Five-Coordination. V. Trigonal-Bipyramidal Nickel(II) Complexes of Tris(3-dimethylarsinopropyl)arsine[1-3]

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Tris(3-dimethylarsinopropyl)arsine, $C_{15}H_{36}As_4$, forms deep blue, diamagnetic, uni-univalent complexes of the types $[Ni(C_{15}H_{36}As_4)X]ClO_4$ and $[Ni(C_{15}H_{36}As_4)X]B(C_6H_5)_4$ as well as the di-univalent $[Ni(C_{15}H_{36}As_4)H_2O](ClO_4)_2$. These crystalline, five-coordinate complexes of nickel(II) are assigned a regular trigonal-bipyramidal (C_{3v} symmetry) structure (Figure 3) on the basis of the close similarity between their electronic absorption spectra and the spectrum of $[Ni(TAP)CN]ClO_4$, which is known to have a trigonal-bipyramidal structure.

Introduction

In a previous paper[5] we described the first five-coordinate nickel(II) complexes resulting from a polydentate "mixed donor atom" ligand. Because flexible tetradentate "tripod" ligands of the type $D(CH_2CH_2CH_2D')_3$ (where $D \neq D'$) permit a controlled and systematic variation of the ligand field strength imposed on the d orbitals of the metal along certain orbital directions, we have undertaken a major investigation of the spectral and magnetic properties of transition metal complexes which result from such ligands.

A series of $D(CH_2CH_2CH_2D')_3$ (where $D \neq D'$) ligands provides an opportunity to vary the peripheral donor atoms, D', with a constant central atom, D, and then to vary the central atom while holding the peripheral atoms constant. A reverse donor atom arrangement (*e.g.*, $P[CH_2CH_2CH_2N(CH_3)_2]_3$ compared with $N[CH_2CH_2CH_2P(CH_3)_2]_3$) should have a profound effect on the electronic spectra and structures of the complexes. The flexible aliphatic linkages ensure that the structures of the complexes will be determined by the bonding characteristics of the metal rather than by the inherent symmetry or steric requirements of the ligand.

Nickel(II) complexes containing the five-coordinate $[Ni(ligand)X]^+$ cations were isolated in our study with the tetradentate ligand $P[CH_2CH_2CH_2As(CH_3)_2]_3$, TAP.[5] A three-dimensional X-ray analysis of $[Ni(TAP)CN]ClO_4$ has shown that the nickel(II) ion is surrounded by a symmetrical trigonal-bipyramidal arrangement of five donor atoms.[6] Since the $[Ni(TAP)X]ClO_4$ complexes could not be oxidized to Ni(III) complexes as Barclay and Barnard[7] had reported for nickel complexes of the analogous tetratertiary arsine $As[CH_2CH_2CH_2As(CH_3)_2]_3$, we have reinvesti-

(1) The authors gratefully acknowledge the financial support of Grant DA-ARO-(D)-31-124-G500 from the U. S. Army Research Office (Durham) and Grant GP-5729 from the National Science Foundation.

(2) Part IV: T. D. DuBois and D. W. Meek, *Inorg. Chem.*, **6**, 1395 (1967).

(3) Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J. Sept 1965, and at the Anniversary Meeting of The Chemical Society (London), Oxford, England, March 1966.

(4) Public Health Service Predoctoral Fellow (No. 1-F1-GM-22), 1964–1966.

(5) G. S. Benner, W. E. Hatfield, and D. W. Meek, *Inorg. Chem.*, **3**, 1544 (1964).

(6) L. F. Dahl and D. L. Stevenson, personal communication, 1965.

(7) G. A. Barclay and A. K. Barnard, *J. Chem. Soc.*, 4269 (1961).

gated the complexes of this ligand. The stable nickel complexes of $As[CH_2CH_2CH_2As(CH_3)_2]_3$ are five-coordinate, trigonal-bipyramidal Ni(II) complexes, $[Ni(ligand)X]ClO_4$, similar to the nickel complexes of $P[CH_2CH_2CH_2As(CH_3)_2]_3$, and not octahedral Ni(III) complexes as reported earlier.[7]

Experimental Section

Preparation of Tris(3-dimethylarsinopropyl)arsine.—The compound was prepared as described by Barclay and Barnard,[7] including modifications reported[5] in the synthesis of $P[CH_2CH_2CH_2As(CH_3)_2]_3$. Since the waxy $As[CH_2CH_2CH_2As(CH_3)_2]_3$ melted at 23°, it was dissolved in benzene or ethanol to give solutions of known concentrations; aliquots of these solutions were used for the following syntheses.

Tetrasulfide of the Ligand.—One-eighth of a gram (0.0039 g-atom) of sulfur, dissolved in 10 ml of ethylenediamine,[8] was added to 6 ml of an 8.8% solution of $As[CH_2CH_2CH_2As(CH_3)_2]_3$ (0.98 mmole) in benzene. After standing 3 min at room temperature, the reaction solution was poured into 100 ml of water, and the resulting slurry was filtered. The white precipitate was recrystallized two times by dissolving the compound in boiling dimethylformamide and then slowly cooling the solution. *Anal.* Calcd for $C_{15}H_{36}As_4S_4$: C, 27.96; H, 5.63; S, 19.90. Found: C, 28.22; H, 5.81; S, 19.57.

Chlorotris(3-dimethylarsinopropyl)arsinenickel(II) Perchlorate, $[Ni(C_{15}H_{36}As_4)Cl]ClO_4$.—A solution of nickel perchlorate hexahydrate (1.2 mmoles) and 0.3 g of nickel chloride hexahydrate (1.3 mmoles) in 25 ml of absolute ethanol was added to 25 ml of a 4.64% solution of $As[CH_2CH_2CH_2As(CH_3)_2]_3$ (2.3 mmoles). After 1 hr, the blue powder was separated by filtration and recrystallized two times by dissolving the sample in a minimum amount of boiling chloroform, then adding boiling ligroin until precipitation just began to occur. The solution was cooled slowly to −78° and the resulting crystals were collected on a sintered-glass filter, washed with ether, and dried *in vacuo* at 56°. *Anal.* Calcd for $C_{15}H_{36}As_4Cl_2NiO_4$: C, 25.38; H, 5.11; Cl, 10.00. Found: C, 25.21; H, 4.99; Cl, 10.04.

Bromotris(3-dimethylarsinopropyl)arsinenickel(II) Perchlorate, $[Ni(C_{15}H_{36}As_4)Br]ClO_4$.—A solution of 0.45 g of $[Ni(H_2O)_6](ClO_4)_2$ (1.2 mmoles) and 0.4 g of $[Ni(H_2O)_6]Br_2$ (1.2 mmoles) in 25 ml of ethanol was added slowly to 25 ml of the ligand solution (2.3 mmoles) with stirring. After 1 hr, the blue powder was collected on a filter, then extracted into chloroform, and precipitated by addition of ligroin. It was then recrystallized two times from methanol. *Anal.* Calcd for $C_{15}H_{36}As_4BrClNiO_4$: C, 23.89; H, 4.81; total halide calcd as Br, 21.19. Found: C, 24.03; H, 4.73; total halide calcd as Br, 21.45.

Attempt to Prepare Dibromotris(3-dimethylarsinopropyl)-

(8) W. A. Hodgson, S. A. Buckler, and G. Peters, *J. Am. Chem. Soc.*, **85**, 543 (1963).

arsinenickel(III) Perchlorate, [Ni(C₁₅H₃₆As₄)Br₂]ClO₄.⁷—An ethanol solution (10 ml) containing 0.16 g of [Ni(H₂O)₆]Br₂ (0.49 mmole) and 0.07 g of sodium perchlorate (0.57 mmole) was added with vigorous stirring to a solution of 0.26 g of As-[CH₂CH₂CH₂As(CH₃)₂]₃ (0.5 mmole) in 5.6 ml of absolute ethanol. After the reaction mixture had stood overnight, the blue powder was collected on a filter, then purified as above. The electronic spectrum of the compound (λ_{max} 624 mμ, ϵ 1884) is nearly identical with that of [Ni(C₁₅H₃₆As₄)Br]ClO₄ (λ_{max} 622 mμ, ϵ 1842). Thus, the compound was [Ni(C₁₅H₃₆As₄)Br]ClO₄, and not [Ni(C₁₅H₃₆As₄)Br₂]ClO₄.

Iodotris(3-dimethylarsinopropyl)arsinenickel(II) Perchlorate, [Ni(C₁₅H₃₆As₄)I]ClO₄.—A solution of 0.45 g of nickel perchlorate hexahydrate (1.2 mmoles) and 0.52 g of nickel iodide hexahydrate (1.2 mmoles) in 25 ml of absolute ethanol was added slowly with stirring to 25 ml of a 4.65% solution of ligand in ethanol (2.3 mmoles). After the mixture had stood overnight, the blue-green product was separated by filtration and purified as for the bromide. *Anal.* Calcd for C₁₅H₃₆As₄ClINiO₄: C, 22.49; H, 4.53; total halide calcd as I, 31.68. Found: C, 22.34; H, 4.63; total halide calcd as I, 31.51.

Cyanotris(3-dimethylarsinopropyl)arsinenickel(II) Perchlorate, [Ni(C₁₅H₃₆As₄)CN]ClO₄.—A solution of 0.15 g of sodium cyanide (3 mmoles) in 50 ml of boiling methanol was added with stirring to a solution of 1.5 g of [Ni(C₁₅H₃₆As₄)Cl]ClO₄ (2.1 mmoles) in 150 ml of boiling methanol. The deep blue solution turned red as soon as the cyanide was added. The volume of the solution was reduced to about 20 ml and the product crystallized when the solution was kept overnight at $-18°$. The red crystals were then recrystallized twice from methanol, washed with ether, and dried *in vacuo* at 56°. *Anal.* Calcd for C₁₆H₃₆As₄ClNNiO₄: C, 27.44; H, 5.18; Cl, 5.06; N, 2.00. Found: C, 27.23; H, 5.03; Cl, 5.27; N, 2.17.

Attempt to Prepare Triphenylphosphinetris(3-dimethylarsinopropyl)arsinenickel(II) Perchlorate, [Ni(C₁₅H₃₆As₄)P(C₆H₅)₃]-(ClO₄)₂: Synthesis of Aquotris(3-dimethylarsinopropyl)arsinenickel(II) Perchlorate, [Ni(C₁₅H₃₆As₄)H₂O](ClO₄)₂.—A solution of 0.54 g (1.5 mmoles) of nickel perchlorate hexahydrate in 10 ml of ethanol and 5 ml of 2,2-dimethoxypropane was added to a boiling solution of 1.8 g of triphenylphosphine (6.9 mmoles) and 1.4 mmoles of As[CH₂CH₂CH₂As(CH₃)₂]₃ in 15 ml of absolute ethanol. The resulting purple powder was collected on a filter, washed with hot tetrahydrofuran, then washed with ether, and dried *in vacuo*. The infrared spectrum of this crude product contained no absorptions characteristic of phenyl groups, but contained bands at ~3500 and 1660 cm^{-1}, characteristic of water. The compound was recrystallized two times from methanol and dried over P₄O₁₀ *in vacuo*. The same compound was obtained when a 1:1:1 mole ratio of triphenylphosphine, nickel(II), and tetraarsine ligand was used. *Anal.* Calcd for C₁₅H₃₈As₄Cl₂NiO₉: C, 22.75; H, 4.84; Cl, 8.96. Found: C, 22.98; H, 4.78; Cl, 8.78.

Spectral and Conductance Measurements.—These were obtained as described previously.⁵,⁹

Magnetic Measurements.—Magnetic moments were determined using a Faraday magnetic susceptibility balance which was constructed recently in this laboratory.¹⁰ The observed susceptibility values were corrected for the diamagnetism of the ligands.¹¹

Discussion

The five-coordinate nickel(II) complexes of tris-(3-dimethylarsinopropyl)arsine, As[CH₂CH₂CH₂As-(CH₃)₂]₃, were synthesized by direct combination of the

(9) (a) G. Dyer and D. W. Meek, *Inorg. Chem.*, **4**, 1398 (1965); (b) G. Dyer and D. W. Meek *ibid.*, **6**, 149 (1967).

(10) The authors gratefully acknowledge the NSF instrument grant (GP-1719) which facilitated purchase of the magnetic susceptibility balance components.

(11) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 403.

reagents in absolute ethanol. Addition of perchlorate ion was required in order to isolate crystalline compounds from the deep blue oils, which resulted from reactions of the ligand with nickel halides. Subsequently, it was simpler to mix an equal number of moles of nickel perchlorate and nickel halide in ethanol to give effectively "NiXClO₄," and then add this resulting solution to the ligand. A deep blue complex usually precipitated immediately when the latter procedure was used.

The above synthetic procedure produced quite a different type of nickel complex from that reported previously.⁷ In order to determine if the two slightly different syntheses produced different complexes, each of Barclay and Barnard's procedures was repeated. In every case, only the deep blue, five-coordinate Ni(II) complex, *i.e.*, [Ni(C₁₅H₃₆As₄)X]ClO₄, was isolated. Also no oxidation of Ni(II) to Ni(III) occurred, even after bubbling air through the reaction mixture.

The cyanide complex was synthesized readily from [Ni(C₁₅H₃₆As₄)Cl]ClO₄ by using a slight excess of sodium cyanide. If a large excess of cyanide ion is used, the tetraarsine complex is destroyed and [Ni(CN)₄]²⁻ is formed.

Attempts to synthesize nickel complexes containing a neutral ligand such as pyridine, thiourea, triphenylphosphine, triphenylarsine, or dipyridyl in the fifth coordination position yielded only the aquo complex [Ni(C₁₅H₃₆As₄)H₂O](ClO₄)₂. This behavior is in contrast to the ready coordination of bulky ligands, such as triphenylphosphine, in the fifth position when the tetradentate ligands TSP and TSeP are used.⁹ These results are understandable now in terms of the structure of the [Ni(TAP)CN]ClO₄ complex. A molecular model, which was constructed from the structural data of [Ni(TAP)CN]ClO₄, indicates that the hole for the fifth ligand position is very small. Apparently only small anions or small molecules such as water can fit into this hole.

Oxidation of Nickel(II) Complexes.—Barclay and Barnard⁷ reported that Ni(III) complexes of As[CH₂-CH₂CH₂As(CH₃)₂]₃ were obtained directly by mixing the ligand with Ni(II) salts and that Ni(II) complexes were isolated only with difficulty. Since our investigation⁵ with the closely related arsine–phosphine ligand P[CH₂CH₂CH₂As(CH₃)₂]₃ yielded only Ni(II) complexes, it was of interest to reinvestigate the nickel complexes of the tetraarsine.

Deliberate attempts to oxidize the [Ni(ligand)X]ClO₄ complexes (where ligand = P[CH₂CH₂CH₂As(CH₃)₂]₃ or As[CH₂CH₂CH₂As(CH₃)₂]₃) by the appropriate halogen, nitrogen(II) oxide, nitrogen(IV) oxide, or nitric acid (a) destroyed the complex (Cl₂, NO₂, HNO₃), (b) failed to produce any change (NO), or (c) produced brown diamagnetic compounds (Br₂ and I₂) which, if monomeric, could not contain Ni(III).

A titration with bromine showed that 2 equiv of oxidant is required in the reactions with the Ni(II) complexes, rather than the 1 equiv expected for eq 1 and 2. The electronic spectra of the brown, diamag-

$$[\text{Ni(ligand)}X_2] + 0.5X_2 \longrightarrow [\text{Ni(ligand)}X_2]X \quad (1)$$

$$[\text{Ni(ligand)}X]ClO_4 + 0.5X_2 \longrightarrow [\text{Ni(ligand)}X_2]ClO_4 \quad (2)$$
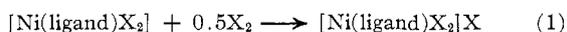
netic oxidation products resemble those of square-planar nickel(II) complexes, and the infrared spectra show a new band characteristic of the As=O group in tertiary arsine oxides. From the properties of the oxidized compounds and the stoichiometry of the reaction, one terminal arsenic atom must become detached from the metal and oxidized by the halogen. The nickel(II) complex is then converted to a square-planar product. Although considerable effort was invested, the oxidized materials did not exhibit reproducible analytical compositions, so the exact course of the reaction has not been established.

It is difficult to explain the discrepancy between the types of complexes reported in the previous study[7] and the present one. However, the following observations may provide a possibility. When $P[CH_2CH_2CH_2As(CH_3)_2]_3$ was mixed with anhydrous nickel bromide or nickel iodide, brown insoluble materials precipitated. The compounds were difficult to purify, mainly because of insolubility in solvents which did not cause decomposition. However, an analytical sample of brown $[\text{Ni(TAP)I}]_2[\text{NiI}_4]$ was obtained from a dichloromethane–ligroin mixture. Elemental analyses, other than nickel, do not distinguish this formulation from $[\text{Ni(TAP)I}_2]I$. The χ_g was 3.19×10^{-6}; by assuming a diamagnetic $[\text{Ni(TAP)I}]^+$ cation, the observed paramagnetism corresponds to $\mu_{eff} = 4.07$ BM. This value is in good agreement for a tetrahedral $[\text{NiI}_4]^{2-}$ ion. If the susceptibility is calculated on the basis of a $[\text{Ni(TAP)I}_2]I$ complex (*i.e.*, an octahedral Ni(III) complex), the $\mu_{eff} = 2.80$ BM. The latter value is somewhat high for a strong-field d^7 case, *i.e.*, Ni(III).

Spectra of the Trigonal-Bipyramidal Complexes.— The electronic absorption spectra (Figure 1 and Table I) of both the $P[CH_2CH_2CH_2As(CH_3)_2]_3$ and $As[CH_2CH_2CH_2As(CH_3)_2]_3$ complexes of nickel(II) are quite similar. The strong, asymmetric band ($\epsilon \sim 2000$) in the 16,000–20,000 cm^{-1} region and a weaker band ($\epsilon \sim 200$) approximately 4000 cm^{-1} higher in energy distinguish these spectra from those typical of four- or six-coordinate Ni(II) complexes. The spectra appear to be characteristic of diamagnetic, trigonal-bipyramidal complexes of d^8 ions.[9,12]

The structure of $[\text{Ni}(C_{15}H_{36}As_3P)CN]ClO_4$ is a regular trigonal bipyramid.[6] Since the electronic spectrum of $[\text{Ni}(C_{15}H_{36}As_4)CN]ClO_4$ (Figure 1) is nearly identical with that of the $P[CH_2CH_2CH_2As(CH_3)_2]_3$ complex (Figure 1), both in solution and in the solid state, the tetraarsine complex must also possess a trigonal-bipyramidal structure. The spectra of the other five-coordinate complexes, *i.e.*, $[\text{Ni(ligand)}X]ClO_4$ (X = Cl, Br, I, NO_2), are very similar. On the basis of the spectral comparison and from the similarity of magnetic, conductivity, and chemical properties, it is con-

(12) G. Dyer and L. M. Venanzi, *J. Chem. Soc.*, 2771 (1965).
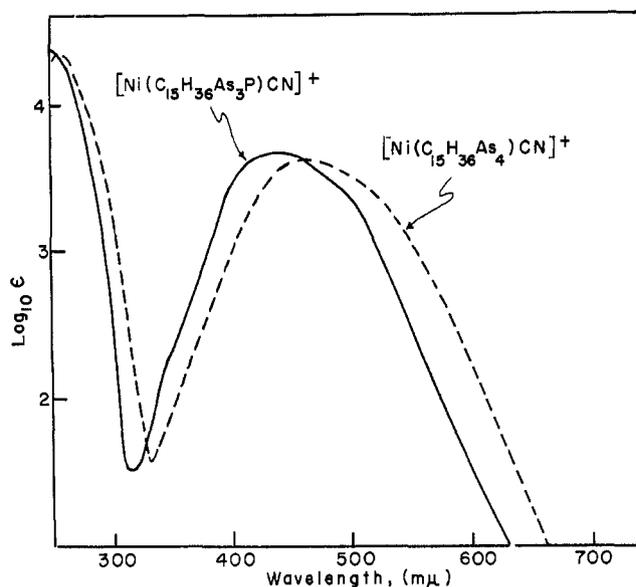
Figure 1.—Electronic absorption spectra of trigonal-bipyramidal $[\text{Ni}(C_{15}H_{36}As_3P)CN]^+$ and $[\text{Ni}(C_{15}H_{36}As_4)CN]^+$ in dichloromethane solutions.

cluded that both ligands form trigonal-bipyramidal cations of general formula $[\text{Ni(ligand)}X]^+$.

The broad, asymmetric electronic absorption band in the visible region can be resolved into two components by Gaussian analysis. Figure 2 illustrates the resolved curves for $[\text{Ni}(C_{15}H_{36}As_4)Cl]ClO_4$ and $[\text{Ni}(C_{15}H_{36}As_3P)Cl]ClO_4$. The higher energy band is considerably more intense in each case. The resolved spectra (Table I) clearly show that both of these bands and also the one at $\sim$21,000 cm^{-1} move to higher energy in the
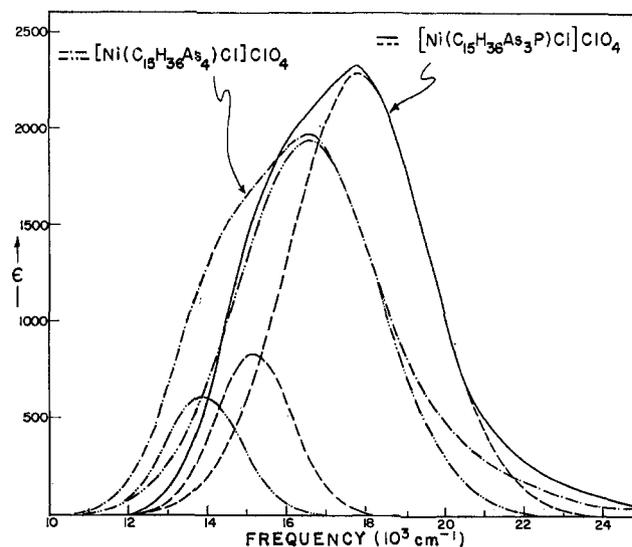
Figure 2.—Peaks which result from Gaussian analysis of the broad, asymmetric absorption bands of $[\text{Ni}(C_{15}H_{36}As_3P)Cl]ClO_4$ and $[\text{Ni}(C_{15}H_{36}As_4)Cl]ClO_4$. Spectra were obtained on dichloromethane solutions.

order: I < Br < Cl < NCS < NO_2 << CN. This series is expected on the basis of the spectrochemical series of ligands observed in four- and six-coordinate

TABLE I

Complex	Obsd spectrum, E_{max}, cm^{-1} (ϵ)	Gaussian analysis,[a] E_{max}, cm^{-1} (ϵ)	Half-band width, cm^{-1}
[Ni(C$_{15}$H$_{36}$As$_3$P)CN]ClO$_4$	22,880 (4540)	20,250 (605)	1100
		22,950 (4540)	2300
		28,600 (140)	
	40,160 (24,140)		
[Ni(C$_{15}$H$_{36}$As$_4$)CN]ClO$_4$	21,740 (3803)	19,300 (1005)	1200
		21,700 (3760)	2160
		26,550 (130)	
	38,460 (21,290)		
[Ni(C$_{15}$H$_{36}$As$_3$P)Cl]ClO$_4$	17,790 (2330)	15,170 (840)	1150
		17,840 (2285)	2050
		22,340 (162)	
	31,250 sh[b]	30,400 (755)	
[Ni(C$_{15}$H$_{36}$As$_4$)Cl]ClO$_4$	16,560 (1975)	13,920 (610)	1110
		16,550 (1940)	2090
		20,700 (203)	
	30,000 sh[b]		
	35,590 (13,460)		
[Ni(C$_{15}$H$_{36}$As$_3$P)Br]ClO$_4$	17,210 (2140)	14,750 (880)	1170
		17,350 (2115)	1930
		21,500 (203)	
	30,300 sh[b]		
	37,450 (17,600)		
[Ni(C$_{15}$H$_{36}$As$_4$)Br]ClO$_4$	16,050 (1847)	13,650 (690)	1165
		16,230 (1800)	2000
		20,500 (185)	
	28,490 sh[b]		
	33,900 (13,460)		
	36,100 (14,080)		
[Ni(C$_{15}$H$_{36}$As$_3$P)I]ClO$_4$	16,670 (1760)	14,170 (676)	1220
		16,740 (1736)	1965
		21,250 (306)	
	26,450 (2780)	26,400 (2780)	1750
	32,360 (12,400)		
	36,760 (14,500)		
[Ni(C$_{15}$H$_{36}$As$_4$)I]ClO$_4$	15,670 (1560)	13,150 (590)	1240
		15,700 (1520)	1970
		19,900 (280)	
	25,570 (3100)	25,030 (2490)	2580
	31,250 (13,250)		
	36,760 (12,000)		

[a] Gaussian analysis was performed on the low-energy, broad, asymmetric absorption band. Three bands were usually evident in the analyzed spectrum, whereas only one maximum was observed in the unresolved curve over the corresponding energy range. [b] sh = a definite shoulder on a more intense absorption.

nickel complexes.[13] Since the field created by the tetradentate ligand should be effectively constant within a given series of complexes, the shift of the spectral bands to higher energy must reflect the increasing ligand field exerted by the fifth ligand.

By comparing the energies of the bands for corresponding P[CH$_2$CH$_2$CH$_2$As(CH$_3$)$_2$]$_3$ and As[CH$_2$CH$_2$-CH$_2$As(CH$_3$)$_2$]$_3$ complexes (Table I), one may conclude that an apical phosphorus atom creates a stronger ligand field than an apical arsenic atom.

For a given monodentate ligand X, analogous five-coordinate complexes of the two ligands have four of the five donor atoms identical, and one might logically expect the band energies of the [Ni(C$_{15}$H$_{36}$As$_3$P)X]$^+$ complexes to be larger than those of [Ni(C$_{15}$H$_{36}$As$_4$)X]$^+$ by a constant value.[9b] This, in fact, is not observed.

The energies of both ν_1 and ν_2 bands show that the differences between the [Ni(C$_{15}$H$_{36}$As$_3$P)X]$^+$ and the [Ni(C$_{15}$H$_{36}$As$_4$)X]$^+$ complexes are smallest for iodide and greatest for chloride (Table II). Thus, the effect of reducing the ligand field difference between P[CH$_2$-CH$_2$CH$_2$As(CH$_3$)$_2$]$_3$ and As[CH$_2$CH$_2$CH$_2$As(CH$_3$)$_2$]$_3$ is the same as the nephelauxetic series,[14] *i.e.*, I > Br > Cl.

The nephelauxetic effect[14] results from the expanded radial function of the bonding molecular orbital because the effective nuclear charge (Z') of the metal ion is decreased by delocalization of the ligand electrons onto the central ion. The donor atoms of both P[CH$_2$CH$_2$CH$_2$-As(CH$_3$)$_2$]$_3$ and As[CH$_2$CH$_2$CH$_2$As(CH$_3$)$_2$]$_3$ are ideal for extensive mixing of ligand and the central metal orbitals; the high intensities observed for the electronic transitions in these five-coordinate complexes reflect

(13) T. M. Dunn, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, pp 229–300.

(14) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Ltd., Oxford, 1962, pp 134–145.

D = P or As
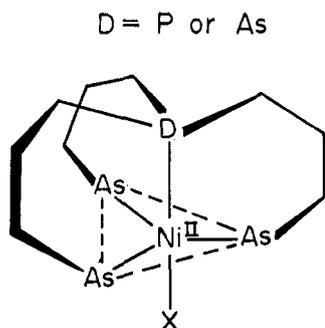
Figure 3.—The structural representation of the trigonal-bipyramidal (C_{3v} microsymmetry or C_3 symmetry over-all) [Ni(ligand)X]$^+$ cations, where ligand = P[CH$_2$CH$_2$CH$_2$As(CH$_3$)$_2$]$_3$ and As[CH$_2$CH$_2$CH$_2$As(CH$_3$)$_2$]$_3$.

TABLE II

THE SHIFT OF THE PEAK MAXIMA IN [Ni(LIGAND)X]$^+$ COMPLEXES
ON CHANGING THE LIGAND FROM As[CH$_2$CH$_2$CH$_2$As(CH$_3$)$_2$]$_3$ TO
P[CH$_2$CH$_2$CH$_2$As(CH$_3$)$_2$]$_3$

	E_{max}, cm^{-1}		
X	As[CH$_2$CH$_2$CH$_2$-As(CH$_3$)$_2$]$_3$	P[CH$_2$CH$_2$CH$_2$-As(CH$_3$)$_2$]$_3$	$\Delta\nu$, cm^{-1}
	ν_1 bands		
Cl	13,920	15,170	1250
Br	13,650	14,750	1100
I	13,150	14,170	1020
	ν_2 bands		
Cl	16,550	17,840	1290
Br	16,230	17,350	1120
I	15,700	16,740	1040

the extensive mixing of metal and ligand orbitals and the "allowedness" of the d → d transitions. Thus, the metal–ligand bonding must involve considerable covalent character.

We[9b] have presented spectral evidence that selenium is more easily polarized and involved in more covalent bonding than sulfur in analogous ligands. Arsenic and phosphorus donor atoms are thought to be even more strongly polarized than sulfur and selenium in nickel(II) complexes. In the trigonal-bipyramidal cations (Figure 3), the extent of mixing, *i.e.*, covalent bonding, between ligand X and the d_{z^2} orbitals of the metal will depend on the polarizability of both X and the apical atom (*i.e.*, As or P in this study) of the tetradentate ligand. The large, easily polarized iodide and bromide ions must compete with the apical arsenic atom in the As[CH$_2$CH$_2$CH$_2$As(CH$_3$)$_2$]$_3$ complexes, whereas they compete with the phosphorus atom in the P[CH$_2$CH$_2$CH$_2$As(CH$_3$)$_2$]$_3$ complexes. If the phosphorus atom is less polarizable (from nickel–donor interactions) than arsenic, the competing bromide and iodide ligands could become more polarized than in the corresponding tetraarsine complex, thereby producing a stronger apparent ligand field and the observed $\Delta\nu$ trend (Table II).