

cm^{-1} .¹⁵ Assignment of the C-S stretching vibration in sulfoxides with an aryl substituent is more difficult.

According to Bellamy²⁴ the C-S stretching vibration of aryl sulfoxides occurs in the 702–607- cm^{-1} region. A very weak band near 670 cm^{-1} is assigned to the C-S stretching vibration in diphenyl sulfoxide and phenyl methyl sulfoxide. In their complexes the assignment is even more difficult because of the very intense bands of the C-H out-of-plane deformation modes of vibration which occur near 750 and 700 cm^{-1} . A weak band observed near 720 cm^{-1} in all diphenyl sulfoxide and phenyl methyl sulfoxide complexes is tentatively assigned to the C-S stretching vibration. A weak absorption near 685 cm^{-1} might be the C-S stretching vibration in di-*n*-propyl sulfoxide and di-*n*-butyl sulfoxide, but that vibration is not observed in any of their complexes.

Selbin, *et al.*,⁶ have proposed the following stability series for dimethyl sulfoxide metal(II) perchlorate complexes: copper(II) > lead(II) > iron(II) > cobalt(II) > manganese(II) > nickel(II). Their order is based on the assumption that the magnitude of the decrease in the S-O stretching vibrational frequency ($\Delta\nu_{\text{SO}}$) of the ligand is a measure of the strength of the metal-oxygen bond. Because of the coupling between ν_{SO} and $\nu_{\text{CH}_3 \text{ rock}}$ in the complexes of dimethyl sulfoxide and phenyl methyl sulfoxide, a stability order based on $\Delta\nu_{\text{SO}}$ is meaningless in these two series of

complexes. No coupling of the S-O stretching frequency has been demonstrated in di-*n*-propyl sulfoxide, diphenyl sulfoxide, and di-*n*-butyl sulfoxide. An average metal ion stability series based on $\Delta\nu_{\text{SO}}$ of these three ligands is: nickel(II) \sim cobalt(II) > iron(II) \sim manganese(II) \geq zinc(II). This order is in basic agreement with the Irving-Williams series. If the average $\Delta\nu_{\text{SO}}$ for all metal ions is considered, the average stability order for the ligands is: (*n*-C₄H₉)₂SO > (C₆H₅)₂SO > (*n*-C₃H₇)₂SO. This order is not easily rationalized. It does not agree with the order expected from a consideration of inductive effects alone: (*n*-C₄H₉)₂SO > (*n*-C₃H₇)₂SO > (C₆H₅)₂SO; nor does it agree with a stability order expected from consideration of steric effects: (C₆H₅)₂SO > (*n*-C₃H₇)₂SO > (*n*-C₄H₉)₂SO. A combination of inductive and steric effects is probably responsible for the observed order. The use of $\Delta\nu_{\text{SO}}$ for determining stability series in hexakis-sulfoxide complexes is at best a gross approximation.

Acknowledgment.—We are grateful to acknowledge the assistance of Miss Joan Rogalski, NSF Summer Undergraduate Student in 1964, who first synthesized many of the complexes. We thank Dr. James D. Morrison for helpful discussions. This research was supported in part by the Central University Research Foundation.

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Five-Coordination. VII. Diamagnetic Nickel(II) Complexes with Polydentate Phosphines Containing Sulfur and Selenium Donor Atoms^{1,2}

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The tridentate ligand bis(*o*-methylthiophenyl)phenylphosphine (DSP, I) forms three types of five-coordinate nickel(II) complexes illustrated by the formulas [Ni(DSP)X₂], [Ni(DSP)₂](ClO₄)₂, and [Ni(DSP)(bidentate)](ClO₄)₂. The bidentate ligand diphenyl(*o*-methylthiophenyl)phosphine (SP, II) gives four-, five-, and six-coordinate nickel(II) complexes, exemplified by the formulas [Ni(SP)Cl₂], [Ni(SP)₂Br]ClO₄, and [Ni(SP)₂Cl₂], respectively. The analogous selenium-phosphine ligand diphenyl(*o*-methylselenophenyl)phosphine (SeP, III) functions similarly. The properties of the SP and SeP complexes, especially the electronic absorption spectra, are compared with those of the phosphorus-arsenic ligand, diphenyl(*o*-diphenylarsinophenyl)phosphine. The spectrochemical series for the different donor groups is established as R₂Se < R₂S < R₃As < R₃P, whereas the absorption band intensities, which may be related to the covalent character of the nickel-ligand bond, produce a different order: S < Se < As.

Introduction

Five-coordinate nickel(II) complexes containing polydentate ligands have become quite numerous during the past 3 years. For example, all of the "tripod-like" tetradentate ligands P(*o*-C₆H₄P(C₆H₅)₂)₃,⁴ As(*o*-C₆H₄-

As(C₆H₅)₂)₃,⁵⁻⁶ P(*o*-C₆H₄SCH₃)₃,⁷ P(*o*-C₆H₄SeCH₃)₃,⁸ P-(CH₂CH₂CH₂As(CH₃)₂)₃,⁹ As(CH₂CH₂CH₂As(CH₃)₂)₃,¹⁰ and N(CH₂CH₂N(CH₃)₂)₃¹¹ form trigonal-bipyramidal nickel(II) complexes. With As(*o*-C₆H₄As(C₆H₅)₂)₃ and

(1) Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstract No. H-84.

(2) Part VI: G. Dyer and D. W. Meek, *J. Am. Chem. Soc.*, **89**, 3983 (1967).

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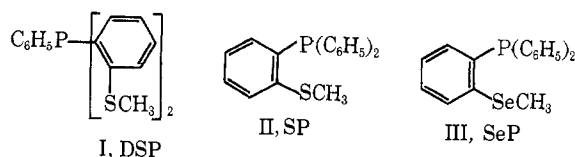
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$P(o-C_6H_4P(C_6H_5)_2)_3$, it was argued that the trigonal structure of the ligand (because of the steric requirements of the bulky *ortho* donor groups) imposed its structure on the metal ion in the resulting complex.⁶ The terminal dimethylamino groups of $N(CH_2CH_2N(CH_3)_2)_3$ are sufficiently bulky to prevent coordination of a second anion and attainment of six-coordination.¹¹ The fact that diamagnetic five-coordinate nickel(II) complexes were isolated with each of the flexible, aliphatic ligands $P(CH_2CH_2CH_2As(CH_3)_2)_3$ and $As(CH_2CH_2CH_2As(CH_3)_2)_3$ suggests that electronic considerations are perhaps more important than steric factors in forming five-coordinate nickel(II) complexes, especially diamagnetic ones^{9,10}

However, it was impossible to dismiss the possibility that the "tripod-like" nature of the above ligands contributed to the trigonal-bipyramidal structures of the resulting complexes. Because tridentate and bidentate ligands have less stringent steric requirements than tetradentate ligands derived from a pyramidal central atom, it was of interest to determine if such ligands would also form five-coordinate nickel(II) complexes. In addition, by properly choosing the ligands, one can determine whether the same ligand field strength and spectral intensity trends are produced in planar and square-pyramidal structures as were observed in the trigonal-bipyramidal complexes.^{7,8}

This paper reports the nickel(II) complexes obtained with the new polydentate phosphines $C_6H_5P(o-C_6H_4SCH_3)_2$ (I, DSP), $(C_6H_5)_2P(o-C_6H_4SCH_3)$ (II, SP) and $(C_6H_5)_2P(o-C_6H_4SeCH_3)$ (III, SeP).



Experimental Section

Synthesis of Bis(*o*-methylthiophenyl)phenylphosphine.—Liquid *o*-mercaptoaniline was treated with sodium and iodomethane in ethanol to yield 87% *o*-aminothioanisole.¹² This compound was subsequently converted to *o*-bromothioanisole.¹³ A solution of *o*-bromothioanisole (77 g, 0.39 mole) in 50 ml of ether was treated with the stoichiometric amount (0.39 mole) of *n*-butyllithium in hexane in 0°. This was followed by the dropwise addition of 34 g (0.19 mole) of dichlorophenylphosphine dissolved in 100 ml of ether. After stirring for several hours, the reaction mixture was hydrolyzed with 0.2 *M* hydrochloric acid. A white solid was collected, washed with ethanol and ether, and dried *in vacuo* (yield 60 g, 87%). The compound (mp 115–116°) was recrystallized from 1-butanol.

Anal. Calcd for $C_{20}H_{19}PS_2$: C, 67.79; H, 5.36; P, 8.75; S, 18.07. Found: C, 67.93; H, 5.51; P, 8.53; S, 18.00.

Other Ligands.—Preparations of the other ligands used in this study have been described previously.^{2,14,15}

Preparation of the DSP Complexes.—All nickel(II) DSP complexes were prepared by dissolving 0.35 g (0.001 mole) of the ligand in 15 ml of boiling acetone. In those cases where an additional neutral ligand was used, equimolar amounts of DSP and the other ligand were dissolved in boiling acetone. To this warm

solution was added dropwise an acetone or ethanol solution containing the stoichiometric amount of the appropriate nickel(II) salt. The nickel(II) complexes crystallized as the solutions were stirred and cooled. The solid products were collected on a suction filter, washed with ether, and dried by a stream of dry air, followed by drying *in vacuo*. The compounds were recrystallized from dichloromethane whenever soluble.

Preparation of the SP and SeP Complexes. $[Ni(SeP)_2Br]ClO_4$.—Diphenyl(*o*-methylselenophenyl)phosphine (0.355 g, 1 mmole) dissolved in dichloromethane (5 ml) was treated with an excess of nickel bromide and nickel perchlorate (0.5 mmole of each) in hot absolute ethanol (20 ml). The volume of the solution was reduced slightly and intensely purple crystals separated; they were recrystallized by dissolving in dichloromethane (15 ml), adding ethanol (30 ml), and boiling off the dichloromethane. The resulting crystals were collected immediately and washed with ethanol (yield 0.22 g, 46.5%).

$[Ni(SP)_2Br]ClO_4$.—This compound was prepared as above using SP ligand (0.3 g, 1 mmole) instead of SeP, except that it was necessary to induce crystallization initially (at 73°) with a seed crystal of the above $[Ni(SeP)_2Br]ClO_4$ complex. For recrystallization, a few crystals of $[Ni(SP)_2Br]ClO_4$ were saved for seeding purposes, and the remainder was dissolved in dichloromethane (15 ml) and ethanol (30 ml). The solution was filtered and concentrated by distillation until the boiling point reached 72°, then the seed crystals were added and the mixture was stirred at 72° for 5 min. On cooling, 0.34 g (78%) of purple crystals was collected.

$[Ni(SP)_2Cl_2]$.—Diphenyl(*o*-methylthiophenyl)phosphine (1.5 g, 5 mmoles) dissolved in warm dichloromethane (25 ml) was treated with a solution of nickel chloride (5 mmoles) and lithium chloride (1.5 g) in hot ethanol (125 ml). The intensely purple solution was then concentrated at its boiling point to 75 ml, removed from the hot plate, and stirred until crystallization commenced in the hot solution. (The free ligand will crystallize preferentially below 50° unless crystallization of the complex has begun.) When the solution had cooled to room temperature, the complex (1.5 g, 80% yield) was collected and recrystallized by dissolving it in 75 ml of dichloromethane, adding 100 ml of warm ethanol, filtering the purple solution, and concentrating it to 75 ml. The pale green compound, which crystallized from the purple solution, was collected and dried *in vacuo*.

$[Ni(SP)_2Cl_2]$.—The $[Ni(SP)_2Cl_2]$ complex (1 g) was dissolved in 50 ml of dichloromethane and treated with 75 ml of petroleum ether (bp 65–110°) while stirring. The solution was filtered and concentrated to 75 ml, and the purple complex, which had separated, was collected immediately (yield 0.55 g, 93%). It was recrystallized from dichloromethane (25 ml) and petroleum ether (40 ml).

$[Ni(SeP)_2Cl_2]$.—This compound was prepared in the same manner as the above $[Ni(SP)_2Cl_2]$ complex, except that it was recrystallized by dissolving the green powder in dichloromethane (40 ml) to give a purple solution, adding 50 ml of warm petroleum ether (bp 65–110°), and concentrating the solution to 60 ml while stirring with a glass rod. Green crystals (70% yield) separated on cooling.

Characterization Measurements.—The conductance data and infrared and electronic absorption spectra were obtained as described previously.^{7–9}

Analyses.—Phosphorus and arsenic analyses were determined colorimetrically.¹⁶ Carbon, hydrogen, sulfur, and halogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Magnetism.—The magnetic susceptibility values were determined at room temperature on a Faraday magnetic balance constructed recently in this laboratory.¹⁷ The values were corrected with Pascal's constants for the diamagnetism of the ligands.¹⁸

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Results and Discussion

Bis(*o*-methylthiophenyl)phenylphosphine, DSP, forms molecular five-coordinate, diamagnetic complexes with nickel(II) halides. The electronic absorption spectrum of each $[\text{Ni}(\text{DSP})\text{X}_2]$ complex is characterized by an intense, symmetric band in which the energy of the maximum produces the series $\text{I} < \text{Br} < \text{Cl}$ (Figure 1). This trend is consistent with the ligand field strengths of the halide ions and indicates that they are present in the first coordination sphere. The molar extinction coefficient increases with the halide's atomic number, *i.e.*, $\text{Cl} < \text{Br} < \text{I}$, as expected on the basis of polarizability.⁸

It may be significant that, whereas the spectra of the chloride and bromide DSP complexes resemble one another fairly closely, the corresponding iodide complex exhibits a much higher extinction coefficient and

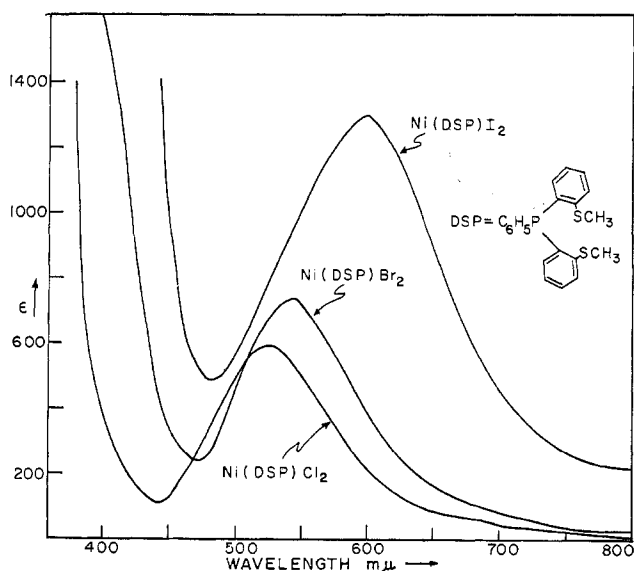


Figure 1.—Electronic absorption spectra of $[\text{Ni}(\text{DSP})\text{I}_2]$, $[\text{Ni}(\text{DSP})\text{Br}_2]$, and $[\text{Ni}(\text{DSP})\text{Cl}_2]$ in dichloromethane solutions.

its absorption maximum is shifted $\sim 2000 \text{ cm}^{-1}$ from that of the bromide. This shift is much larger than usually observed between the bromide and iodide in five-coordinate nickel(II) complexes of the same stereochemistry.⁵⁻¹⁰ The spectrum of the iodide is more characteristic of a trigonal-bipyramidal structure than either the bromide or chloride complex. Steric interactions of the large iodide ions may cause the trigonal-bipyramidal structure to be preferred in this case.

The $[\text{Ni}(\text{DSP})\text{X}_2]$ complexes exhibit increasing conductance values with increasing size of the halide ion (Table I), indicating increasing solvation by acetonitrile. Molecular weight, conductivity, and electronic spectral measurements demonstrate that polar solvents such as acetonitrile and dimethylformamide decompose the DSP complexes at $10^{-4} M$. To illustrate the extent of solvation, the apparent molecular weight of $[\text{Ni}(\text{DSP})\text{Br}_2]$ was 204, 222, and 223 at 0.0237, 0.0475, and 0.0570 *M*, respectively, in dimethylformamide, whereas the apparent molecular weight expected for $[\text{Ni}(\text{DSP})\text{Br}_2]$ and $[\text{Ni}(\text{DSP})(\text{Sol})_x]^{2+} + 2 \text{ Br}^-$ is 573 and 191, respectively. Thus, the experimental molecular weight values show that the bromide ions in $[\text{Ni}(\text{DSP})\text{Br}_2]$ are almost completely displaced in DMF at $\sim 10^{-2} M$. Conductivity measurements over the range 10^{-1} to $10^{-2} M$ in DMF fully support the molecular weight data and also indicate increasing ion pairing at the higher concentrations.

An olive-green bis-DSP complex was obtained with nickel(II) perchlorate. With two tridentate ligands a six-coordinate complex might be expected; however, the compound is diamagnetic and a di-univalent electrolyte, thereby excluding from consideration a regular octahedral structure and perchlorate coordination. Alternate likely possibilities involve five- and four-coordinate complexes in which some of the possible donor atoms are not coordinated. To help elucidate the type of coordination present in $[\text{Ni}(\text{DSP})_2](\text{ClO}_4)_2$, a series of complexes was prepared in which a similar

TABLE I
PROPERTIES AND ANALYTICAL DATA OF THE NICKEL(II)-POLYDENTATE PHOSPHINE COMPLEXES^a

Compound	Color	Λ_M^b , cm ² /ohm mole	Analyses, %							
			C		H		P		Halogen	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[\text{Ni}(\text{DSP})\text{Cl}_2]^c$	Purple	19	49.62	49.57	3.96	4.14	6.40	5.84	14.65	14.40
$[\text{Ni}(\text{DSP})\text{Br}_2]$	Purple	23	41.92	42.02	3.34	3.37	5.41	5.47	27.89	27.63
$[\text{Ni}(\text{DSP})\text{I}_2]^d$	Green-blue	154	36.01	35.83	2.87	3.05	4.64	4.53	38.05	38.21
$[\text{Ni}(\text{DSP})_2](\text{ClO}_4)_2$	Olive-green	311	49.71	49.56	3.96	4.05	6.41	6.86	7.34	7.40
$[\text{Ni}(\text{DSP})(\text{SP})](\text{ClO}_4)_2^e$	Brown	304	52.08	52.00	3.81	4.02	6.90	6.76	7.80	8.00
$[\text{Ni}(\text{DSP})(\text{AP})](\text{ClO}_4)_2^f$	Brown	260	55.52	54.29	4.01	4.02	5.73	5.75	6.65	7.03
$[\text{Ni}(\text{DSP})(\text{PP})](\text{ClO}_4)_2^g$	Brown	287	55.72	55.38	4.37	4.64			7.25	7.06
$[\text{Ni}(\text{SP})_2\text{Cl}_2]$	Maroon	8.6 ^h	52.10	51.90	3.91	4.04			16.18	16.40
									Other	
$[\text{Ni}(\text{SP})_2\text{Br}]\text{ClO}_4$	Deep purple	87 ^b	53.39	53.38	4.00	4.18	7.49	7.32 (S)		
$[\text{Ni}(\text{SeP})_2\text{Br}]\text{ClO}_4^h$	Deep purple	89 ^b	48.12	47.99	3.61	3.83	16.64	16.45 (Se)		
$[\text{Ni}(\text{SP})_2\text{Cl}_2]$	Pale green	6.4 ^b	61.15	60.96	4.59	4.74			9.49	9.62

^a All of these complexes are diamagnetic, *i.e.*, $< 0.4 \text{ BM}$, except $[\text{Ni}(\text{SP})_2\text{Cl}_2]$, which has $\mu_{\text{eff}} = 3.15 \pm 0.03 \text{ BM}$ at two different magnetic field strengths. ^b Molar conductance value of $\sim 10^{-3} M$ solution of the compound in acetonitrile, except that the SP and SeP complexes were determined at $10^{-3} M$ in nitromethane. Uni-univalent and di-univalent electrolytes exhibit Λ_M values in the ranges 75-95 and 160-190 in nitromethane, whereas the values are 145-160 and 260-310 for acetonitrile. ^c DSP, $\text{C}_6\text{H}_5\text{P}(\text{o}-\text{C}_6\text{H}_4\text{SCH}_3)_2$. ^d Calculated molecular weight, 667; found, 665 in chloroform. ^e SP, $(\text{C}_6\text{H}_5)_2\text{P}(\text{o}-\text{C}_6\text{H}_4\text{SCH}_3)$. ^f AP, $(\text{C}_6\text{H}_5)_2\text{P}(\text{o}-\text{C}_6\text{H}_4\text{As}(\text{C}_6\text{H}_5)_2)$. ^g PP $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$. ^h SeP, $(\text{C}_6\text{H}_5)_2\text{P}(\text{o}-\text{C}_6\text{H}_4\text{SeCH}_3)$.

bidentate ligand was substituted for one DSP ligand. The bidentates used were $(C_6H_5)_2P(o-C_6H_4SCH_3)$, SP, $(C_6H_5)_2P(o-C_6H_4As(C_6H_5)_2)$, AP, and $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, PP, and the three compounds are represented as $[Ni(DSP)(PD')](ClO_4)_2$ (where $D' = S, As, P$).

The resulting complexes containing one tridentate DSP and one bidentate ligand are quite similar to $[Ni(DSP)_2](ClO_4)_2$ in solubility properties, so that electronic spectra could not be obtained in noncoordinating solvents such as dichloromethane. However, the transmission spectra of Nujol mulls of the solid compounds (Figure 2) show the same band maxima as those obtained in acetonitrile solutions. Each compound exhibits a three-band spectrum in which the first maximum occurs at 15,500–17,500 cm^{-1} , the second at 21,500–23,000 cm^{-1} , and the third at 27,000–29,000 cm^{-1} . The spectral data of acetonitrile solutions are given in Table II and compared with $[Ni(DSP)_2](ClO_4)_2$. The characteristic spectra show definite similarities among all five compounds, but they differ from either the $[Ni(DSP)X_2]$ series or the known trigonal-bipyramidal complexes.^{4–10} Four-coordinate, planar structures can definitely be eliminated by comparing the spectra in Figure 2 with those of $[Ni(SP)_2](ClO_4)_2$ (Figure 3) and $[Ni(AP)_2](ClO_4)_2$ (Figure 3 of ref 19). The most significant difference is the absence of an absorption band below 21,000 cm^{-1} in the planar complexes. Since four- and six-coordinate compounds are ruled out for $[Ni(DSP)(bidentate)]^{2+}$ and $[Ni(DSP)_2]^{2+}$ on the basis of magnetic and spectral data, and since their electronic spectra differ from those of trigonal-bipyramidal complexes,^{4–10} we tentatively propose a five-coordinate, probably distorted square-pyramidal structure for these compounds.

The relative energies of the bands fit quite well into the qualitative pattern expected for square-pyramidal d^8 complexes.² Four of the five donor atoms are held constant (two phosphorus atoms and two sulfur atoms) throughout the series; changes in absorption maxima seem to be related to the donor ability of the fifth atom, *i.e.*, $S < As < P$. Electronic absorption intensities increase progressively as the energies increase and also as the variable donor atom is changed from sulfur to arsenic to phosphorus (Table II). This same spectrochemical trend was observed in several series of trigonal-bipyramidal Ni(II) complexes.^{7–9}

Each of the three bidentate ligands, AP, SP, and SeP, forms yellow, diamagnetic $[Ni(\text{ligand})_2](ClO_4)_2$ complexes. It appears that no diamagnetic nickel(II) complexes of a neutral bidentate ligand containing a thioether or a selenoether group have been reported previously.²⁰ The $[Ni(\text{bidentate})_2](ClO_4)_2$ complexes are converted instantly into the purple, five-coordinate $[Ni(\text{bidentate})_2X]ClO_4$ compounds by halide ion in solution. When the five-coordinate complex is formed, the lowest electronic absorption band ($\sim 22,000$ cm^{-1}) of the corresponding $[Ni(\text{ligand})_2](ClO_4)_2$ shifts ~ 3000

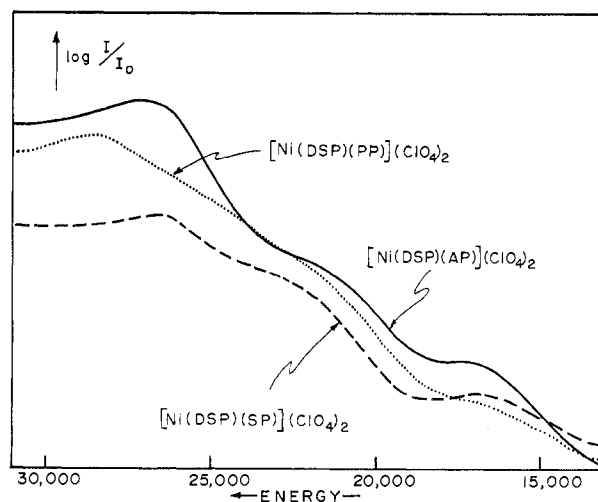


Figure 2.—Electronic absorption spectra of solid $[Ni(DSP)(AP)](ClO_4)_2$, $[Ni(DSP)(SP)](ClO_4)_2$, and $[Ni(DSP)(PP)](ClO_4)_2$ in Nujol mulls.

TABLE II
ELECTRONIC SPECTRAL DATA FOR THE
 $[Ni(DSP)(bidentate)](ClO_4)_2$
COMPLEXES DISSOLVED IN ACETONITRILE

Compound	Energy of absorption bands, cm^{-1} (ϵ^a)		
$[Ni(DSP)_2](ClO_4)_2$	15,600 (150)	21,800 (575)	27,000 (3000)
$[Ni(DSP)(SP)](ClO_4)_2$	16,000 (200)	21,000 (750)	26,000 (5500)
$[Ni(DSP)(AP)](ClO_4)_2$	16,500 (450)	21,000 (1300)	27,500 (13,200)
$[Ni(DSP)(PP)](ClO_4)_2$	17,500 (400)	22,500 (1350)	28,500 (13,400)

^a ϵ , molar extinction coefficient.

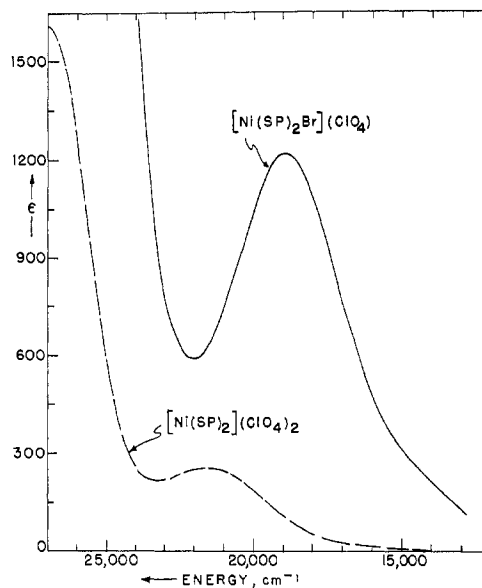


Figure 3.—Absorption spectra of $[Ni(SP)_2](ClO_4)_2$ and $[Ni(SP)_2Br]ClO_4$ in dichloromethane solutions.

cm^{-1} to lower energy and the extinction coefficient increases 2–3 times (Figure 3). The spectral maxima of the five-coordinate compounds in dichloromethane solution are essentially identical with those in the solid state, indicating that no structural rearrangement occurs on dissolving the solid.

The electronic spectra of the four- and five-coordinate compounds have two maxima in the visible and near-ultraviolet region. The extinction coefficient of the

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higher energy band indicates that it is a charge-transfer band, and since it occurs at the same position ($\sim 28,000$ cm^{-1}) in both $[\text{Ni}(\text{SP})_2](\text{ClO}_4)_2$ and $[\text{Ni}(\text{SP})_2\text{Br}]\text{ClO}_4$, it must be due to a common transition not involving the bromide ligand. The energy of a charge-transfer band should be related to the ionization potential of the atom involved. Triarylphosphines have the lowest ionization potentials of all the donor atoms used in this study;^{21,22} therefore, the band ($\sim 28,000$ cm^{-1}) probably results from a ligand \rightarrow metal electron transition involving the lone pair of electrons on phosphorus (used in the P-Ni σ bond) and the empty b_1 ($d_{x^2-y^2}$) orbital of nickel. The spectra in Figure 4 provide additional evidence for this assignment. Since phosphorus is common to all three ligands, the $\sigma\text{P}\rightarrow\text{Ni}$ electron transition should occur at essentially the same energy in the three complexes, as observed.

The lower energy band in the planar $[\text{Ni}(\text{ligand})_2](\text{ClO}_4)_2$ complexes is assigned to the ligand field transition involving the orbitals b_2 (d_{xy}) \rightarrow b_1 ($d_{x^2-y^2}$). The spectra of the five-coordinate $[\text{Ni}(\text{ligand})_2\text{X}]\text{ClO}_4$ complexes resemble those of the analogous planar complexes more closely than the known trigonal-bipyramidal ones.⁵⁻⁷ For diamagnetic, square-pyramidal nickel(II) complexes, the first ligand field transition should occur at $\sim 20,000$ cm^{-1} ,²³ in excellent agreement with the observed maxima ($\sim 19,000$ cm^{-1}).

The spectra in Figure 5 indicate a strong structural similarity between $[\text{Ni}(\text{SP})_2\text{Br}]\text{ClO}_4$ and $[\text{Ni}(\text{DSP})\text{Br}_2]$. The increases in extinction coefficient and E_{max} of $[\text{Ni}(\text{SP})_2\text{Br}]\text{ClO}_4$ are consistent with ligand field considerations when a bromide ion in $[\text{Ni}(\text{DSP})\text{Br}_2]$ is replaced by a phosphine donor.^{2,8,19} These same effects are also apparent in the spectra of $[\text{Ni}(\text{AP})_2\text{Br}]\text{ClO}_4$, $[\text{Ni}(\text{SP})_2\text{Br}]\text{ClO}_4$, and $[\text{Ni}(\text{SeP})_2\text{Br}]\text{ClO}_4$ (Figure 4).

The apparent ligand field strength observed previously⁸ with tetradentate ligands, *i.e.*, $\text{Se} < \text{S} < \text{As}$, is also produced by these bidentate ligands. The intensities of the electronic transitions produce an increasing effect in a different order: $\text{S} < \text{Se} < \text{As}$. This intensity trend was observed in trigonal-bipyramidal nickel(II) complexes with tetradentate ligands.^{7,8}

The existence of both low-spin phosphine, arsine, and thioether complexes of Fe(II), Co(II), and Ni(II) and high-spin tertiary amine¹¹ complexes suggests a rather dramatic variation of the ratio between the orbital energy differences and interelectronic repulsion parameters. Subtle changes in the nature of the ligand can produce a profound effect on the ground state of the complex. This is demonstrated particularly well with the bidentate ligands used in this study. All three ligands give diamagnetic, four-coordinate $[\text{Ni}(\text{ligand})\text{X}_2]$ and diamagnetic, five-coordinate $[\text{Ni}(\text{ligand})_2\text{X}]^+$ complexes, whereas only SP and SeP generally yielded six-coordinate, paramagnetic $[\text{Ni}(\text{ligand})_2\text{Cl}_2]$ com-

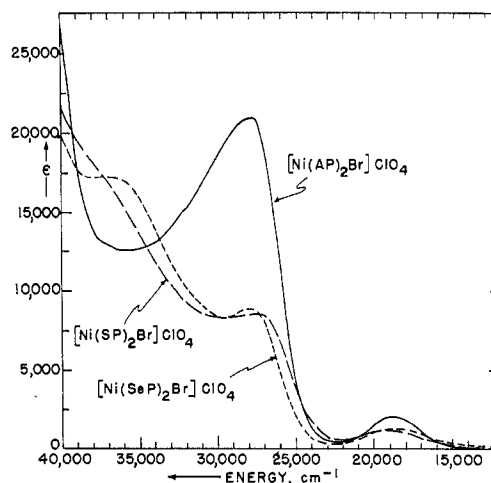


Figure 4.—Visible and ultraviolet absorption spectra for $[\text{Ni}(\text{AP})_2\text{Br}]\text{ClO}_4$, $[\text{Ni}(\text{SP})_2\text{Br}]\text{ClO}_4$, and $[\text{Ni}(\text{SeP})_2\text{Br}]\text{ClO}_4$ in dichloromethane solutions.

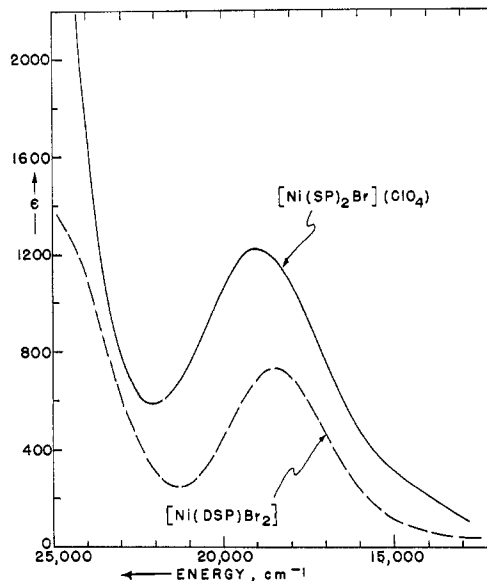


Figure 5.—Visible absorption spectra of $[\text{Ni}(\text{SP})_2\text{Br}]\text{ClO}_4$ and $[\text{Ni}(\text{DSP})\text{Br}_2]$ in dichloromethane solutions.

plexes. The specific compound isolated with each ligand also is a sensitive function of the solvent and synthetic conditions. In our hands, only nickel thiocyanate yielded a six-coordinate complex with AP.

Conclusions.—Because no structural data are available for a regular square-pyramidal nickel compound, the absorption spectra do not permit a definitive structural assignment for these five-coordinate nickel(II) complexes with tridentate and bidentate ligands; however, it is apparent from the electronic spectra that five donor atoms probably occupy similar positions around the nickel ion for the case of two bidentate ligands with one halide and for the case of one tridentate ligand with two halides (Figure 5). The spectra are not characteristic of trigonal-bipyramidal complexes nor the one known distorted square-pyramidal complex, *i.e.*, $[\text{Ni}(\text{triarsine})\text{Br}_2]$.²⁴ Certainly, the low-energy bands of the five-coordinate complexes reported here are more sym-

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metrical and well defined than those of $[\text{Ni}(\text{triarsine})\text{-Br}_2]$. A square-pyramid (with the $L_{\text{apex}}\text{-Ni-L}_{\text{base}}$ angle probably $>90^\circ$) is the easiest structure to visualize for the complexes containing two bidentates and one halide, with the bidentate ligands forming the square base and the halide in the apical position. The absorption spectra are consistent with a square-pyramidal structure. Obviously, the spectral and structural correlation will be definitive only when one or two of these structures are determined by X-ray crystallography and must be considered tentative until then.

In any case, a very significant conclusion from this investigation is that five-coordination with nickel(II) is quite general for ligands containing π -bonding atoms such as phosphorus, arsenic, sulfur, and selenium, and it does not depend on using a ligand with highly specific steric effects, such as a "tripod" tetradentate, at least in the diamagnetic series of nickel(II) complexes.^{25,26}

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(25) A referee has pointed out that all of the ligands used in this study contain a phenyl-phosphorus linkage and that the *o*-hydrogen may be partially responsible for denying stereochemical access of a sixth ligand to the coordination sphere. Such an effect is important in the case of $[\text{Ru}(\text{P}(\text{C}_6\text{H}_5)_2)_2\text{Cl}_2]$.²⁶ The fact that we have prepared (this paper) paramagnetic, pseudo-octahedral $[\text{Ni}(\text{SP})_2\text{Cl}_2]$ and $[\text{Ni}(\text{SeP})_2\text{Cl}_2]$ complexes illustrates that the sixth coordination site is not blocked. Also, the electronic ground state of all these five-coordinate complexes is a singlet. If the *o*-hydrogen functioned to block access to one of the coordination positions, the electronic ground state should be a triplet due to the use of thiomethyl and selenomethyl donors.²⁰ Therefore, we believe the primary factor involved in formation of these diamagnetic, five-coordinate complexes is the use of the π -bonding donor atoms, which reduce the interelectronic repulsion parameters and create a favorable electronic state for five-coordination. In any case, the results of an X-ray investigation, currently underway, should settle this point.

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High-Spin Five-Coordinate Nickel(II) and Cobalt(II) Complexes with a Tridentate NNN Schiff Base

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The tridentate Schiff base formed from *N*-methyl-*o*-aminobenzaldehyde and *N,N*-diethylethylenediamine (MABen-NEt₂, set of donor atoms NNN) forms high-spin complexes with Ni(II), Co(II), and Mn(II) salts of the general formula $M(\text{MABen-NEt}_2)_2\text{X}_2$. The stereochemistry of these complexes, both in the solid state and in solution, has been studied with magnetic and spectrophotometric measurements. The complexes of metal halides are five-coordinate; those with nickel(II) thiocyanate and nickel(II) nitrate are six-coordinate, the former through bridging linkages, the latter through bidentate and monodentate nitrate groups. In solution the Ni(II)-halide complexes give rise to a five-coordinate \rightleftharpoons tetrahedral equilibrium.

Introduction

The first examples of high-spin five-coordinate complexes of nickel(II) and cobalt(II) have recently been described and characterized.¹ The most favorable ligands appear to be those which have strongly electronegative donor atoms (oxygen, nitrogen, halogens) and have little tendency to form π bonds with the metal ion. Moreover, to obtain five-coordination the ligands should provide steric hindrance, so that six-coordination is prevented, and be polydentate, so that rigidity may be imparted to the complex.

Some Schiff bases, which are formed from ring-substituted salicylaldehydes and *N,N*-disubstituted ethylenediamines, having the general formula $\text{XC}_6\text{H}_3(\text{OH})\text{-CH}=\text{N}(\text{CH}_2)_2\text{N}(\text{R})\text{R}'$ ($\text{X-SALen-N}(\text{R})\text{R}'$), appear to

be able to form high-spin five-coordinate complexes.^{1a,b} X-Ray structure analysis has shown that 5-Cl-SALen-NEt₂ forms nickel(II) and cobalt(II) complexes with a distorted square-pyramidal configuration in which one ligand molecule is bidentate while the other is tridentate.² The steric hindrance and the electronic effects caused by two ethyl groups on the β nitrogen seem to be critical. In fact, among a large number of ligands with different substituents on the β nitrogen, only the diethyl derivatives form five-coordinate complexes, while the others give four- or six-coordinate complexes.^{1a,3} Other ligands such as those formed from polymethyl polyamines like $\text{MeN}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2$ (Me₃dien) or $\text{N}(\text{CH}_2\text{CH}_2\text{NMe}_2)_3$ (Me₆tren) function as tri- or tetradentates with donor atom sets N₃ or N₄, to give five-coordinate complexes with the bivalent metals of the first transition series by coordination of

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