

It is of interest to compare the electronic spectra of the DPEA series of complexes with those of the structurally similar tridentate, $\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)_2$, studied by Ciampolini and Speroni⁴ to which five-coordinate structures have been attributed. The spectra of the two series of complexes are similar. However, the absorption bands in the spectra of the DPEA series occur at positions about 3000 cm^{-1} higher in energy. Assuming the same stereochemistry, this represents a very substantial increase in effective ligand field strength. There are two possible interpretations of this effect. Either there is greater steric hindrance (which is not apparent from an examination of molecular models) in the aliphatic triamine complex causing reduced metal-ligand interaction or there is a measure of metal-pyridine π overlap in the DPEA (and DPES) complexes. The latter explanation seems the more likely. Evidence for nickel-to-pyridine π bonding in (six-coordinate) nickel(II) complexes has been presented previously.^{12,13}

(13) S. M. Nelson and T. M. Shepherd, *Inorg. Chem.*, **4**, 813 (1965).

Finally, it is of interest to note that, in the aliphatic polyamine complexes studied by Ciampolini and co-workers,^{3,4} the chelate rings are five membered. In both ligands reported in the present work, the chelate rings have six member atoms. When the ring size is reduced to five as in chelates of di(2-pyridylmethyl)amine (DPMA), stable six-coordinate complex ions containing two ligand molecules are formed,¹⁴ e.g., $[\text{Ni}(\text{DPMA})_2]^{2+}$. Solutions containing this complex ion have spectra typical of nickel(II) complexes of O_h symmetry with $Dq = 1255\text{ cm}^{-1}$, a value only 10 cm^{-1} lower than that observed for the very stable tris(dipyridyl)nickel(II) cation.

Acknowledgments.—The authors are indebted to Miss Ida Woodward for guidance in the X-ray measurements and to Mr. W. J. Swindell and Mr. B. McKnight for microanalyses. Thanks are also due to the government of Northern Ireland for a research studentship to J. R. and to the Science Research Council for a grant to S. M. N. for apparatus.

(14) S. M. Nelson and J. Rodgers, Proceedings of the 9th International Symposium on Coordination Chemistry, St. Moritz, Switzerland, 1966.

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Five-Coordination. IV. Nickel(II) Complexes of Diphenyl(*o*-diphenylarsinophenyl)phosphine¹⁻³

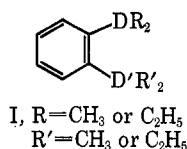
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Received November 28, 1966

Diphenyl(*o*-diphenylarsinophenyl)phosphine forms four-coordinate, diamagnetic $[\text{Ni}(\text{ligand})\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$) complexes, five-coordinate, diamagnetic $[\text{Ni}(\text{ligand})_2\text{X}]\text{ClO}_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_2, \text{NCS}, \text{NCSe}$) complexes, and the six-coordinate, paramagnetic $[\text{Ni}(\text{ligand})_2(\text{NCS})_2]$ complex. These compounds have been characterized by magnetic and conductivity measurements, electronic and infrared spectra, and elemental analyses. The electronic spectra of the five-coordinate complexes differ significantly from those of trigonal-bipyramidal nickel(II) complexes with ligands containing similar donor atoms and may be interpreted in terms of a square-pyramidal structure.

Introduction

Several *o*-phenylene compounds (I) in which D and D' are phosphorus, arsenic, or nitrogen or any com-



bination of them have been prepared and the properties of selected coordination compounds investigated.^{4,5}

For example, the ligand *o*-phenylenebisdimethylarsine ($\text{D} = \text{D}' = \text{As}$ and $\text{R} = \text{R}' = \text{CH}_3$) forms the tetragonal, six-coordinate complexes $[\text{M}(\text{diarsine})_2\text{I}_2]$ (where $\text{M} = \text{Ni}, \text{Pd}, \text{ and Pt}$) in the solid state,^{6,7} however, these compounds are uni-univalent electrolytes and five-coordinate in solution.⁸ This ligand also forms $[\text{Ni}(\text{diarsine})_3](\text{ClO}_4)_2$, which is thought to be the only regular octahedral, diamagnetic nickel(II) complex.⁹ In contrast to the diarsine ligand, only planar $[\text{Ni}(\text{diphos-}$

(1) The authors gratefully acknowledge the financial support of this research by the National Science Foundation (Grant No. GP-5729).

(2) Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966; Abstracts, No. H-64.

(3) Part III: G. Dyer and D. W. Meek, *Inorg. Chem.*, **6**, 149 (1967).

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(5) F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.*, 1269 (1955); E. R. H. Jones and F. G. Mann, *ibid.*, 4472 (1955); W. Cochran, F. A. Hart, and F. G. Mann, *ibid.*, 2816 (1957); F. A. Hart and F. G. Mann, *Chem. Ind. (London)*, 574 (1956); *J. Chem. Soc.*, 3939 (1957); F. G. Mann and H. R. Watson, *ibid.*, 3945, 3950 (1957).

(6) N. C. Stephenson and G. A. Jeffrey, *Proc. Chem. Soc.*, 173 (1963).

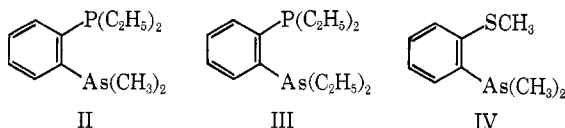
(7) N. C. Stephenson, *J. Inorg. Nucl. Chem.*, **24**, 791, 797 (1962).

(8) C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 4379 (1960).

(9) B. Bosnich, R. Bramley, R. S. Nyholm, and M. L. Tobe, *J. Am. Chem. Soc.*, **88**, 3926 (1966).

phine)₂]²⁺ complexes have been reported with the similar diphosphine, *o*-phenylenebisdiethylphosphine.¹⁰

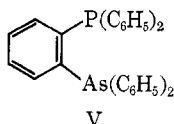
Palladium(II) and platinum(II) complexes of II and copper(I), silver (I), and gold(I) complexes of III were



investigated;⁵ however, no complexes of nickel were reported with either arsine-phosphine.

The substitution of one dimethylarsino group in *o*-phenylenebisdimethylarsine by one thiomethyl group markedly alters the properties of the nickel(II) complexes.¹¹ In contrast to the diarsine complexes mentioned above, the nickel(II) complexes of IV are paramagnetic and essentially nonelectrolytes in nitrobenzene.¹¹ Also, the palladium(II) complexes of ligand IV are four-coordinate nonelectrolytes in nitrobenzene, in contrast to the complexes of *o*-phenylenebisdimethylarsine which tend to have higher coordination numbers. Recently, tetrahedral [Ni(ligand)X₂] (where X is Cl, Br), planar [Ni(ligand)(NCS)₂] and [Ni(ligand)₂](ClO₄)₂, and octahedral [Ni(ligand)₂I₂] complexes have been isolated with β-(diphenylphosphino)ethyl-2-pyridine.¹²

In view of the different coordination numbers and structures observed in nickel(II) complexes, it was of interest to determine the types of compounds that would be formed with the bidentate arsine-phosphine, diphenyl(*o*-diphenylarsinophenyl)phosphine, V. This



paper reports the preparation and characterization of the four-, five-, and six-coordinate nickel(II) complexes with this ligand.

Experimental Section

Reagents.—Reagent grade 1-butanol was refluxed over anhydrous barium oxide and then distilled (bp 116.5°) from magnesium butoxide. Technical grade dichloromethane was refluxed over calcium chloride and then distilled (bp 40.0°) from fresh calcium chloride. Nitromethane was washed with 5% aqueous sodium bicarbonate and then 5% aqueous sulfuric acid, dried over calcium chloride, and fractionated (bp 101°). Acetonitrile was stirred over barium oxide, filtered, and distilled (bp 81.0°) from a small amount of P₂O₁₀. Absolute ethanol, reagent grade acetone, reagent grade chlorobenzene, and anhydrous diethyl ether were used without further purification.

Preparation of the Complexes.—Diphenyl(*o*-diphenylarsinophenyl)phosphine, C₃₀H₂₄AsP, was prepared by Dr. G. Dyer according to the procedure of Nicpon and Meek.¹³ Unless stated otherwise, all preparations were performed under a dry nitrogen atmosphere to prevent possible oxidation of the ligand before it was coordinated.¹⁴ All compounds were collected on a sintered-glass funnel, recrystallized from a 1:1 mixture of dichlorometh-

ane and 1-butanol, washed with 1-butanol and then diethyl ether, dried in a stream of dry nitrogen, and then dried further *in vacuo* at room temperature. Yields of recrystallized products are given in Table I.

[Ni(C₃₀H₂₄AsP)₂X]ClO₄ (where X = Cl, Br, I, NO₂, NCS, and NCS₂).—Solutions of "NiXClO₄" were prepared *in situ* by treating 1-butanol solutions of nickel(II) nitrate hexahydrate (0.5 mmole) with 1 mmole of the sodium salt of the desired univalent anion, filtering the mixture to remove sodium nitrate, and then adding 0.5 mmole of nickel(II) perchlorate hexahydrate to the filtrate. The resulting solution was heated to reflux and 0.98 g (2 mmoles) of diphenyl(*o*-diphenylarsinophenyl)phosphine, C₃₀H₂₄AsP, dissolved in a hot mixture of 1-butanol (10 ml) and chlorobenzene (10 ml) was added. The resulting deep blue solutions were refluxed for an additional 15 min and then allowed to cool to room temperature to deposit blue crystals.

[Ni(C₃₀H₂₄AsP)₂](where X = NCS, Cl, Br, and I).—To the appropriate hydrated nickel(II) salt (1 mmole) was added 0.49 g (1 mmole) of ligand in a mixed solvent containing 10 ml of 1-butanol and 10 ml of chlorobenzene. The deep blue solution was refluxed for 15 min; on cooling the solution to room temperature, red crystals separated. The halide complexes were recrystallized as in the above general preparation but [Ni(C₃₀H₂₄AsP)(NCS)₂] was recrystallized from dichloromethane and isopropyl ether.

[Ni(C₃₀H₂₄AsP)₂](ClO₄)₂.—To 0.98 g (2 mmoles) of ligand was added 1 mmole of nickel(II) perchlorate hexahydrate in a hot 2:1 mixture of chlorobenzene and 1-butanol (30 ml).

[Ni(C₃₀H₂₄AsP)₂(NCS)₂].—A warm solution of nickel(II) thiocyanate (0.5 mmole) in 20 ml of ethanol was added to 0.49 g (1 mmole) of ligand in dichloromethane (20 ml). The solution immediately turned deep purple and then brown. When the reaction mixture had cooled to room temperature, a yellow-green solid separated.

Spectra.—Infrared spectra were obtained with a Perkin-Elmer Model 337 grating spectrophotometer and a high-resolution Beckman IR-9 spectrophotometer¹⁵ using Nujol mulls between crystalline potassium bromide plates. Visible and ultraviolet spectra of the complexes in solution were taken with a Cary Model 14 recording spectrophotometer using a set of matched 1-cm quartz cells. The spectra of the complexes in the solid state were obtained with the same instrument by using Nujol mulls supported on filter paper.¹⁶

Conductance Measurements.—The measurements were performed at 23° with an Industrial Instruments Model RC-16B conductivity bridge on approximately 10⁻³ M nitromethane solutions.

Magnetic Measurements.—Magnetic moments were determined using a Faraday magnetic susceptibility balance equipped with a Cahn Gram electrobalance and a Varian 4-in. electromagnet fitted with specially shaped pole pieces. Samples were used in 20–25-mg quantities and the values reported are the averages of at least two determinations. The magnetic measurements were determined at two different field strengths to check for ferromagnetic impurities. The observed susceptibility values were corrected for the diamagnetism of the ligands.¹⁷

Results and Discussion

Diphenyl(*o*-diphenylarsinophenyl)phosphine, V, forms deep red, diamagnetic, nonelectrolyte complexes of the composition [Ni(C₃₀H₂₄AsP)₂X₂] when mixed with nickel(II) halides on a 1:1 stoichiometric ratio (Table

(14) Although precautions were taken throughout this study against ligand oxidation, subsequent preparations without using the nitrogen atmosphere gave equally good yields.

(15) The authors are grateful to the National Science Foundation for the instrument grant with which the Beckman IR spectrophotometer and components for the magnetic balance were purchased.

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TABLE I
 ANALYTICAL DATA AND PHYSICAL PROPERTIES OF DIPHENYL(*o*-DIPHENYLARSINOPHENYL)PHOSPHINE-NICKEL(II) COMPLEXES

Compound	Color	% yield	M, cm^3/mole ^a	10 ³ χ'_M ^b	Analyses, %									
					C		H		P		Halogen		N	
					Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
[Ni(C ₃₀ H ₂₄ AsP) ₂ Cl]ClO ₄	Purple	95	84.1	351	61.35	61.33	4.12	4.06	5.27	5.24	6.03	6.22		
[Ni(C ₃₀ H ₂₄ AsP) ₂ Br]ClO ₄ · 0.5CH ₂ Cl ₂	Purple	56	83.6	299	57.61	57.74 57.42	3.92	4.06 4.04	4.91	4.85	(8.43) 5.62 Cl 6.34 Br	(8.46) ^c 5.63 Cl 6.34 Br		
[Ni(C ₃₀ H ₂₄ AsP) ₂ I]ClO ₄	Deep blue	88	91.0	460	56.92	57.15	3.83	3.96	4.89	4.87	2.80 Cl	3.12 Cl		
[Ni(C ₃₀ H ₂₄ AsP) ₂ (NO ₂)]ClO ₄	Purple	34	96.7	110	60.81	60.52	4.08	4.16			2.99	3.21	1.18	1.09
[Ni(C ₃₀ H ₂₄ AsP) ₂ (NCS)]ClO ₄	Purple	80	80.7	000	61.20	61.44	4.04	4.01	5.17	5.22	2.96	2.91	1.17	1.22
[Ni(C ₃₀ H ₂₄ AsP) ₂ (NCS) ₂]ClO ₄	Purple	58	90.2	216	59.00	60.99	3.90	4.22	4.99	5.05	2.85	2.79	1.13	1.17
[Ni(C ₃₀ H ₂₄ AsP) ₂](ClO ₄) ₂	Yellow	86	175	104	58.18	57.89	3.91	3.97	5.00	4.98	5.72	5.75		
[Ni(C ₃₀ H ₂₄ AsP)(NCS) ₂] ^d	Red-brown	40	13.4	103	57.77	57.09 57.8	3.64	3.68 3.50					4.21	4.17 4.15
[Ni(C ₃₀ H ₂₄ AsP)Cl ₂]	Red	86	8.58	178	58.11	57.86	3.90	3.71	5.00	4.80	11.43	11.63		
[Ni(C ₃₀ H ₂₄ AsP)Br ₂]	Brick red	90	20.7	79	50.82	51.09	3.41	3.31	4.37	4.46	22.54	22.15		
[Ni(C ₃₀ H ₂₄ AsP)I ₂]	Violet	80	23.6	158	44.88	44.92	3.01	3.11	3.85	3.87	31.61	31.61		
[Ni(C ₃₀ H ₂₄ AsP) ₂ (NCS) ₂] ^d	Yellow-green	78	62.4 ^e	4153	64.43	64.67 64.0	4.19	4.29 4.13	5.36	5.60			2.42	2.12 2.27

^a Molar conductance values obtained on approximately 10^{-3} M solutions in nitromethane. ^b χ'_M , corrected molar susceptibility values. All of the compounds, except [Ni(C₃₀H₂₄AsP)₂(NCS)₂], are effectively diamagnetic with a paramagnetic contribution from the temperature-independent paramagnetism. μ_{eff} calculated for [Ni(C₃₀H₂₄AsP)₂(NCS)₂] is 3.18 ± 0.04 BM, fully consistent with an octahedral nickel(II) complex, as proposed in the discussion. ^c Total halide calculated and reported as chloride. The dichloromethane was not removed when pumped at 56° (10^{-2} mm) for 24 hr. ^d Analytical data from both Galbraith, Knoxville, Tenn., and Bernhardt, Mulheim, Germany. ^e The nitromethane solution used for the conductance reading was purple, indicating that the complex dissociated extensively to the five-coordinate [Ni(C₃₀H₂₄AsP)₂NCS]⁺ cation.

I). The integrated intensity¹⁸ of the C≡N infrared frequency ($6.96 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}$) of [Ni(C₃₀H₂₄AsP)(NCS)₂] in dichloromethane solution clearly indicates that the thiocyanate groups are bonded through nitrogen and are not bridging. These complexes exhibit one symmetrical electronic absorption band in the visible region (Figure 1), consistent with a four-coordinate, planar structure. Since the positions of the electronic absorption maxima are the same in the solid compounds as in solution, no polymerization and increase in coordination number occur in the solid state.

When mixed with solutions of "NiXClO₄," ligand V also forms the five-coordinate complexes [Ni(ligand)₂X]ClO₄, which are diamagnetic and uni-univalent electrolytes in nitromethane. This behavior is similar to that of *o*-phenylenebisdimethylarsine; however, one important difference should be noted. Whereas the *o*-phenylenebisdimethylarsine complexes of nickel and palladium are five-coordinate in solution, the iodide complexes become tetragonal, six-coordinate compounds in the solid state.⁶ Since the electronic spectra of the [Ni(C₃₀H₂₄AsP)₂X]ClO₄ complexes (where X = Cl, Br, I) are identical both in dichloromethane solution and the solid state (Figure 2), these compounds maintain discrete five-coordinate cations in both states. The solution spectrum of the solvated example, [Ni(C₃₀H₂₄AsP)₂Br]ClO₄ · 0.5CH₂Cl₂, is identical with that obtained in other noncoordinating solvents and quite similar to the spectra of the unsolvated [Ni(C₃₀H₂₄AsP)₂X]ClO₄ (X = Cl, I) complexes. Therefore, the dichloromethane molecule is trapped in the crystal lattice and the structure of the [Ni(C₃₀H₂₄AsP)₂Br]⁺ cation must be the same in solution as in the solid state (Figure 2). Also, the infrared spectra show no splitting of the ~ 1100 - and ~ 625 -cm⁻¹ perchlorate bands,¹⁹

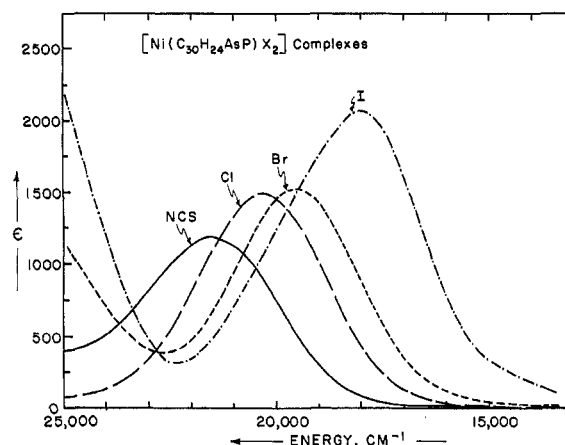


Figure 1.—Electronic absorption spectra of the [Ni(C₃₀H₂₄AsP)₂X₂] (X = NCS, Cl, Br, I) complexes dissolved in dichloromethane.

thereby eliminating the possibility of perchlorate coordination.

The solid-state electronic spectra of the five-coordinate thiocyanate and selenocyanate compounds differ somewhat from those obtained on dichloromethane solutions of the same compounds. In dichloromethane solutions, both the integrated intensity¹⁸ and the position of the C≡N infrared band in the thiocyanate ($5.14 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}$; 2103 cm^{-1}) and selenocyanate (2108 cm^{-1}) indicate that these groups are N bonded.²⁰ No infrared peak around 2140 – 2150 cm^{-1} for a bridging thiocyanate group was discernible. Thus, the splitting in the electronic absorption band between $18,000$ and $19,000 \text{ cm}^{-1}$ in the solid-state electronic spectra of the thiocyanate and selenocyanate compounds may arise from structural distortions caused by packing in the crystalline lattice.

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(19) S. F. Pavkovic and D. W. Meek, *ibid.*, **4**, 1091 (1965), and references therein.

(20) The frequencies assigned to the C–S and C–Se stretching vibrations in the thiocyanate and selenocyanate complexes occur at 850 and 590 cm^{-1} , respectively.

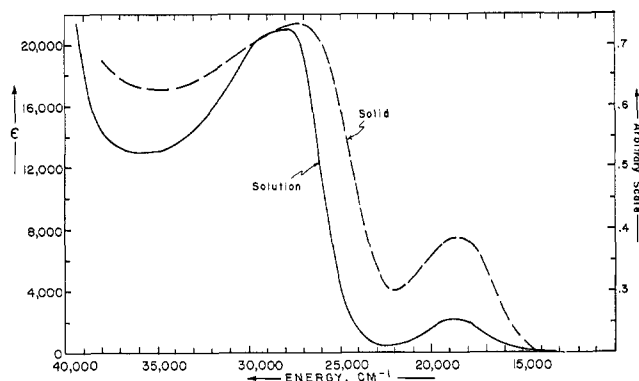


Figure 2.—Electronic absorption spectra of $[\text{Ni}(\text{C}_{30}\text{H}_{24}\text{AsP})_2\text{Br}]\text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2$ dissolved in dichloromethane (—) and the solid compound suspended in a thin Nujol mull (---). An arbitrary scale is used for the solid-state spectrum.

A comparison of the visible portions of the electronic spectra of $[\text{Ni}(\text{C}_{30}\text{H}_{24}\text{AsP})_2](\text{ClO}_4)_2$, $[\text{Ni}(\text{C}_{30}\text{H}_{24}\text{AsP})_2\text{Br}]\text{ClO}_4$, and $[\text{Ni}(\text{TAP})\text{Br}]\text{ClO}_4$ (where TAP is $\text{P}[\text{CH}_2\text{CH}_2\text{CH}_2\text{As}(\text{CH}_3)_2]_3$) (Figure 3) illustrates that both diphenyl(*o*-diphenylarsinophenyl)phosphine complexes possess absorption bands at considerably higher energy than the trigonal-bipyramidal $[\text{Ni}(\text{TAP})\text{Br}]\text{ClO}_4$ complex. When compared with the spectrum of the planar $[\text{Ni}(\text{C}_{30}\text{H}_{24}\text{AsP})_2](\text{ClO}_4)_2$ complex, the spectrum of the five-coordinate complex $[\text{Ni}(\text{C}_{30}\text{H}_{24}\text{AsP})_2\text{Br}]\text{ClO}_4$ is considerably more intense and shifted to lower energy (Figure 3).

The absorption band at $\sim 22,000\text{ cm}^{-1}$ in the planar complexes corresponds to the transition which has the d -orbital character $d_{xy} \rightarrow d_{x^2-y^2}$. On introducing an anion into the complex along the z axis to form a square-pyramidal compound, the relative energies of the d_{xy} and $d_{x^2-y^2}$ orbitals (both in the xy plane) will be affected to exactly the same extent. Therefore, since the ligand field band maximum of each of the five-coordinate complexes occurs at lower energy than in the corresponding planar complex, this band must involve a transition from another orbital to the $d_{x^2-y^2}$ orbital. The metal orbital most drastically affected by addition of a ligand along the z axis is clearly the d_{z^2} orbital.

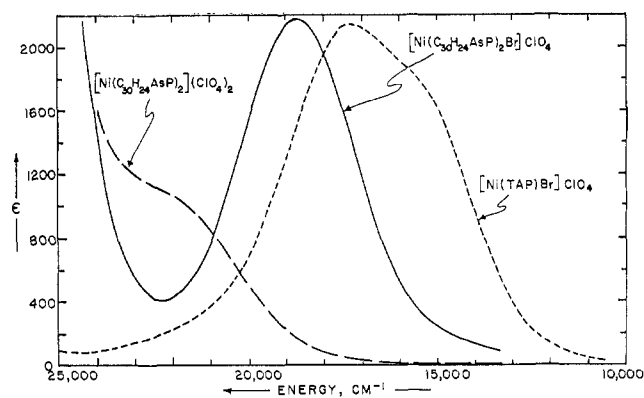


Figure 3.—Electronic absorption spectra of the planar $[\text{Ni}(\text{C}_{30}\text{H}_{24}\text{AsP})_2](\text{ClO}_4)_2$ (—), the five-coordinate $[\text{Ni}(\text{C}_{30}\text{H}_{24}\text{AsP})_2\text{Br}]^+\text{ClO}_4$ cation (---), and the trigonal-bipyramidal $[\text{Ni}(\text{TAP})\text{Br}]\text{ClO}_4$ (TAP = $\text{P}[\text{CH}_2\text{CH}_2\text{CH}_2\text{As}(\text{CH}_3)_2]_3$) (-.-.-) dissolved in dichloromethane.

Since the spectra are not typical of diamagnetic trigonal-bipyramidal $\text{Ni}(\text{II})$ complexes and are sensitive to the anion that is added in the fifth position, the $[\text{Ni}(\text{C}_{30}\text{H}_{24}\text{AsP})_2\text{X}]^+$ cations probably possess a square-pyramidal structure. Unfortunately, there are no structural data for a regular, square-pyramidal d^8 complex, whose electronic spectrum could be compared. Until the X-ray study of one of these complexes is finished, the structural assignment must be considered tentative.

The yellow-green six-coordinate compound $[\text{Ni}(\text{C}_{30}\text{H}_{24}\text{AsP})_2(\text{NCS})_2]$ exhibits properties of a tetragonal complex. The solid-state electronic spectrum contains three principal absorption bands, the two at lower energies being split into two bands, indicative of a tetragonal distortion from octahedral symmetry. Also, the infrared spectrum contains very sharp, strong absorptions at 825 and 2080 cm^{-1} in the $\text{C}-\text{S}$ and $\text{C}\equiv\text{N}$ regions, respectively, indicating only N-bonded thiocyanate groups.¹⁸ The compound converts to the purple five-coordinate $[\text{Ni}(\text{C}_{30}\text{H}_{24}\text{AsP})_2\text{NCS}]^+$ cation in all solvents in which it will dissolve.