta^2 = \frac{-3\cos\theta}{1 - \cos\theta}$$

where the parameter ε is defined such that $(1 + \varepsilon)$ is the number of electrons of each P-X bond that belongs to the phosphorus atom. Therefore, except for the sign, the parameter ε is the same as the fractional ionic character term and may be estimated by the above equation. When X is more electronegative than phosphorus, ε acquires a negative sign before substitution into the third equation. X_A and X_B are the electronegativities of atoms A and B, respectively, D' is the p electron imbalance, β is a parameter representing the extent of hybridization of the lone pair, and δ is the P^{31} chemical shift. Therefore, using Pauling electronegativities (34) for P, C, and O and the chemical shift values of VIII listed in Table 2, the following bond angles were obtained in solving the quadratic expression for β^2: C-P-C, 104° 18' and 93° 9'; O-P-O, 104° 29' and 93° 1'. For the phosphine end of the molecule, the larger value appears more tenable since it does not seem reasonable that the angle should decrease from its value in trimethylphosphine (98.9°) (25) when oxygen substiments are placed on the alkyl groups. For the phosphite end, the larger value again seems more reasonable for steric reasons and is more consistent with the OPO bond angle of 103.5° found for IIa from X-ray studies (35), A similar calculation of possible CPC bond angles in THP gave 104°7' and 93°27'. Therefore, if these equations of Muller, et al. (33) and Parks (32) have any validity, the above result can be interpreted to mean that chemical shifts are very sensitive to small changes in XPX bond angles.

It should be pointed out that the equations discussed above are empirical and unreliable. Because δ depends upon an exponential term, it is very sensitive to the third significant figure. The calculation of ε, however, is justified to only two. Thus an uncertainty of one in the second significant figure with typical values of D' leads to an error of 50 p.p.m.

The value for C-P-C is not close to the tetrahedral angle and thus, such a calculation detracts further from the hybridization arguments in explaining the trends in J_{PCH} and lends more support for the consideration of relative signs of coupling constants.

In Table 2, values for J_{PP} observed in the P^{31} n.m.r. spectra are listed for VIII, VIIIa, and VIIIb. There is no precedent for this type of compound and comparison to similar compounds is very difficult. The diphosphite anion, having two phosphorus atoms bonded directly to each other, has associated with it a J_{PP} value of 480 Hz. (36), while the isohypophosphate anion, wherein the two phosphorus atoms are linked together by an oxygen atom, exhibits a J_{PP} value of 17 Hz. (36). Separating the phosphorus atoms by two atoms, as in VIII, causes the value of J_{PP} to increase by a factor of two over that observed for the isohypophosphate anion. This phenomenon may be explained by the fact that there are three paths for a through-bond coupling mechanism to occur in the bicyclic system, whereas there is only one in the isohypophosphate anion. A through-space coupling mechanism has been considered for J_{POCCH} in 2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (IX) (22). Such a mechanism calls for a decrease in J_{POCCH} upon oxidation of IX. For upon increasing the



IX

sp^3 character of the phosphorus, the per cent s character in the phosphorus lone pair would be reduced which consequently reduces the amount of s character in the non-bonding lobe through which a through-space interaction might take place. Although this decrease is indeed observed for IX and its oxide derivative (22), oxidation of VIII to VIIIa and VIIIb results in large increases in J_{PP}. It may be more attractive to postulate, therefore, that the large increase in J_{PP} upon oxidation of VIII is due to an increase in the per cent s character in the $P(O)_3$ and $P(C)_3$ bonds.

Infrared spectra

The characteristic P = O and P = S stretching frequencies observed in the infrared region for VIIIa, VIIIb, and VIIIc along with other stretching frequencies are shown in Table 3. The values reported for the P = O stretching frequencies in VIIIa are assigned by comparing them to the P = O stretching frequencies observed for the IIa (1325 cm^{-1}) (2) and Va (1208 cm^{-1}) (28). The P = S stretching frequency (807 cm^{-1}) was determined by a close comparison of all spectra, noting its definite absence in VIIIa and its constancy in VIIIb and VIIIc. Also, a similar value, 800 cm^{-1}, was reported for IIb (2) and Thomas and Chittenden (37) have set a range of 800 - 844 cm^{-1} for $(RO)_3P = S$ compounds.

The P = O stretching frequencies found for VIIIa are considerably higher than those predicted for the corresponding trialkyl compounds. Thomas and Chittenden (38) give a range of 1050 - 1183 cm^{-1} for $R_3P = O$ and 1258 - 1286 cm^{-1} for $(RO)_3P = O$, where R is alkyl. When R is aryl for $(RO)_3P = O$, a higher range is found, 1290 - 1314 cm^{-1}. This indication of a strong P = O bond may account for the absence of the monooxo

Table 3. Characteristic infrared frequencies for VIII and derivatives

Compound	Phase	Phosphite P = O	Phosphite P = S	Phosphine P = O	P-O-C region 905-1060 cm^{-1}	P - C
$P(CH_2O)_3P$ (VIII)	CCl_4				1046(s)[a], 964(s)	713(w)[b], 676(s)
$OP(CH_2O)_3PO$ (VIIIa)	KBr	1325(s)		1220(s)	1050(s), 1015(s)	744(m)[c], 704(w)
$P(CH_2O)_3PS$ (VIIIb)	KBr		807(s)		1022(s), 957(s)	747(s), 695(w)
$OP(CH_2O)_3PS$ (VIIIc)	KBr		807(s)	1215(s)	1013(s), 988(s)	744(m)

[a] Strong.

[b] Weak.

[c] Medium.

compound. However, it is not clear why the 1,4-disulfo compound could not be prepared.

VIII as a Ligand

The prime purpose in preparing VIII was to compare the coordination properties of a phosphite and a phosphine in a ligand of low steric requirements. Although monodentate coordination was expected, the possibility of polymerization by VIII acting as a bridge between metal atoms could not be ruled out. This phenomenon may have been the cause of the insoluble and intractable compounds which were obtained.

In all cases, the colors that were observed for the complexes exactly parallel those which had previously been observed for the polycyclic phosphites (9, 10, 12, 13) and trimethyl phosphite (see Part II). In particular, $Ni(NO_3)_2$ reacts with phosphines to give green-colored complexes (17) and phosphine complexes of cobalt halides are either blue or green (17). (The green color observed for the reaction of VIII with $CoCl_2$ was probably due to the presence of the $CoCl_4^{2-}$ anion (39).) The colors observed for $Co(NO_3)_2$ are typical for the phosphite disproportionation of Co(II) (10, 12) and the reduction of Cu(II) to Cu(I) has been observed before (9, 13). Finally, the explosive nature of the $Ni(ClO_4)_2$ complex with VIII may be indicative of phosphite coordination. Bonding through the phosphite end might place the phosphine phosphorus in close proximity to the perchlorate anion, and the slight scraping may have caused an immediate and explosive oxidation of the phosphine phosphorus by the perchlorate anion.

Although little more than a preliminary investigation was carried out on the ligand properties of VIII, it was deemed expedient in view of the intractable nature of the complexes to proceed with the related topic described in Part II. It may be said in conclusion that for bicyclic phosphites and phosphines, the former exhibits stronger ligand properties. This was the same conclusion reached by Boros (28) in considering the infrared frequencies of some metal carbonyl complexes of V and the 4-ethyl derivative of II.

SUGGESTIONS FOR FUTURE WORK

The ligand properties of VIII should be explored more thoroughly with transition metals. Even though the complexes that have been prepared are uncharacterized because of their insolubility, other methods may be employed for characterization. If the compounds are formed by phosphite coordination, they should possess solid state visible, ultraviolet, and infrared spectra similar to complexes of I, II, and trimethyl phosphite (L). Complexes of VIII might then also be isomorphous with those of I, II, and L. Gross differences observed in the solid spectra might be ascribed to coordination through the phosphine phosphorus in VIII.

In view of the reduced reactivity of the phosphine in VIII, it may be of interest to study in detail the Lewis base character of VIII towards boron Lewis acids. Such a study could involve the reaction of VIII with B_2H_6, noting the number of moles of BH_3 taken up under various conditions. This study could also include the VIIIb derivative.

The reactions of polycyclic phosphites and V with metal carbonyls has been mentioned and it may be informative to extend these reactions to VIII, observing in particular, which phosphorus coordinates in these systems. Again, the study could be extended to VIIIb which is similar to V.

Utilization of both phosphorus nuclei in VIII could result in some homo or hetero bi-metallic compounds wherein VIII could act as a bridge between two metal atoms. Ideally, this may be facilitated by forming a mono-substituted compound with a metal atom which typically forms stronger complexes with phosphites followed by a reaction with a metal carbonyl forming a complex with the phosphine end. It is also conceivable that the uncomplexed phosphorus in a coordination compound of VIII could be quaternized with a metal or carbonium ion.

Finally, some insight into the large J_{PP} values observed for VIII and its derivatives may be obtained by preparing organophosphorus compounds with one and two P-O-C-P links and measuring J_{PP} from their P^{31} n.m.r. spectra. Although appreciable changes in the geometry of the bonding system might take place, they may not be sufficiently large to override the effect of decreasing the number of coupling paths.

PART II. THE STUDY OF SOME TRANSITION METAL COMPLEXES OF TRIMETHYL PHOSPHITE (L) AND SOME POLYCYCLIC PHOSPHITES

INTRODUCTION

The coordination reactions of phosphorus ligands with transition metals has been extensively investigated in the case of phosphines. An excellent review of the complexes formed with transition metals and tertiary phosphines has recently appeared (17) containing a listing of the many compounds prepared. Transition metal complexes with phosphites are found to be far fewer. Huttemann (13) recently reviewed the coordination chemistry of trialkyl phosphites and concluded that relatively few complexes have been prepared and characterized and those complexes which have been prepared involve coordinating anions and are usually polymeric. Jensen, et al. (16) have attempted the preparation of nickel halide complexes with various trialkyl phosphites. Although some solid complexes were isolated, the products were generally very unstable in comparison to the analogous nickel halide phosphine complexes.

It was believed (9, 10) that trialkyl phosphites possessed poor coordinating properties because of their steric requirements and low dipole moments. Thus the freely rotating motion of the alkoxy groups can allow several orientations which when viewed with molecular models are seen to produce large ligand-ligand repulsions upon coordination. Moreover, it was observed that the dipole moments of trialkyl phosphites (ca. 2 D.) (40) were only about half the value found for the bicyclic phosphites I and II (4.7 D. and 4.15 D., respectively (40)).

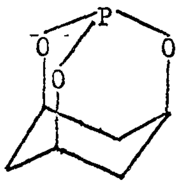
Well-characterized coordination complexes have been reported for a series of polycyclic phosphites. Huttemann et al. reported transition metal complexes of 2,8,9-trioxa-1-phospha-adamantane (I) (12, 13), and

Verkade and Piper (9, 10) discussed the coordination chemistry of the bicyclic phosphite ligand, 4-methyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane (II) with various transition metal ions. These polycyclic phosphites are shown in Figure 1. A large number of substituted carbonyl complexes have also been reported for I and II by Hendricker et al. (11, 14). The conclusion reached by these authors was that monomeric complexes were obtained in which maximum coordination of the metal ions was attained with only the phosphite ligand in the coordination sphere. This was attributed to the constraint of the ligands which reduced ligand-ligand repulsions. The high Dq values (comparable to CN^-) for these ligands in the Co(III) complexes, were attributed to possible d pi-p pi back bonding from the metal which would be enhanced by the electronegative oxygens on the phosphorus.

In view of the work cited above involving polycylic phosphites, it became of interest to investigate the ligand properties of trialkyl phosphites. For this purpose, trimethyl phosphite (L) was selected since minimum ligand-ligand repulsions would be expected (Figure 1). Primarily, non-coordinating anions were selected for this study to enhance the possibility of filling the metal coordination sphere with L molecules only.

During the course of this investigation, some five-coordinate complexes were isolated as well as those wherein nitrate ion is coordinated. Because of the somewhat unusual nature of these phenomena, a discussion of these topics follows.

Two reviews have recently appeared on pentacoordination (41, 42) with many pertinent references. The review by Muetterties and Schuun



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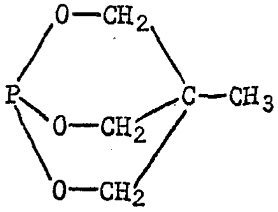

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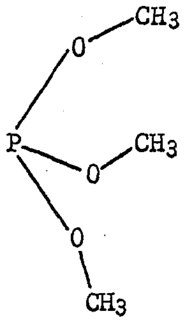


L

Figure 1. Schematic representations of the polycyclic phosphites I and II and of trimethyl phosphite (L)

is more extensive in its scope. A five-coordinate complex may possess one of two idealized geometries, trigonal bipyramid (D_{3h}) or tetragonal pyramid (C_{4v}), or some distorted form of these configurations. Gillespie (43) indicated that complexes which possess a large amount of covalent character will favor a trigonal bipyramidal over a tetragonal pyramidal geometry, with the latter configuration being favored by more ionic bonding. For the five-coordinate complexes prepared in this work, it is impossible to firmly establish their geometry from methods other than an X-ray analysis, but it is presumed that trigonal bipyramidal geometry dominates. Support for this postulate stems from the known structure of $Ni\ II_5(ClO_4)_2$ (44), which is very nearly trigonal bipyramidal.

In reviewing five-fold coordination, the absence of MP_5 species (where M is a transition metal and P is a phosphorus containing ligand) became very apparent. In all the reported cases of five-fold coordination involving phosphorus ligands, the coordinated phosphorus was part of a polydentate ligand or functioned as a monodentate ligand. In both cases, however, donors other than phosphorus were also coordinated. Only recently Huttemann (13) described the synthesis of $NiL_5(ClO_4)_2$ which represents the first reported example of a five-coordinate complex containing five monodentate phosphorus ligands.

Ciampolini and Nardi (45) and Dori and Gray (46) stated that if bulky, polydentate ligands are used, a five-coordinate complex will be favored over an octahedral complex. For the most part, the constitution of five-coordinate complexes has involved polydentate amines, arsines, and phosphines with the remaining coordination site(s) occupied by anions. The examples involving monodentate phosphorus ligands are very few;

notable among these are the tris(diphenylphosphine)nickel(II) complexes reported by Hayter (47). By three dimensional X-ray analysis (48), the analogous cobalt(II) bromide complex has been shown to be nearly trigonal bipyramidal with two diphenylphosphines on the C_3 axis. The related complexes of cobalt(II) iodide, nickel(II) bromide and iodide were also stated to have similar structures. Chatt and Shaw (49) have also reported the five-coordinate complex $Ni(C{\equiv}CPh)_2(PPhEt_2)_3$ and Jensen, *et al.* (50) have described the synthesis of $NiBr_2(PMe_3)_3$ which is almost black in color.

One of the further distinguishing features of five-coordinate complexes is their magnetism. It has been generally observed that when polydentate phosphines or arsines (47-60), arsino-phosphines (61), thiophosphines (62), and seleno-phosphines (63) are used, dimagnetic complexes are obtained. This has been attributed to a stabilization of the low-spin state by the *pi*-bonding ability of these ligands (61-63). For polydentate amine ligands, which cannot particpate in *pi*-bonding, high-spin five-coordinate complexes have been reported (64-68). Ciampolini has determined a crystal field model for high-spin five-coordinate Ni(II) complexes considering both trigonal bipyramidal and tetragonal pryamidal geometries (49). He concludes that a triplet ground state is favored for dipole strengths from zero to slightly above 8 D., and that it does not seem reasonable that polydentate phosphines and arsines should have larger dipole strengths than polydentate amines. Therefore, it would seem that spin pairing is favored by extensive formation of covalent bonds between the nickel and donor atoms. The intense d-d transitions observed in the visible spectra of these compounds have therefore been interpreted in terms of extensive mixing of metal and ligand orbitals (53). Ciampolini also implied that a large nephalauxetic effect could give rise to more covalent character in these complexes (69).

The study of the coordination chemistry of L was also extended to include coordinating anions, namely, nitrate and cyanide. Two reviews on nitrate coordination have recently appeared (70, 71). Nitrate coordination is complicated by the possibility that this ion can coordinate in three distinct manners which in some aspects are very similar. Thus it can coordinate as a monodentate ligand involving one *sigma* metal-oxygen bond, as a bidentate ligand involving two *sigma* metal-oxygen bonds, and as a bridging ligand to two metal atoms. A possibility of a fourth type of coordination suggested by Addison (40) involves the use of a three-center-bond utilizing two nitrate oxygen orbitals and one metal orbital. Electronically this is the same as monodentate coordination although geometrically it resembles bidentate chelation. The first three types of coordination along with ionic nitrate are schematically represented in Figure 2 with their respective symmetry point groups.

Evidence for coordinated nitrate is most easily obtained through infrared spectroscopy. This is a very convenient tool for distinguishing between coordinated and ionic nitrate, but it can be very misleading in attempts to determine the type of coordination. This is because the three types of coordination all have the same symmetry point group with the result that the associated infrared spectra would be and are observed to be quite similar. Therefore no attempt will be made here

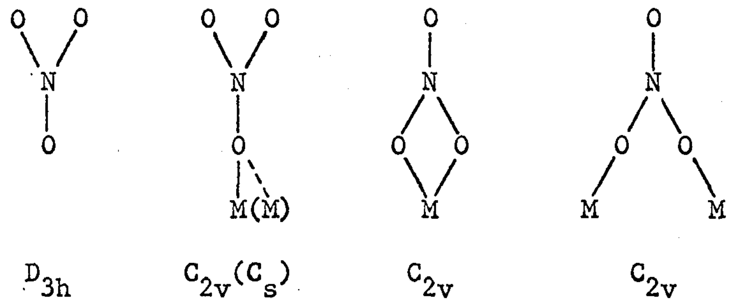


Figure 2. Coordination modes of the nitrate group with respective symmetry point groups

to correlate infrared spectra with molecular structure, other than in distinguishing ionic and coordinated nitrate.

Finally, it is interesting to note that there appears to be no obvious environmental influences which give rise to nitrate coordination nor the mode of coordination adopted. Coordinated nitrate has been found with a host of metals in the transition, actinide, and lanthanide series and also with Be, Ca, Zn, Hg, Tl, and Sn. Moreover, the type of ligand found in conjunction with coordinated nitrate does not appear to be restricted to any particular class. Such ligands range from weak to strong *sigma* donors and monodentate to tetradentate amines. Representative of this group are H_2O, $OP(NMe_2)_3$, $OPMe_3$, $OPPh_3$, $OAsPh_3$, C_5H_5NO, Me_3NO, NH_3, Py, en, and dipy. Well represented also, are ligands which may very well *pi* bond with the metal such as PEt_3, PPh_3, $SC(NH_2)_2$, P$PPh_2)_3$, and as reported here, L.

For most of the complexes reported here, it was possible to obtain P^{31} n.m.r. spectra. Although a considerable amount of P^{31} n.m.r. work has been reported for trivalent phosphorus compounds and some of their adducts, it is noteworthy that relatively little has been reported on the P^{31} absorptions of transition metal complexes. In 1961 Meriwether and Leto (72) reported the P^{31} chemical shifts of some disubstituted nickel carbonyl complexes of both phosphines and phosphites. In all cases, the chemical shift of the complex was downfield of the free ligand. For the phosphite complexes, the downfield shift was about one-half as great as that observed for the phosphine complexes and this was attributed to a lessened net electron drift form the phosphorus to nickel. These authors have summarized the factors which could affect the P^{31} chemical shift of transition metal complexes as follows: 1) temperature independent paramagnetic contributions, 2) _sigma_-bond formation, 3) d _pi_-p _pi_ back donation, 4) aromatic ring currents, 5) inductive effects of substituents on phosphorus, 6) bond rehybridization effects due to changes in phosphorus bond angles, 7) electronegativities of atoms on phosphorus, and 8) steric effects. In their particular study, it was thought that the dominant effect was produced by the stronger _pi_-bonding ability of phosphites. Thus the increased back donation from nickel resulted in more shielding of the phosphorus than in analogous phosphine complexes.

Downfield chemical shifts have also been reported for some Rh(III) and Rh(I) phosphine complexes (73) and some tungsten carbonyl complexes of phosphines (74). Similar downfield shifts have been reported for some molybelenum carbonyl complexes of L (75). Pidock, _et al_. (76) have reported the downfield shifts of some Pt(II) and Pt(IV) phosphine complexes. Although they attempt no correlation of chemical shifts it is interesting that a Pt(IV) complex is shifted downfield by approximately 10 p.p.m. from that of a similar Pt(II) complex. This phenomenon, which may be due to a charge effect, was explored further by Shupack and Wagner (77) for a series of trialkyl phosphite complexes. These authors concluded that the greater the charge on the metal ion, the greater the shielding of the phosphorus nucleus due to the electron drift form the alkoxy oxygens to the phosphorus. Such a mechanism was proposed to account for the upfield shifts of the complexes relative to the free phosphite ligand.

Recently, Reddy and Schmutzler (78) have reported downfield shifts in complexes of fluorine-containing phosphine ligands. These shifts are discussed in terms of five factors: 1) changes in the electronegativity of the phosphorus atom, 2) anisotropy of the metal atom, 3) an increase in the coordination number of phosphorus, 4) changes in the bond angles in the ligands, and 5) polarization of the lone pair orbital. The fourth factor, although considered to be very critical by some workers (79), was neglected because of a lack of data and the third and fifth factors were expected to be small in comparison to the first two. The first two factors were expected to produce a negative contribution to the chemical shift. Increased electronegativity of phosphorus would increase pi-bonding and magnetic shielding in the magnetically anisotropic region was expected to produce a downfield shift. The authors further explained upfield shifts observed for some chlorophosphine ligands in terms of larger changes in the hybridization and bond angles on complexation attributable to the larger size of the chlorine ligands.

EXPERIMENTAL

Analytical Methods

Carbon, hydrogen, nitrogen, chlorine, and phosphorus analyses

Carbon, hydrogen, nitrogen, chlorine and phosphorus analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tenn.

Cobalt analysis

Cobalt analyses were performed on 8-15 mg. samples by decomposing them with 3 ml. of concentrated HNO_3, heating to near dryness, followed by treatment with 1 ml. of 70% $HClO_4$, and evaporating to near dryness again. The remaining solutions were diluted to 50 ml. with a 50% aqueous-acetone solution containing 5 g. of NH_4CNS and were analysed spectrophotometrically using a molar extinction coefficient of 1842 l. mole^{-1} cm.$^{-1}$ for the $Co(CNS)_4^{-2}$ ion.

Nickel analysis

Nickel analyses were performed on approximately 30-50 mg. samples which were suspended in 1 ml. of water and decomposed by slowly adding 5 ml. of concentrated HNO_3. The resultant solution was evaporated to near dryness, cooled slightly and treated with 1 ml. of 70% $HClO_4$ which was added slowly. Again the solution was evaporated to near dryness and finally diluted with 40 ml. of distilled water.

After the pH was adjusted to 6-7 with concentrated NH_4OH, the solutions were reheated to near boiling and then treated with a 1% ethanol solution of dimethylglyoxime (DMG). The volume of DMG added was determined by the relation that 1 ml. approximately equals 0.0025 g. of Ni.

A 1-2 ml. excess of DMG solution was added to insure complete precipitation. The pH was then adjusted to 9-10 and the solutions allowed to stand at room temperature for 1 hr. The precipitates were filtered into preweighed filter crucibles, washed with cold water and dried at 110° for 1 hr. If too large an excess of DMG was used, it was washed from the precipitate with 50% ethanol solution. The weight of Ni was then determined by the factor, (wt. of $Ni(DMG)_2$ x 0.2032).

Instrumentation

Infrared spectra

Infrared spectra were obtained in KBr pellets, nujol and hexachlorobutadiene mulls and CCl_4 solutions using a Perkin-Elmer Model 21 double-beam spectrometer with sodium chloride optics.

Ultraviolet and visible spectra

All solution spectra were scanned in the ultraviolet and visible regions on a Cary Model 14 spectrophotometer and a Bausch and Lomb Model 505 Spectrophotometer. Reflectance spectra were obtained with a Beckman DU Spectrophotometer equipped with the Beckman 2580 reflectance attachment. Magnesium carbonate was used as a reference and diluent.

Nuclear magnetic resonance spectra

Proton n.m.r. spectra were obtained in approximately 15% solutions on Varian HR-60 and A-60 spectrometers. Tetramethylsilane was used as an internal standard. The P^{31} n.m.r. spectra were obtained in approximately 30% solutions with 85% aqueous phosphoric acid as an external standard on a Varian HR-60 spectrometer equipped with a P^{31} r.f. unit and matching probe.

Molecular weights

Molecular weight determinations were performed on a Mechrolab Model 301A vapor pressure osmometer. A standard curve of machine reading *vs*. molar concentration was determined for the solvent used by measuring prepared solutions of known concentrations (0.01-0.03 molar) of benzil.

Molar conductivities

Conductivities were measured at 25° with an Industrial Instruments Incorporated Model RC-16B2 conductivity bridge at 1000 c.p.s. Approximately 0.001 molar solutions were prepared with reagent grade solvents and these were measured in a cell with a constant of 0.077 cm^{-1}.

Materials

Trimethyl phosphite

Trimethyl phosphite was purchased from Eastman Kodak Co., Rochester, N.Y., and used without further purification.

2,2-Dimethoxypropane

2,2-Dimethoxypropane was purchased from Eastman Kodak Co., Rochester, N.Y., and used without further purification.

Coordination Compounds of Trimethyl Phosphite (L)

Preparations

All the complexes were prepared in a similar manner by reacting an acetone solution of the metal hydrate with an excess of L. Where indicated, the hydrates were dehydrated with a 100% excess of 2,2-dimethoxypropane (DMP), previous to adding L.

$[CoL_5]ClO_4$ and $[CoL_6](ClO_4)_3$

To 0.757 g. (2.07 mmoles) of $Co(ClO_4)_2 \cdot 6H_2O$, dissolved in an acetone-DMP solution, 2.82 g. (22.8 mmoles) of L was slowly added. The solution was allowed to stir for 3 hr. after which the more insoluble Co(III) compound was filtered from the solution as a nearly colorless powder. It should be noted that the Co(III) complex is shock-sensitive and was therefore was handled in mg. quantities. The Co(I) compound was obtained by adding ether to the filtrate to initiate precipitation followed by cooling to 0°. Yellow, needle-like crystals were thus obtained. Several recrystallizations from acetone were necessary in order to obtain the Co(I) compound free of the Co(III) complex.

Anal. Calcd. for $[CoL_6](ClO_4)_3$: Co, 5.38. Found: Co, 5.47.

Due to the explosive nature of this compound it was not analyzed further.

Calcd. for $[CoL_5]ClO_4$: C, 23.15; H, 5.78; Cl, 4.52; P, 19.91. Found: C, 22.97; H, 5.78; Cl, 4.55; P, 19.82.

$[CoL_5]NO_3$, $[CoL_5]_2[Co(NO_3)_4]$, and $[CoL_5][CoL(NO_3)_2]$

To 0.944 g. (3.25 mmoles) of $Co(NO_3)_2 \cdot 6H_2O$, dissolved in an acetone-DMP solution, 4.40 g. (35.8 mmoles) of L was slowly added. The dark green solution was allowed to stir for 1/2 - 3/4 hr. after which a small amount of ether (3-5 ml.) was added and the solution cooled to 0°. There first appeared a dark red oil from which the solution was separated by decantation. Further treatment of the red acetone solution with ether gave the solid complexes. This process was repeated with cooling over a 4-5 day period. First precipitated was a dark violet solid, $[CoL_5][CoL(NO_3)_2]$, followed by a dark red solid, $[CoL_5]_2[Co(NO_3)_4]$, and lastly the yellow solid, $[CoL_5]NO_3$. Throughout these precipitations a small amount of white solid was a persistent contaminant. This may have been the $[CoL_6](NO_3)_3$, which coprecipitated with the compounds. Thus far it has not been possible to obtain this compound in sufficient quantity for analysis. The complexes were purified by recrystallizing several times from an acetone-ether mixture.

Anal. Calcd. for $[CoL_5]NO_3$: C, 24.27; H, 6.08; P, 20.93. Found: C, 24.17; H, 6.02; P, 20.75.

Calcd. for $[CoL_5]_2[Co(NO_3)_4]$: C, 21.61; H, 5.41; N, 3.37; P, 18.63. Found: C, 21.68; H, 5.67; N, 3.46; P, 18.84.

Calcd. for $[CoL_5][CoL(NO_3)_2]$: C, 21.92; H, 5.48; N, 2.84; P, 18.88; Co, 11.9. Found: C, 21.96; H, 5.64; N, 2.93; P, 18.78; Co, 11.7.

$[CoL_5]_2[Co(NO_3)_4]$ was also prepared by dissolving 0.096 g. (0.13 mmole) of $[CoL_5]NO_3$ in acetone and adding to it an acetone-DMP solution containing 0.039 g. (0.13 mmole, 100% excess) of $Co(NO_3)_2 \cdot 6H_2O$. The dark red complex was obtained by adding ether and cooling the solution to 0°.

$[Ph_4As][CoL(NO_3)_2]$

To 0.12 g. (0.17 mmole) of $[CoL_5][CoL(NO_3)_2]$ dissolved in 3 ml. of acetonitrile, 1.6 ml. of a 0.10 M acetonitrile solution of Ph_4AsNO_3 (0.16 mmole) was added with stirring. Addition of ether produced a dark blue solid which was recrystallized from CH_2Cl_2 and ether to give well-formed azure blue crystals.

Anal. Calcd. for $[Ph_4AS][CoL(NO_3)_2]$: Co, 8.54. Found: Co, 8.49.

$[CuL_4]NO_3$

To 0.665 g. (2.76 mmoles) of $Cu(NO_3)_2 \cdot 3H_2O$, dissolved in an acetone DMP solution was slowly added 3.42 g. (27.6 mmoles) of L. The light blue solution first turned dark blue but became colorless with the addition of all the ligand. The solution was diluted with ether slightly and cooled to 0°C. producing colorless crystals. The solid was recrystallized from an acetone-ether mixture.

Anal. Calcd. for $[CuL_4]NO_3$: C, 23.19; H, 5.79; N, 2.25. Found: C, 22.97; H, 5.70; N, 2.48.

$[AgL_2NO_3]$

To 5 ml. of L (40 mmoles) was very slowly added 0.61 g. (3.6 mmoles) of $AgNO_3$. After the exothermic reaction ceased, the solution was allowed to stir for 1/2 hr. Adding a large volume of ether to the solution produced a white solid which was recrystallized from an acetone-ether mixture.

Anal. Calcd. for [AgL_2NO_3]: C, 17.25; H, 4.31; N, 3.35.
Found: C, 17.72; H, 4.31; N, 3.19.

A molecular weight determination in acetone gave an average value of 436; calculated for [AgL_2NO_3], 418.

[$NiL_3(NO_3)_2$]

To 0.723 g. (2.49 mmoles) of $Ni(NO_3)_2 \cdot 6H_2O$, dissolved in an acetone-DMP solution, 1.54 g. (12.5 mmoles) of L was added all at once to give a brown-red solution. This was allowed to stir for approximately 1 min. and then the entire solution was poured into 250 ml of ether and stirred vigorously for several hr. The resulting orange powder could be recrystallized from acetone but not without rapid decomposition. Therefore, the compound was analyzed as the well-washed powder.

Anal. Calcd. for [$NiL_3(NO_3)_2$]: C, 19.47; H, 4.87; N, 5.05; Ni, 10.60. Found: C, 19.29; H, 5.08; N, 5.27; Ni, 11.07.

This compound is very unstable and loses L very easily, especially under vacuum. A nickel analysis performed two days after the above value was determined gave an average value of 11.81%.

[$NiL_3(CN)_2$]

To a suspension of 3.01 g. (16.5 mmoles) of $Ni(CN)_2 \cdot 4H_2O$ in 25 ml. of acetone was added 10.2 g. (82.4 mmoles) of L all at once. The solution was stirred for 3 hr. and then filtered to remove the unreacted $Ni(CN)_2 \cdot 4H_2O$. Concentrating the solution under vacuum and cooling yielded dark red-orange crystals. The solid was not washed with ether since it was partially soluble in ether and also reacted with it (see following preparation). Thus, it was washed in cold acetone several times and recrystallized from this solvent.

Anal. Calcd. for $[NiL_3(CN)_2]$: C, 27.35; H, 5.50; N, 5.81; Ni, 12.18. Found: C, 27.55; H, 5.50; N, 5.82; Ni, 12.22.

$[NiL_2(CN)_2]$

A small sample (ca. 0.5 g.) of $[NiL_3(CN)_2]$ was dissolved in about 100 ml. of ether and the solution stirred vigorously for 1 hr. The yellow powder produced was filtered from the yellow solution and washed with ether until the wash was colorless. The yellow powder was then analyzed:

Anal. Calcd. for $[NiL_2(CN)_2]$: C, 26.75; H, 5.02; N, 7.81; P, 17.27. Found: C, 26.75; H, 5.08; N, 8.08; P, 17.24.

$[NiL_2(CN)_2]$ was quite insoluble in most organic solvents and decomposed in them to give $Ni(CN)_2$. Because of this, it was not possible to determine a molecular weight for this compound.

If the filtrate from the above reaction was cooled to 0°, $[NiL_3(CN)_2]$ could be obtained as red-orange crystals. If this solid was treated with more ether as above, it all eventually converted to $[NiL_2(CN)_2]$.

When a sample of $[NiL_3(CN)_2]$ was subjected to high vacuum for approximately 10 hrs., it lost its red-orange color and became more yellow. The infrared spectra of the yellow product and that of an anthentic sample of $[NiL_2(CN)_2]$ were identical.

Coordination Compounds of Some Bicyclic Phosphites

$[NiII_3(CN)_2]$

To 0.50 g. (1.7 mmole) of $Ni(NO_3)_2 \cdot 6H_2O$, dissolved in 10 ml. of absolute ethanol, 1.28 g. (8.65 mmoles) of II dissolved in 5 ml. of absolute ethanol was added all at once to give a yellow-green solution after stirring for 1/4 hr. Then 0.17 g. (3.4 mmoles) of NaCN, dissolved in 5 ml. of absolute ethanol, was added all at once to give a yellow powder. The powder was washed well with boiling ethanol to remove $NaNO_3$ and analyzed as the powder since it is quite insoluble in most organic solvents.

Anal. Calcd. for $[NiII_3(CN)_2]$: C, 36.77; H, 4.87; N, 5.05; P, 16.78; Ni, 10.6. Found: C, 36.51; H, 5.01; N, 4.76; P, 16.29; Ni, 10.6.

$[NiII_3(NO_3)_2]$

To 0.350 g. (1.21 mmoles) of $Ni(NO_3)_2 \cdot 6H_2O$ dissolved in an acetone-DMP solution, 1.07 g. (7.23 mmoles) of II dissolved in 10 ml. of acetone was added all at once to give a yellow powder after about 1 min. of stirring. The mixture was allowed to stir for 5 min. after which the powder was collected, washed well with cold acetone and ether, and then analyzed as the powder since it is quite unstable and insoluble in most organic solvents.

Anal. Calcd. for $[NiII_3(NO_3)_2]$: C, 28.75; H, 4.32; N, 4.47; Ni, 9.37. Found: 29.64; H, 4.81; N, 4.54; Ni, 9.77.

$[\mathrm{NiI_5(NO_3)_2}]$

To 1.55 g. (5.33 mmole) of $Ni(NO_3)_2 \cdot 6H_2O$ dissolved in an acetone-DMP solution, 5.12 g. (32.0 mmole) of I, dissolved in 20 ml. of acetone, was added all at once. After several min. of stirring, a yellow powder precipitated. This powder was recrystallized form cold acetone to give yellow, needle-like crystals. These crystals contained occluded acetone as shown from the infrared spectrum. Therefore the solid was ground to a fine powder under ether and dried under vacuum at the temperature of refluxing acetone previous to analysis.

Anal. Calcd. for $[\mathrm{NiI_5(NO_3)_2}]$: C, 36.55; H, 4.58; N, 2.85; P, 15.62; Ni, 5.97. Found: C, 36.81; H, 4.75; N, 3.11; P, 15.54; Ni, 5.95.

DISCUSSION

Transition Metal Complexes of L, I and II

Listed below in Figure 3 are all the complexes prepared in this work. Table 1 contains molar conductances which are consistent with the formulations of these compounds as shown in this Table.

$[CoL_5]ClO_4$
$[CoL_6](ClO_4)_3$
$[CoL_5]NO_3$
$[CoL_5]_2[Co(NO_3)_4]$
$[CoL_5][CoL(NO_3)_2]$
$[Ph_4As][CoL(NO_3)_2]$
$[CuL_4]NO_3$
$[AgL_2NO_3]$
$[NiL_3(NO_3)_2]$
$[NiII_3(NO_3)_2]$
$[NiI_5(NO_3)_2]$
$[NiL_3(CN)_2]$
$[NiL_2(CN)_2]$
$[NiII_3(CN)_2]$

Figure 3. Transition metal complexes of L, I, and II prepared in this work

The proton n.m.r. data in Table 2 and the ultraviolet-visible spectral data in Table 3 will be included in the following discussion of the complexes where appropriate.

$[CoL_5]ClO_4$ and $[CoL_6](ClO_4)_3$

The disproportionation reaction of Co(II) to give the yellow, five-coordinate Co(I) complex and the nearly colorless six-coordinate Co(III) complex has been observed before for I (12) and II (10). The strong-field nature of L in the Co(III) complex is demonstrated by the

Table 1. Molar conductances of transition metal complexes of L, I and II[a]

Complex	Molar Conductance (mhos cm^{-1} $mole^{-1}$)	Solvent
$[CoL_5]ClO_4$	113	Acetone
$[CoL_6](ClO_4)_3$	460	Acetonitrile
$[CoL_5]NO_3$	146	Acetone
$[CoL_5]_2[Co(NO_3)_4]$	253	Acetone
$[CoL_5][CoL(NO_3)_2]$	118	Acetone
$[Ph_4As][CoL(NO_3)_2]$	142	Acetonitrile
$[CuL_4]NO_3$	113	Acetone
$[AgL_2NO_3]$	13	Acetone
$[AgL_2NO_3]$	167	Acetonitrile
$[Cu(Ph_3P)_2NO_3]$[b]	0	Nitrobenzene
$[Ag(Ph_3P)_4]NO_3$[b]	19.3	Nitrobenzene
$[NiL_3(NO_3)_2]$	25	Acetone
$[NiL_3(CN)_2]$	0	Acetone
$[NiL_2(CN)_2]$[c]		
$[NiII_3(NO_3)_2]$	11	Acetone
$[NiII_3(CN)_2]$[d]		
$[NiI_5(NO_3)_2]$	26	Acetone
$[NiI_5(NO_3)_2]$	47	Ethanol

[a] The following compounds and their molar conductivities were used for comparison: $(n\text{-}C_4H_9)_4NBr$, 123(acetone); $[Ph_4As]_2[Co(NO_3)_4]$, 252(acetone); $(n\text{-}C_4H_9)_4NNO_3$, 158(acetonitrile); $[Ni(en)_3](ClO_4)_2$, 312(acetonitrile); $[Co(H_2O)_6](ClO_4)_2$, 53(ethanol); $[Co(P(OCH)_3(CH_2)_3)_6](ClO_4)_3$, 430(acetonitrile).

[b] See reference 80.

[c] Compound decomposes to $Ni(CN)_2$ in most solvents.

[d] Insoluble.

Table 2. Proton n.m.r. data for transition metal complexes of L

Compound	δCH_3[a]	J_{POCH}[b]	Solvent
L	3.50	10.7	---[c]
$[CoL_5]ClO_4$	3.67	10.5	Acetonitrile
$[CoL_6](ClO_4)_3$	4.02	---[d]	Acetonitrile
$[CoL_5]NO_3$	3.67	10.5	Acetonitrile
	3.67	10.5	Deuteriochloroform
$[CoL_5][CoL(NO_3)_2]$	3.59, 2.18	8, 6	Benzonitrile
	3.39[e]	---[f]	Deuteriochloroform
	3.35[g]	---[f]	Deuteriochloroform
	3.68[h]	---[f]	Deuteriochloroform
$[Ph_4As][CoL(NO_3)_2]$	---, 2.16	---, 6	Benzonitrile
$[AgL_2NO_3]$	3.68	12.3	Acetone
	3.69	12.9	Deuteriochloroform
$[NiL_3(CN)_2]$	3.83	9.7	Acetone
$[NiL_2(CN)_2]$ + L[i]	3.81	10.5	Acetone
$[NiL_3(CN)_2]$ + L	3.53	10.8	Acetone

[a] p.p.m.

[b] Hz.

[c] Spectrum run neat.

[d] Resonance is a very complex multiplet.

[e] Spectrum run at 40°.

[f] Resonance consists of broad singlet.

[g] Spectrum run at 0°.

[h] Spectrum run at -40°.

[i] One drop of L was added to a suspension of $[NiL_2(CN)_2]$ in acetone.

Table 3. Ultraviolet and visible spectra of complexes of L, I, and II

Compound	Phase	Wavelength mμ[a]
$[CoL_5]ClO_4$	CH_2Cl_2	$230(1.3 \times 10^4)$, $253(1.6 \times 10^4)$, $382(1.0 \times 10^3)$
$[CoL_6](ClO_4)_3$[b]	CH_3CN	$261(4.4 \times 10^4)$, $285(7.5 \times 10^3)$, $306(1.7 \times 10^3)$, $340(1.1 \times 10^3)$
$[CoL_5]NO_3$	CH_2Cl_2	$230(1.4 \times 10^4)$, $253(1.2 \times 10^4)$, $382(1.0 \times 10^3)$
$[CoL_5]_2[Co(NO_3)_4]$	CH_2Cl_2	$230(1.5 \times 10^4)$, $253(1.2 \times 10^4)$, $382(1.0 \times 10^3)$, 538(102)
$[CoL_5][CoL(NO_3)_2]$[c]	CH_2Cl_2	$230(1.5 \times 10^4)$, $253(1.2 \times 10^4)$, $382(1.0 \times 10^3)$, 525(67), 573(120), 615(59)
$[Ph_4As][CoL(NO_3)_2]$[d]		
$[Ph_4As]_2[Co(NO_3)_4]$	CH_3NO_2	538(135)
$[NiL_5](ClO_4)_2$[e]	CH_2Cl_2	$259(1.6 \times 10^4)$, $404(2.5 \times 10^3)$
	Solid	265 425
$[Co(Me_3PO)_2(NO_3)_2]$[f]	$CHCl_3$	525(sh), 560(144)
$[NiL_3(NO_3)_2]$	Solid	265, 410
$[NiII_3(NO_3)_2]$	Solid	260, 370
$[NiI_5(NO_3)_2]$	Solid	260, 395
	Acetone	365(427)[g]

Table 3. (Continued)

Compound	Phase	Wavelength mμ[a]
$[NiL_3(CN)_2]$	Solid	260(sh), 395
	CH_2Cl_2	295(2.7 x 10^3), 345(1.8 x 10^3), 420(sh)(2.9 x 10^2)[h]
$[NiL_2(CN)_2]$	Solid	340(sh), 425(sh)
$[NiII_3(CN)_2]$	Solid	267, 365

[a] Extinction coefficients in units of l. mole^{-1} cm^{-1} appear in parentheses.

[b] Bands were resolved by gaussian analysis.

[c] Bands for the anion were resolved by gaussion analysis.

[d] Spectrum in CH_2Cl_2 was identical to $[CoL_5][CoL(NO_3)_2]$ except for the yellow band due to $[CoL_5]^{+1}$.

[e] See reference 15.

[f] See reference 81.

[g] This very low extinction coefficient is indicative of decomposition in acetone.

[h] Estimated extinction coefficient.

diamagnetism of the complex and a calculated Dq value similar to that observed for polycyclic phosphites (10, 12). If it can be assumed that the bands at 340 and 306 mμ (Table 3) correspond to the spin-allowed transition, $^1A_{1g}(t_{2g})^6 \rightarrow {}^1T_{1g}(t_{2g})^5(eg)$ and $^1A_{1g}(t_{2g})^6 \rightarrow {}^1T_{2g}(t_{2g})^5(eg)$, respectively, then Dq is 3100cm^{-1} according to a method of calculation employed by Ballhausen (82). The Dq value of 3100 cm.$^{-1}$ for L compares favorably to values of 3350 and 3320 cm.$^{-1}$ for I (12) and II (10), respectively, and to a value of 3350 cm.$^{-1}$ (83) for cyanide ion in $Co(CN)_6^{-3}$.

The five-coordinate Co(I) complex is also diamagnetic which is consistent with the observation that nearly all five-coordinate Ni(II) complexes (with which the Co(I) complex is isoelectronic) containing phosphorus ligands are of low spin (see Introduction). Jorgensen (84) has suggested an energy level diagram for the MX_5 chromophore (Figure 4) in which the eight d elections of the Co(I) complex would completely fill the two doubly-degenerate e' and e'' levels to attain a low-spin configuration. In low-spin d^8 complexes of polydentate phosphines and arsines (53), two low-energy absorptions at approximately 570 and 370 mμ were typically observed which were assigned to the two transitions $e'' \rightarrow a_1'$ and $e' \rightarrow a_1'$ (Figure 4). Thus the intense charge-transfer absorption at 382 mμ (Table 3) in $[CoL_5]ClO_4$ may overshadow any d-d bands for this compound.

The proton n.m.r. spectrum of the $[CoL_5]^{+1}$ cation (Table 2) consisted of a doublet with J_{POCH} = 10.5 Hz. and a chemical shift of 3.67 p.p.m. The spectrum of the Co(III) compound was not as simple in that it consisted of a complex, yet symmetrical multiplet, from which no

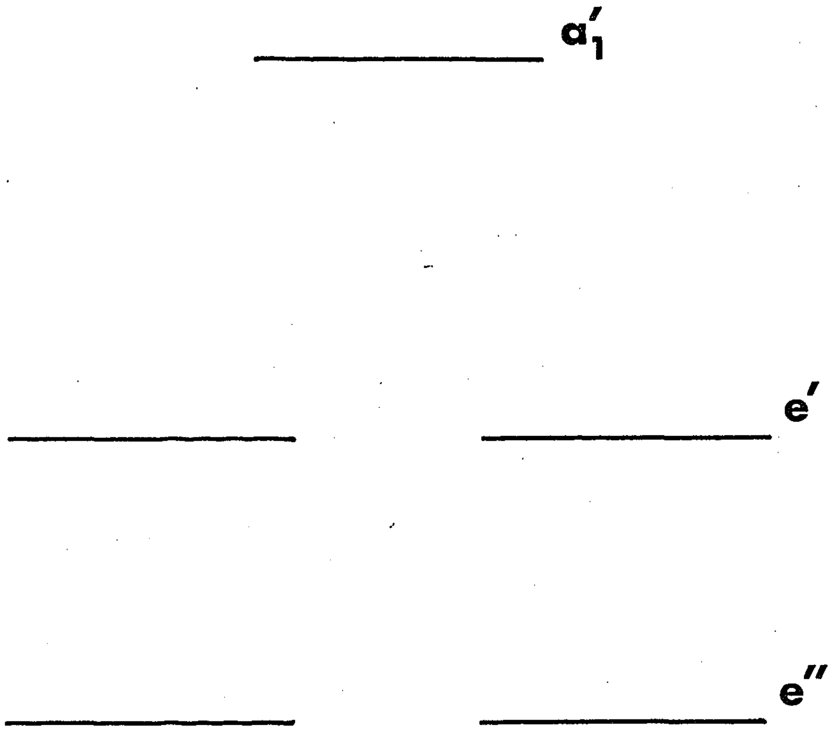
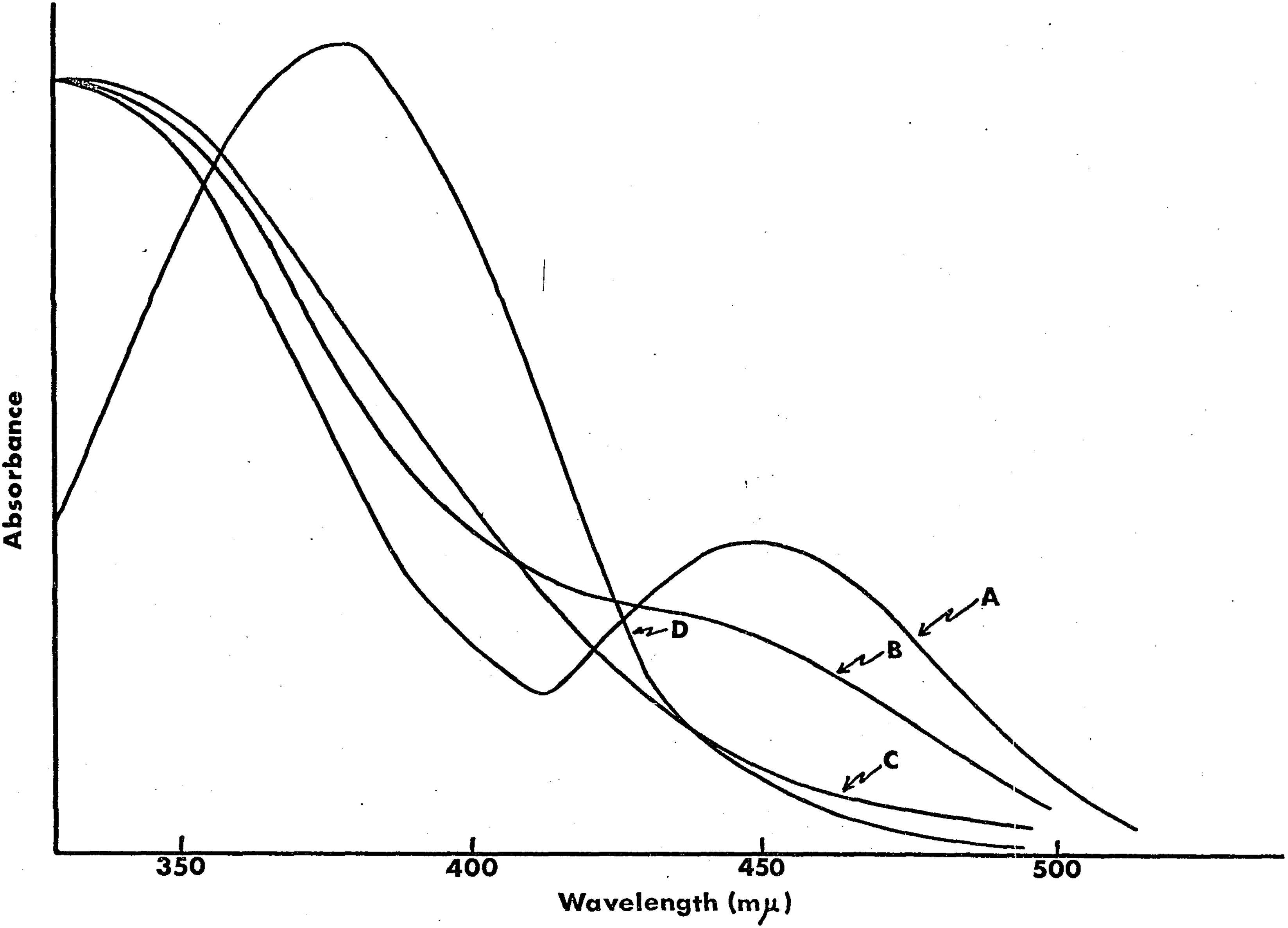


Figure 4. Relative orbital energies of the partly filled shell in the trigonal bipyramidal chromophore MP_5

coupling constants could be obtained. However, the chemical shift (4.02 p.p.m.) is consistent with a downfield shift ascribable to an increase in metal oxidation state. The origin of this multiplet probably lies in the extensive P^{31}-P^{31} coupling through the metal atom. Although analysis of complexes containing only two phosphorus atoms have yielded values for this coupling (11, 14), analysis of more complicated spectra found for systems such as $[CoL_6]^{+3}$ have not been carried out.

The reaction for the preparation of the Co(I) and Co(III) compounds was followed in the visible and ultraviolet regions of the spectrum and evidence for a possible intermediate was observed. The procedure consisted of sampling a small portion of the reaction mixture at various times, removing the precipitated Co(III) complex by centrifugation, and measuring the spectrum of the centrifugate. Some of the results of these experiments are shown in Figure 5. It can be seen that there is initially an intense band in the ultraviolet with a shoulder at approximately 440 mμ. With time, this shoulder disappears as does the intense ultraviolet band and only after approximately 20 hr. does the band for $[CoL_5]^{+1}$ appear at 382 mμ. Although the nature of this possible intermediate was not investigated thoroughly at this time it is interesting to speculate on its origin. It should be noted that even though the Co(III) complex is insoluble in the reaction solvent, it does not begin to precipitate from the solution for several minutes and complete precipitation is accomplished only after about 20 hr. This could mean that the oxidation-reduction process is not immediate and that a Co(III) intermediate can not be ruled out. Some supporting evidence for a Co(I)

Figure 5. Time study of the ultraviolet-visible spectrum of the disproportionation of $Co(ClO_4)_2$ by L at 0 hr. (A), 3 hr. (B), 14 hr. (C), and 20 hr. (D)


Absorbance
350
400
450
500
Wavelength (mμ)
A
B
C
D

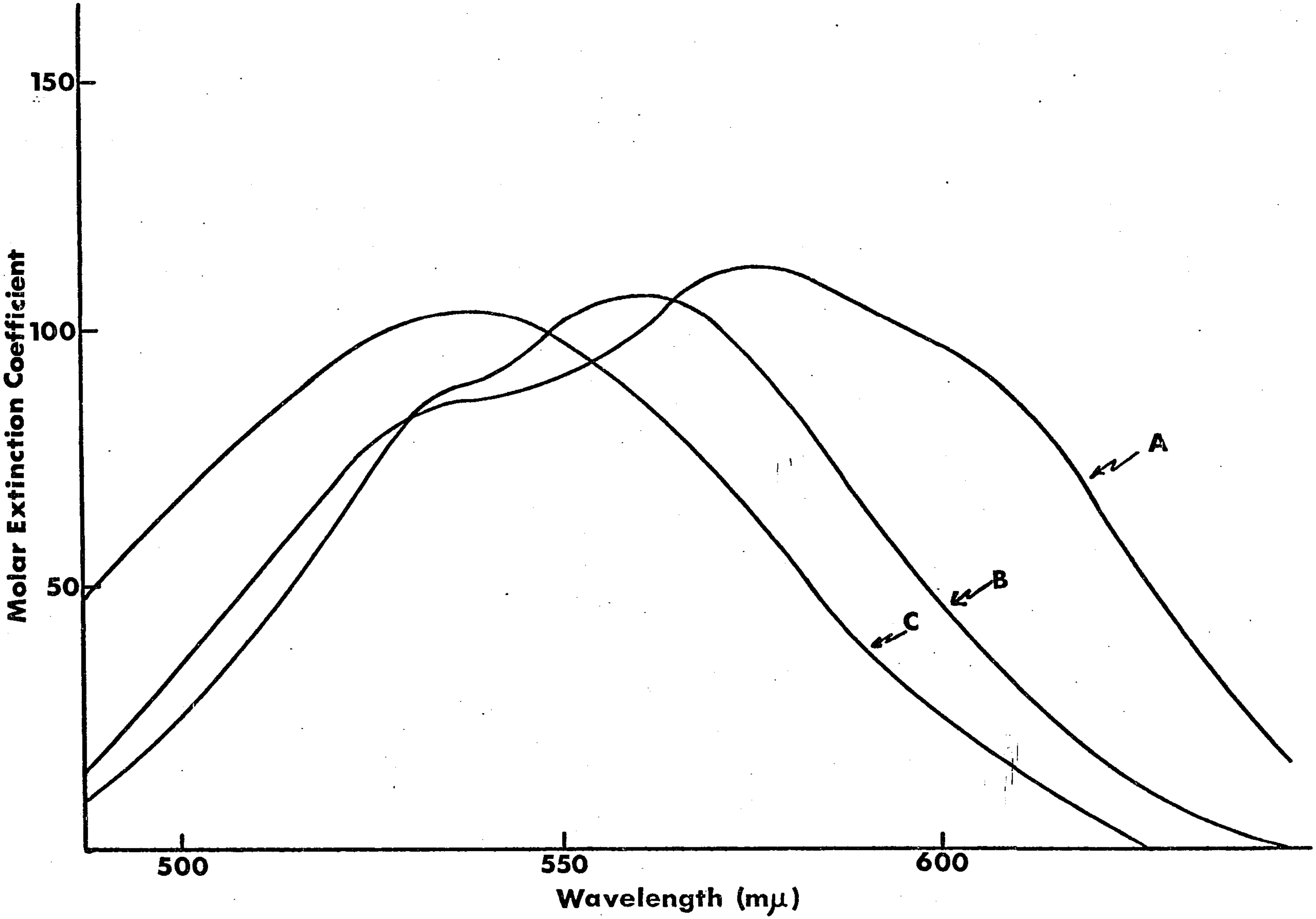
intermediate was obtained. By assuming that a ligand/metal ratio of 4/1 to 6/1 was not unreasonable for any intermediate, the conductivity of an acetone solution of the isolated orange intermediate was most consistent with that of a 1:1 electrolyte, which tends to indicate the presence of a Co(I) complex which is less stable than the one obtained finally.

$[CoL_5]NO_3$, $[CoL_5]_2[Co(NO_3)_4]$, $[CoL_5][CoL(NO_3)_2]$, and $[Ph_4As][CoL(NO_3)_2]$

The isolation of $[CoL_5]NO_3$ is not surprising in view of the reaction with cobalt perchlorate discussed above. The large, reasonably symmetrical $[CoL_5]^{+1}$ cation could be largely responsible for the stablization of the $[Co(NO_3)_4]^{-2}$ anion. The isolation of the dark violet $[CoL_5][CoL(NO_3)_2]$ is, however, worthy of note since it contains both an anionic and a cationic complex Co(I) atom bound to L. The Co(I) anion, also isolated as the tetra-phenylarsonium salt, is interesting in that nitrate coordination takes place. Although a complex anion containing both L and nitrate was not expected, the isolation of $[CoL_5]_2[Co(NO_3)_4]$ indicates that nitrate can compete successfully with L for metal ions.

Support for monovalent cobalt in the anion was obtained by conductance measurements and the diamagnetism of the anion was shown by its normal n.m.r. spectrum. Thus a cobalt(II) species was ruled out. It is somewhat surprising, therefore, that the ultraviolet-visible spectrum is typical of a nitrato cobalt(II) species rather than of $[CoL_5]^{+1}$. In Figure 6, the spectrum of $[CoL(NO_3)_2]^{-1}$ is reproduced along with the spectrum of $[Co(NO_3)_4]^{-2}$ and the Co(II) compound, $[Co(Me_3PO)_2(NO_3)_2]$, reported by Cotton, et al., (81). A crystal structure analysis

Figure 6. Visible spectra of: $[CoL(NO_3)_2]^{-1}$ (A) in CH_2Cl_2, $[Co(Me_3PO)_2(NO_3)_2]$ (B) in $CHCl_3$, and $[Co(NO_3)_4]^{-2}$ (C) in CH_3NO_2


Molar Extinction Coefficient
150
100
50
500
550
600
Wavelength (mμ)
A
B
C

of the latter compound has been completed and it was determined that the overall structure was a very distorted octahedron with bidentate nitrates (85). The close similarity in the visible spectra for a nitrato cobalt (II) and cobalt(I) series shown in Figure 6 casts some doubt on the formulation of the anion as $[CoL(NO_3)_2]^{-1}$, but in view of the conductivities, normal n.m.r. spectra, and analyses, it is the only reasonable formulation.

As stated in the Introduction, and pictured in Figure 2, the nitrate group can coordinate in a monodentate, bidentate, and bridging fashion. All of these types have C_{2v} point symmetry. Therefore, by performing a group theoretical analysis to determine the symmetry types of the normal modes, the same spectrum would be expected for the three types of coordination. Such an analysis has been performed by Addison and Simpson (86) for C_{2v} symmetry and by Gatehouse, et al., (87) for D_{3h} symmetry (ionic nitrate). The results are shown in Tables 4 and 5.

For D_{3h} symmetry, only four modes are generated and one of these, ν_1,is infrared inactive. Therefore, in the case of ionic nitrate, only three bands are possible with ν_3 (NO_2 asymmetric stretch) being the strongest. For C_{2v} symmetry, six modes are generated and all are infrared active. Addison and Simpson have also gone a step further and distinguished between monodentate and bidentate nitrate on the basis of rather minor spectral differences. Although their conclusion based on their infrared data for bidentate nitrate in $Ti(NO_3)_4$ is supported by an X-ray study (88), it is not believed that these assignments are sufficiently unambiguous that they can be universally applied to all compounds.

Table 4. Infrared and Raman modes for ionic nitrate

Symmetry	Type[a]	Absorption (cm^{-1})	Assignment
D_{3h}	A_1'[b]	ν_1(1050)	N-O stretch
	A_2'[c]	ν_2(831)	NO_2 deformation
	E'	ν_3(1390)	NO_2 asym. stretch
	E'	ν_4(720)	planar rocking

[a] All modes are infrared and Raman active unless specified otherwise. Within a point group the vibrational modes are numbered from the highest symmetry species and from the highest frequency within any symmetry species.

[b] Infrared inactive.

[c] Raman inactive.

Table 5. Infrared and Raman modes for coordinated nitrate

Symmetry	Type[a]	Absorption (cm^{-1})		Assignment
		monodentate	bidentate	
C_{2v}	A_1	ν_1(1290)	ν_2(985)	NO_2 sym. stretch
	A_1	ν_2(1000)	ν_1(1630)	N-O stretch
	A_1	ν_3(740)	ν_3(785)	NO_2 sym. bend.
	B_1	ν_4(1480-1550)	ν_4(1250)	NO_2 asym. stretch
	B_1	ν_5(715)	ν_5(750)	NO_2 asym. bend.
	B_2	ν_6(800)	ν_6(700)	out of plane rock

[a] All modes are infrared and Raman active unless specified otherwise. Within a point group the vibrational modes are numbered from the highest symmetry species and from the highest frequency within any symmetry species.

Lever (89) believes that such assignments for compounds in which only nitrate groups function as ligands, can not be carried over to systems wherein other ligands are present. An example of such a system is [Co(Me$_3$PO)$_2$(NO$_3$)$_2$], whose infrared data tabulated in Table 7 are inconsistent with Addison and Simpson's predictions (86).

Upon changing from D_{3h} symmetry (ionic nitrate) to C_{2v} (coordinated nitrate) the degeneracy of $\nu_3(E')$ is lifted and the band is split into two components, $\nu_1(A)$ and $\nu_4(B)$. A close analysis of this splitting in various spectra reveals that there is further splitting of ν_1 and ν_4 into as many as three bands.

In Tables 6 and 7 are listed the infrared data in the nitrate region for the compounds which contain ionic and coordinated nitrate, respectively. Compounds containing ionic nitrate exhibit only the one sharp band ($\nu_3(D_{3h})$) while compounds containing coordinated nitrate exhibit definite splitting of $\nu_3(D_{3h})$ in the nitrate stretching region. In this manner, the $[Co(NO_3)_4]^{-2}$ anion in $[CoL_5]_2[Co(NO_3)_4]$ was identified and the Co(I) anion distinguished from it.

Assuming that the oxidation state of cobalt is plus one and that both nitrate groups are coordinated in $[CoL(NO_3)_2]^{-1}$, it is interesting to speculate on its possible structure. From the infrared spectrum alone it is impossible to determine the type of nitrate coordination and nothing short of a three-dimensional X-ray analysis can possibly do so with any certainty. A thorough literature search of compounds containing coordinated nitrate, as determined by X-ray analysis, has revealed the compounds listed in Table 8. There are some cases of

Table 6. Infrared data in the nitrate region for ionic nitrate[a]

Compound	ν_3	ν_1	ν_2
Ionic Nitrate[b]	1390	1050[c]	820
$[CoL_5]NO_3$	1368		828
$[CuL_4]NO_3$	1350		828
$[Ag(Ph_3P)_4]NO_3$[d]	1343		

[a] Spectra were run in either nujol or HCBD mulls and values are in cm^{-1}.

[b] See reference 90.

[c] ν_1 is sometimes weakly observed, even though it is infrared inactive.

[d] See reference 80.

Table 7. Infrared data in the nitrate region for coordinated nitrate[a]

Compound	ν_4	ν_1	ν_2	ν_6
$[CoL_5]_2[Co(NO_3)_4]$[b]	1462	1320, 1285	1022	812
$[Ph_3AsMe]_2[Co(NO_3)_4]$[c]	1462	1285	1022	807
$[Ph_4As]_2[Co(NO_3)_4]$[b]	1478, 1462, 1435	1305, 1285	1015	810
$[CoL_5][CoL(NO_3)_2]$[b]	1490, 1462	1305, 1285	1018	810
$[Ph_4As][CoL(NO_3)_2]$[b]	1500, 1479, 1435	1305, 1285	1018	808
$[Co(Me_3PO)_2(NO_3)_2]$[d]	1517, 1492, 1469	1312, 1304, 1282	1024	812
$[AgL_2NO_3]$	1448, 1423	1350, 1285	1025	818
$[Cu(Ph_3P)_2NO_3]$[e]	1475	1275	1022	810
$[NiL_3(NO_3)_2]$[f]				
$[NiII_3(NO_3)_2]$[g]	1457, 1430, 1385, 1365	1300br[h]		
$[NiI_5(NO_3)_2]$[g]	1435, 1418	1300		

[a] Spectra were run in either nujol or HCBD mulls and values are in cm^{-1}.

[b] Resolution was not sufficient to see shoulder peaks.

[c] See reference 91.

[d] See reference 81.

[e] See reference 80.

[f] Compound would not form mull.

[g] Very poor resolution.

[h] Broad.

Table 8. X-ray analyses of compounds containing coordinated nitrate

Compound	Postulated Coordination	Reference
$Cu(NO_3)_2$	bidentate[a] and bridging	93
$Ti(NO_3)_4$	bidentate	88
$[Ph_4As]_2[Co(NO_3)_4]$	bidentate	94
$[(Me_3PO)_2Co(NO_3)_2]$	bidentate	85
$RbUO_2(NO_3)_3$	bidentate	95
$[UO_2(NO_3)_2(H_2O)_2]H_2O$	bidentate	96
$Ce_2Mg_3(NO_3)_{12}\cdot 24H_2O$	bidentate	97
$[UO_2(NO_3)_2(H_2O)_2]4H_2O$	bidentate	98
$Pr(NO_3)_2\cdot 6H_2O$	bidentate	99
$UO_2(NO_3)_2(OP(OEt)_3)_2$	bidentate	100
$AgC_8H_8NO_3$	monodentate[b]	101
$C_7H_8\cdot 2AgNO_3$	bridging	102
$[(C_5H_5NO)Cu(NO_3)_2]$[c]	monodentate	92

[a] Bidentate in all cases is meant to imply that two oxygen atoms per nitrate are found to be within bonding distance to the metal.

[b] Because of the nearness of one nitrate oxygen to the metal, it was concluded that some degree of covalency existed.

[c] Exists as dimer.

bridging nitrate, only one concrete example of monodentate nitrate (92), and an overwhelming number of cases of bidentate nitrate. It is most reasonable, therefore, to assume that like the $[CoL_5]^{+1}$ cation, $[CoL(NO_3)_2]^{-1}$ is also five-coordinate and attains this coordination number by employing the bidentate nature of the nitrate group.

In view of the known trigonal bipyramidal structure for $[NiI_5](ClO_4)_2$ (44), it seems quite reasonable that the isoelectronic $[CoL_5]^{+1}$ should also be trigonal bipyramidal. However, the symmetry imposed by the steric requirements of the bidentate nitrate groups may cause the $[CoL(NO_3)_2]^{-1}$ anion to assume a tetragonal pyramidal rather than a trigonal bipyramidal geometry, or some distortion of both possible configurations. Considering the extreme differences in the visible spectra of these two ions, very different geometries would not be unexpected.

The proton n.m.r. spectrum of $[CoL_5][CoL(NO_3)_2]$ in benzonitrile exhibits two doublets (Table 2). The resonance at higher field is ascribed to the protons of the single ligand in the anion because of the smaller intensity of the resonance and the expected upfield shift upon decreasing the positive oxidation state of the metal ion. In deuteriochloroform the resonance consists of a broad singlet which does not split into two resonances upon cooling the solution to -40°. Presumably, the singlet resonance is due to a rapid intramolecular exchange of ligands in this solvent which could not be stopped with cooling. Credence to this postulate is obtained by considering the chemical shift of the singlet in deuteriochloroform at 3.39 p.p.m. It is between the two values observed for the doublets in benzonitrile and is nearly equal to a weighted average of the two doublet values (3.37 p.p.m.), as should be the case for such an exchange.

$[CuL_4]NO_3$ and $[AgL_2(NO_3)]$

The reduction of Cu(II) salts by phosphite ligands has been observed previously for polycyclic phosphites (9, 13) and L (15). The behavior of $[CuL_4]NO_3$ as a 1:1 electrolyte in acetone indicates that the maximum coordination number of four has been reached by the metal ion. Its diamagnetism and P^{31} spectrum (103) support the postulate that the complex is tetrahedral.

The complex formed with $AgNO_3$ and L is molecular in acetone (Table 1) with a coordinated nitrate group as shown by the infrared spectrum (Table 7). Since the complex is also monomeric in acetone, polymers involving bridging nitrate are ruled out in solution. Unless the silver is three-coordinate and, therefore, bonded to a monodentate nitrate or perhaps a bidentate nitrate involving a three-center bond, a tetrahedral structure containing a normal bidentate nitrate is expected. Because of the coordinating ability of acetonitrile, it is not surprising that nitrate is displaced from $[AgL_2NO_3]$, thereby resulting in a conductivity corresponding to a 1:1 electrolyte. No such nitrate coordination with silver ion was noticed when the polycyclic ligands I (9) and II (13) were used. This may indicate that L is a somewhat weaker ligand since the nitrate group is able to compete with it.

An interesting comparison can be made with $[CuL_4]NO_3$ and $[AgL_2NO_3]$ and the Cu(I) and Ag(I) nitrate complexes of PPh_3. Cotton and Goodgame (80) have shown that an ionic compound is obtained with Ag(I), $[Ag(PPh_3)_4]NO_3$ and a molecular complex with Cu(I), $[Cu(PPh_3)_2NO_3]$ (Tables 1, 4, and 5). The reason for the reversal observed with L is not clear, but it should be noted that the preparation conditions are different in that the PPh_3 complexes were prepared in acetonitrile.

$[NiL_3(NO_3)_2]$, $[NiII_3(NO_3)_2]$ and $[NiI_5(NO_3)_2]$

The $Ni(NO_3)_2$ complexes of L, I, and II also constitute interesting examples of nitrate coordination. The complex with L is very unstable in most solvents and also when exposed to the air. The orange color of the solid disappears quite readily in acetone, which is why the compound is precipitated and isolated from the acetone reaction solution almost immediately. Also, the complex loses L very easily at atmospheric pressure and when subjected to long periods of dynamic vacuum. This instability of the complex is almost certainly the cause of the poor elemental analyses obtained for this compound. Easy ligand loss was verified by observing that the precent nickel increased substantially (see Experimental section) after subjecting the sample to vacuum pumping for two days. The complex with II is considerably more stable to the atmosphere, but decomposes in solution. Dissolving the compound in acetone with heat, produces a green solution from which a greenish-yellow solid is obtained. The green tinge to the color of this solid was never completely eliminated. If the green contaminant were nickel(II) ion, the observed high nickel analysis would be expected. Finally, the complex with I containing five ligands, is very different from the other complexes. It tends to be insoluble in most solvents, but can be recrystallized from acetone to give nicely shaped needle-like crystals and it is considerably more stable than the other two nickel complexes.

The near-zero conductivities observed for these compounds in acetone (Table 1), demonstrates the coordination of the nitrate ion. The conductances that are observed probably represent decomposition of the complexes in the solvent in view of their instability. For $[NiI_5(NO_3)_2]$, an increase in conductivity was observed with time, and an extrapolation back to zero time gave a near-zero conductivity. Moreover, this latter compound was found to be a three-ion electrolyte in the more polar solvent ethanol.

From the infrared spectra in the nitrate region of these compounds (Table 7), it can be established quite firmly that the nitrate groups in all cases are coordinated in the solids. The presence of ionic nitrate gives rise to a very intense band, $\nu_3(D_{3h})$, at approximately 1360 cm^{-1} (90). This type of band was not observed for these compounds, but at the same time, the excellent resolution obtained for the nitrato cobalt compounds was not observed either. Therefore it was not possible to clearly distinguish the ν_1 and ν_4 (C_{2v}) bands.

A possible formulation for the complexes $[NiL_3(NO_3)_2]$ and $[NiII_3(NO_3)_2]$ is the dimer $[NiP_6][Ni(NO_3)_4]$, where P equals L or II. In addition to the fact that elemental analyses are of no aid in resolving this question, the insolubility of the monomer prevented a molecular weight determination. However, the reflectance spectra (Table 3) did not show the presence of the $[Ni(NO_3)_4]^{-2}$ anion (91) nor did the conductance data (Table 1) support such a formulation.

The solid state visible-ultraviolet spectra of $[NiL_3(NO_3)_2]$ and $[NiII_3(NO_3)_2]$ consist primarily of one very broad absorption at approximately 370 mμ. This is very similar to that observed for $[NiI_5](ClO_4)_2$ (Table 3) whose structure is known to be trigonal bipyramidal (44). Therefore, the structures of $[NiL_3(NO_3)_2]$ and $[NiII_3(NO_3)_2]$ are probably also five-coordinate and trigonal bipyramidal. The arrangement of the ligands in this geometry is not known with certainty, but D_{3h} point symmetry with trans-axial nitrate groups seems most reasonable for steric reasons.

For $[NiL_3(NO_3)_2]$ and $[NiII_3(NO_3)_2]$ to be five-coordinate, both nitrate groups are expected to be monodentate. This would be somewhat surprising in view of the few reported cases of monodentate nitrate, but any other structure does not seem as plausible. In considering the Ni(II) and Co(I) nitrate complexes of L, it is also very interesting that an ionic nitrate complex is formed only with Co(I). Moreover, the nickel nitrate complex of I is a very interesting case of nitrate coordination. Although the coordination of five phosphite ligands is not surprising in view of the well-characterized complex $[NiI_5](ClO_4)_2$ (12, 44), the non-ionic character of the nitrate analogue in acetone and the apparent nitrate coordination as revealed by the infrared spectrum is highly unusual. Even though it is not possible to rule out a coordination number of seven for this complex, the formation of ion pairs is perhaps more reasonable in view of the similarity of the visible spectrum to those of other five coordinate nickel(II) phosphite complexes. The ion-pairing interaction is probably rather weak in comparison to the other cases of nitrate coordination reported here, because it does not take place in more polar solvents such as ethanol. If the nitrate is an outer sphere ligand, the ethanol may preferentially complex the outer sphere of the cation and thus ionize the complex.

$[NiL_3(CN)_2]$, $[NiL_2(CN)_2]$, and $[NiII_3(CN)_2]$

Recently, Raymond and Basolo (104) and Rick and Pruett (105) have isolated five-coordinate Ni(II) complexes with coordinated cyanide ions.

Raymond and Basolo isolated the $[Ni(CN)_5]^{-3}$ anion for the first time in the solid form. This ion represents one of the first examples of five-coordinate Ni(II) complexes with only identical mono-dentate ligands in the coordination sphere. A preliminary X-ray analysis reveals that the anion exists both as a trigonal bipyramid and a tetragonal pyramid in the crystal lattice (106). The compound prepared by Rick and Pruett was $[Ni(PhP(OEt)_2)_3(CN)_2]$. The authors stated that the phosphite complex was monomeric and dissociatively stable in acetone. A trigonal bipyramidal structure was postulated because the visible spectrum, consisting of two bands at 350 mμ and a shoulder at 415 mμ with molar extinction coefficients of 3.16×10^3 and 2.5×10^3, respectively, was concluded to be characteristic of d^8, low-spin, trigonal bipyramidal structures (62). Furthermore, the cyanide groups were predicted to be in the trans-axial positions since only one band at 4.75 μ was observed in the cyanide region of the infrared spectrum.

The complex prepared with L, $[NiL_3(CN)_2]$, shows a strong similarity to $[Ni(PhP(OEt)_2)_3(CN)_2]$ in that it is a red-orange crystalline complex which is diamagnetic and non-electrolytic. Also prepared in this work are the complexes, $[NiL_2(CN)_2]$ and $[NiII_3(CN)_2]$, which are both insoluble yellow powders. The conductivities of the latter complexes are not known because of their insolubility, but they are assumed to be non-ionic and diamagnetic.

The visible-ultraviolet spectrum of $[NiL_3(CN)_2]$ in CH_2Cl_2 (Table 3) consists of three absorptions at 295, 345, and 420(sh) mμ. The latter two absorptions are in very good agreement with that observed for $[Ni(PhP(OEt)_2)_3(CN)_2]$ (105). Interestingly, the reflectance spectrum of [$NiL_2(CN)_2$] (Table 3) is nearly identical to the solution spectrum of [$NiL_3(CN)_2$], for it also shows two bands at 340 and 425 mμ. Finally, the reflectance spectrum of [$NiL_3(CN)_2$] (Table 3), shows no similarity to its solution spectrum nor to the reflectance spectrum of [$NiL_2(CN)_2$]. It consists rather of two absorptions at 260 and 395 mμ, the latter being very broad. It is therefore concluded that in solution, $NiL_3(CN)_2$ dissociates to [$NiL_2(CN)_2$] and L. Hence the compound reported by Rick and Pruett, [$Ni(PhP(OEt)_2)_3(CN)_2$], is probably acting in the same manner in that in the solution phase they observed [$Ni(PhP(OEt)_2)_2(CN)_2$]. Although these authors state that their compound is dissociatively stable on the basis of molecular weight studies, they do not mention the method of their measurements. If a cryoscopic method was employed, the low temperature involved could have suppressed any dissociation.

The postulate by Rick and Pruett that the solution spectrum of [$Ni(PhP(OEt)_2)_3(CN)_2$] was characteristic of d^8, low-spin, trigonal bipyramidal complexes thus does not seem to be substantiated.

The possibility of a dimer for [$NiL_2(CN)_2$] can not be ruled out. If such is the case, then each nickel atom could be five-coordinate and trigonal bipyramidal by sharing a common edge with two bridging cyanides. Such a postulate could explain the similarity in the visible spectrum of [$NiL_2(CN)_2$]$_2$ with those of other five-coordinate phosphite complexes. Finally, the reflectance spectrum of [$NiL_3(CN)_2$] is very similar to that observed for [$NiII_3(CN)_2$] (Table 3). The latter compound shows no tendency to dissociate and its spectrum is consistent with those of five-coordinate complexes. In addition, very similar solution and solid spectra were observed for [NiI_5](ClO_4)$_2$ (Table 3).

The possibility of an equilibrium between $[NiL_3(CN)_2]$ and $[NiL_2(CN)_2]$ and L seems to be indicated by the spectral data discussed above. The manner in which $[NiL_2(CN)_2]$ is prepared from $[NiL_3(CN)_2]$ apparently makes use of this phenomenon. It is surprising that $[NiL_3(CN)_2]$ can be recrystallized many times from acetone, yet the addition of ether causes formation of $[NiL_2(CN)_2]$. For some obscure reason, ether removes L from the equilibrium system, but acetone does not.

That the postulated equilibrium is reversible, was shown by n.m.r. spectroscopy (Table 2). Addition of a drop of L to an acetone suspension of $[NiL_2(CN)_2]$ resulted in the formation of an orange-red solution which exhibited a chemical shift nearly identical to that of an authentic sample of $[NiL_3(CN)_2]$ in acetone. The chemical shift observed is undoubtedly an exchange chemical shift between $[NiL_2(CN)_2]$ and L since the free ligand proton absorptions were absent. Thus adding more L to the acetone solution of $[NiL_3(CN)_2]$, produced a chemical shift near that of free ligand (Table 2) as expected for an exchange process (107).

The infrared spectral data in the cyanide region for $[NiL_3(CN)_2]$, $[NiL_2(CN)_2]$, and $[NiII_3(CN)_2]$ is shown in Table 9. In Figure 7 the cyanide stretching bands are pictured. For $[NiL_3(CN)_2]$ and $[NiII_3(CN)_2]$ only one band is observed for the cyanide stretching frequency. These five-coordinate complexes, therefore, are undoubtedly trigonal bipyramidal with <u>trans</u>-axial cyanides since only the D_{3h} point group symmetry is consistent with one cyanide stretching frequency.

The infrared spectrum for $[NiL_2(CN)_2]$ shows that the symmetry possessed by the five-coordinate complex has been removed. If

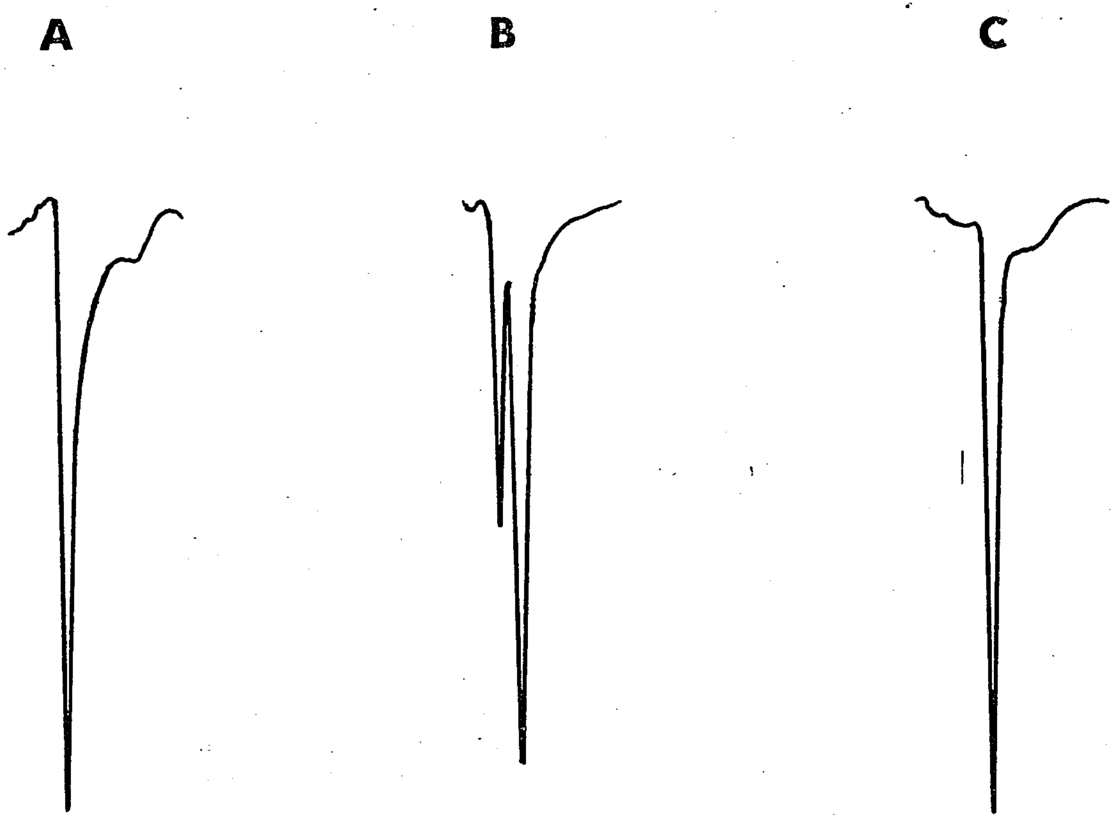


Figure 7. Infrared spectra in the cyanide region for $[NiL_3(CN)_2]$ (A), $[NiL_2(CN)_2]$ (B), and $[NiII_3(CN_3)_2]$ (C)

Table 9. Infrared spectral data for the cyanide region of the nickel cyanide complexes

Compound	Phase	Wavelength[a]
[$NiL_3(CN)_2$]	KBr Nujol	4.71 4.72
[$NiL_2(CN)_2$]	Nujol	4.65, 4.71
[$NiII_3(CN)_2$]	KBr	4.68

[a] Values reported in microns.

[$NiL_2(CN)_2$] is a monomer, the two possible structures are cis-square planar and tetrahedral; both of which should produce two infrared-active modes. If the compound is a dimer, the infrared spectrum can also be accounted for by ascribing the two stretching frequencies to two terminal and two bridging cyanides. Possible dimeric structures consistent with the infrared data are shown in Figure 8.

P^{31} N.M.R. of Complexes

It was initially hoped that the P^{31} chemical shifts (δ_{PM}) obtained for the complexes of L, I, and II could be compared and some insight into the nature of the metal phosphorus bond obtained. Such a comparison does not seem unreasonable in view of the very similar complexes prepared with each of these ligands and their comparable spectral and magnetic properties.

The P^{31} chemical shifts for the complexes of L are shown in Table 10. Also shown are values obtained for similar complexes of I and II.

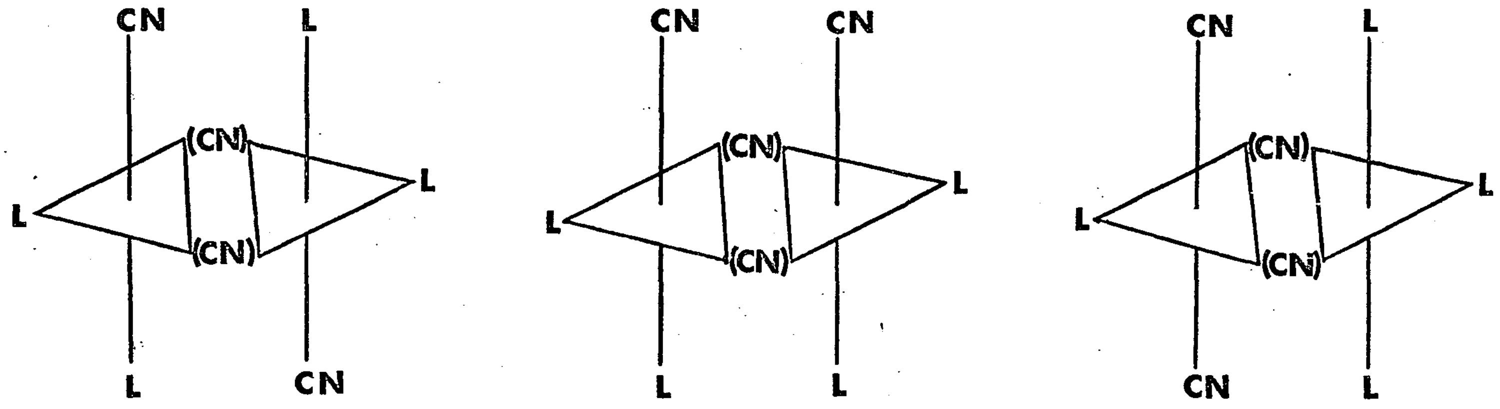


Figure 8. Possible dimeric structures for $[NiL_2(CN)_2]_2$

Table 10. P^{31} chemical shifts of complexes

Compound	L	I	II[a]
P[b]	-141	-137[c,d]	-93[d]
$[NiP_5](ClO_4)_2$[e]	-110(+31)[f]	-125(+12)[g]	-108(-15)[h]
$[NiP_3(CN)_2]$	-120(+21)[f]		
$[CuP_4]NO_3$	-129(+12)[f]		
$[AgP_4]ClO_4$[i]	-132(+9)[f]		
$[AgP_4]NO_3$[j]		-134(+3)[k]	-99(-6)[h]
$[AgP_2NO_3]$	-134(+7)[f]		
$[CoP_5]NO_3$[l]	-147(-6)[f]		-138(-45)[h]
$[CoP_5]ClO_4$[m]		-138(-1)[h]	
$[NiP_4]$[n]	-163(-22)[d]		-129(-36)[d]

[a] The 4-ethyl derivative of II was used in all cases.

[b] P equals L, I, or II.

[c] See reference 29.

[d] Spectrum obtained in chloroform.

[e] For P = L, I, and II, see references 15, 12, and 10, respectively.

[f] Spectrum obtained in acetone.

[g] Spectrum obtained in N,N-dimethylformamide.

[h] Spectrum obtained methylene chloride.

[i] See reference 15.

[j] For P = I and II, see references 13 and 9, respectively.

[k] Spectrum obtained in dimethylsulfoxide.

[l] For P = II, see reference 12.

[m] For P = I, see reference 12.

[n] For P = L and II, see references 13 and 12, respectively.

The values in parentheses represent an upfield (positive) or downfield (negative) shift relative to free ligand.

From Table 10 it can be seen that for the complexes of L, δ_{PM} is at higher field than the free ligand in all cases except for the Co(I) and Ni(0) complexes. For I, δ_{PM} does not vary appreciably and shifts at lower and higher fields than the free ligand are observed. For II, however, all shifts are at lower field than the free ligand.

The individual factors mentioned in the Introduction are felt to be influential in determining phosphorus chemical shifts in transition metal complexes (72, 77, 78), but their individual contributions are difficult to assess. The charge effect seems to be demonstrable for a series of isostructural and isoelectronic complexes of the same ligand wherein changes in the other factors might be expected to be minimal. Thus $[CuL_4]^{+1}$ and $[AgL_4]^{+1}$ are seen to have similar chemical shifts whereas $[NiL_4]^{\circ}$ appears further downfield. The same can be said for $[AgII_4]^{+1}$ and $[NiII_4]^{\circ}$. Similarly, the shift of $[NiP_5]^{+2}$ is upfield of $[CoP_5]^{+1}$ where P is either L, I, or II.

The importance of bond angle changes in the phosphite ligand upon coordination may be evident in the resonances of $[NiL_5]^{+2}$ and $[NiII_5]^{+2}$. These resonances are upfield and downfield, respectively, from the free ligands. Shielding effects should be about the same in the two complexes, but inasmuch as bond angle changes in II would be minimal due to its rigid structure, changes in the OPO bond angles of L upon coordination may be appreciable. Furthermore, Verkade and King (29) have shown that small OPO bond angle variations in trivalent phosphorus compounds seem to be responsible for large changes in P^{31} shifts.

In view of the relatively few metal complexes containing a specific phosphorus ligand for which P^{31} shift values are known, it does not seem profitable to attempt correlations of a few bond parameters with P^{31} shifts. However, it is believed that paramagnetic contributions are dominant and any diamagnetic shielding resulting from back bonding is probably small.

CONCLUSION

In every comparable case, coordination compounds of L were prepared which parallel those obtained with I and II. Furthermore, the ligand properties of L have been shown to be very comparable to those of I and II from its Dq value in $[CoL_6]^{+3}$ and the stable complexes prepared.

The postulate that trialkyl phosphites were poor ligands because of steric reasons and a low permanent dipole in comparison to I and II (9, 10), is apparently incorrect.

The excellent ligand properties of L can be accounted for by considering possible electronic and geometrical changes that may take place in L upon coordination and the possible pi-bonding ability of L. A metal ion in solution with L may set up a strong inducing electrostatic field whereby the total dipole moment of L is increased by an induced dipole effect. Livingstone (108) has developed an equation relating these effects:

$$\mu = P + p' = P + \alpha E$$

where μ is the total dipole moment, P is the permanent dipole moment, p' is the induced dipole moment, α is the polarizability, and E is the inducing electrostatic field. From this equation it can be seen that the total dipole moment of L would be increased by any effect due to the induced moment. The important term in this equation is α, the polarizability. In the presence of a cation with high polarizing power, L should be polarized very easily because of the lone pair electrons on the three oxygen atoms as well as on phosphorus.

Moreover, any constraint of the alkoxy groups to C_{3v} symmetry, which might be necessary for minimum ligand-ligand repulsion, would enhance the permanent dipole of L since directional character would be given to the oxygen lone pairs (40). The net result of the electronic and constraining effects could result in a dipole moment of L comparable to those of I and II (*ca*. 4 D.) in spite of the low moment for unperturbed L (*ca*. 2 D.).

Pi-bonding effects for L have been postulated by Chatt, *et al*. (109), to account for unusually energetic d-d transitions in platinum (II) complexes and have been cited as a possible cause for the extraordinarily strong ligand properties of I and II (13, 29). *Pi*-bonding, if present, should be about the same for all three ligands with back bonding occurring from the filled metal d orbitals to the empty d orbitals on phosphorus. This could account for the apparently substantial covalent bonding in these complexes.

Support for large metal-ligand interactions is demonstrated by the five-coordinate Co(I) and Ni(II) complexes of I (12), II (10), and L. These cations exhibit an intense charge-transfer bond in the near ultraviolet regions with no observable ligand bands. For the large number of five coordinate Ni(II) complexes with polydentate phosphines and arsines (47-60) and monodentate phosphines (47-50), absorptions attributed to ligand-field bands were observed well into the visible region. That these bands are not observed for the Ni(II) and Co(I) five-coordinate complexes may indicate that the intense charge-transfer bands mask the d-d transitions. If this is the case, the energies associated with these transitions are at least in the near ultraviolet and are indicative of a large ligand-field separation of the levels.

SUGGESTIONS FOR FUTURE WORK

The extension of the work described in this thesis to longer-chain trialkyl phosphites does not appear to be advantageous or otherwise rewarding. Huttemann (13) reported that color changes take place when triethyl, thriisopropyl, and tri-n-butyl phosphites are reacted with metal ions, but only unstable solids or oils could be obtained.

The reactions of L with nickel and cobalt salts of coordinating anions such as halides should be of interest. Although incompletely characterized complexes of the type $[NiP_2X_2]$ (where P is a trialkyl phosphite and X is a halide ion), have been reported (16, 77), it seems unlikely that they are four-coordinate in view of the five-coordinate complexes reported here which involve two coordinated cyanides. Preliminary results of a reinvestigation of these complexes by Jenkins[1] indicate that the complex reported by Jensen is indeed five-coordinate.

The nature of the postulated dissociation of $[NiL_3(CN)_2]$ to L and $[NiL_2(CN)_2]$ may be elucidated by low-temperature proton n.m.r. spectroscopy. It may be possible to slow the exchange process to the point where the spectrum due to each of the species becomes visible. Some insight into this equilibrium may also be obtained by attempting to isolate a compound like $[NiL_2P(CN)_2]$ where P is some other phosphorus ligand, in particular, a polycyclic phosphite. Upon the addition of

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[1] Work performed by Dr. J. M. Jenkins, Post-Doctoral Fellow, Department of Chemistry, Iowa State University, Ames, Iowa.

excess P to a solution of [$NiL_3(CN)_2$], dissociation of the complex may be reversed to form [$NiL_2P(CN)_2$] because of the greater insolubility observed for P complexes of nickel(II). Dissociation of [$NiL_2P(CN)_2$] could give rise to [$NiL_2(CN)_2$] and/or [$NiLP(CN)_2$]. The latter compound would be the first example of a disubstituted mixed phosphite complex. The extent of phosphorus-phosphorus coupling could be directly measured from the phosphorus n.m.r. spectrum since both phosphorus atoms are chemically and magnetically different.

The studies on nickel(II) cyanide phosphite complexes might be extended to cobalt(II) cyanide. Since Co(II) undergoes a disproportionation reaction in the presence of phosphites, the Co(I) compound may represent an interesting comparison to [$NiL_3 CN)_2$]. If non-ionic species are formed, compounds of the formulation [CoL_4CN] and [$CoL_3(CN)_3$] may be anticipated with the possibility of isomers in the case of the latter complex. A complex analogous to [$CoL(NO_3)_2$]$^{-1}$ (i.e., [CoL_3 $(CN)_2$]$^{-1}$) is also not unexpected if the former compound is five-coordinate.

The bidentate nature of the nitrate group is apparently employed in [$CoL(NO_3)_2$]$^{-1}$, whereas in [$NiL_3(NO_3)_2$], they are probably monodentate. The ease with which L is lost in the latter compound may indicate that compounds like [$NiL_2(NO_3)_2$] and [$NiL(NO_3)_2$] can be isolated. If [$NiL(NO_3)_2$] contains bidentate nitrates, it may also be isostructural with [$CoL(NO_3)_2$]$^{-1}$ in addition to being isoelectronic.

Studies of P^{31} n.m.r. spectra of metal phosphite complexes should be extended to as many examples as possible in order to document trends. Only then can speculations on the origin of P^{31} shifts be of maximum value. Although a study of isoelectronic and isostructural systems seems most advantageous at present, the known examples for a series of oxidation states seems limited to two in each case. Some attempts should be made to synthesize $[FeL_5]^{\circ}$ to ascertain the variation of P^{31} shift with charge on the metals in proceeding to $[CoL_5]^{+1}$ and $[NiL_5]^{+2}$. Similarly, some attempts should be made to isolate tetrahedral L complexes of divalent zinc, cadmium, and mercury to compare their P^{31} shifts with those of $[AgL_4]^{+1}$ and $[NiL_4]^{\circ}$.

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