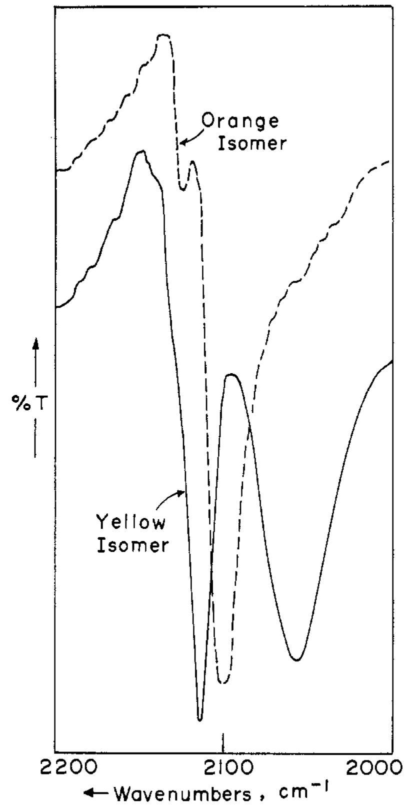

Figure 2.—The $C{\equiv}N$ region in the infrared spectra of the (———) yellow and (– – – –) orange palladium thiocyanate complexes of diphenyl(*o*-diphenylarsinophenyl)phosphine in Nujol mulls.

tronic spectra suggest that one thiocyanate ion is N bonded and one is S bonded in the yellow isomer, *i.e.*, [Pd($C_{30}H_{24}AsP$)(SCN)(NCS)].

The yellow isomer represents an unusual case among thiocyanate complexes because it is one of only two (or perhaps three) molecular complexes which contain both N- and S-bonded thiocyanate groups.[25] It is the only example where the type of thiocyanate bonding is controlled by use of a chelating ligand containing two different donor atoms. The compound can be prepared either by recrystallizing the orange compound from DMF–ethanol or by heating the solid at 220° for 45 min. The infrared spectra of the compounds which result from the two preparative routes are identical. We are currently studying palladium(II) thiocyanate complexes of other "mixed" donor atom bidentate ligands to determine which thiocyanate group is *trans* to phosphorus.

Summary.—These palladium(II), platinum(II), gold(I), and copper(I) complexes demonstrate that I functions as a chelating ligand involving coordination of the $P{=}S$ group. "Class b" metals form stable complexes, whereas no complexes of "class a" metals were obtained. A comparison of the electronic absorption spectra of palladium(II) complexes of the phosphine sulfide, I, and phosphine, II, shows that the ligand field strength of II is greater than that of I.

Acknowledgments.—The authors thank Professor A. Wojcicki for stimulating discussions, Professor F. Basolo for a preprint of his study, and Dr. R. Sievers and Mr. C. S. Springer, Jr., for the differential thermal analysis experiment.

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[25] After this study was completed, Raymond and Basolo [*Inorg. Chem.*, **5**, 1632 (1966)] reported a copper complex which contains both S- and N-bonded thiocyanate groups, and Bertini and Sabatini [*ibid.*, **5**, 1025 (1966)] suggest this possibility for a palladium complex.

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Five-Coordination. III. Trigonal-Bipyramidal Nickel(II) Complexes with a Phosphorus–Selenium Tetradentate Ligand[1-4]

BY G. DYER AND DEVON W. MEEK

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The new tetradentate ligand, tris(*o*-methylselenophenyl)phosphine, TSeP, IV, has been synthesized, and the resulting series of five-coordinate, trigonal-bipyramidal nickel(II) complexes has been characterized. The intensely blue complexes are diamagnetic and uni-univalent electrolytes, consistent with the formula [Ni(TSeP)X]ClO_4, when the fifth ligand is an anion, and di-univalent electrolytes when the fifth ligand is a neutral molecule. A comparison of the electronic absorption spectra of these complexes with those of similar trigonal-bipyramidal nickel(II) complexes containing sulfur, arsenic, or phosphorus atoms gives a spectrochemical series for the donor groups. A different order of the first spectral band intensity is obtained.

Introduction

One of the most interesting recent developments in the field of coordination chemistry has been the investigation of the unusual structures and the stereochemistries which occur among complexes of polydentate ligands. For example, several series of the previously unusual five-coordinate nickel(II) complexes have been obtained by use of polydentate ligands during the

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(1) The authors gratefully acknowledge the financial support of the U. S. Army Research Office (Durham) (Grant No. DA-ARO-(D)-31-124-G500) and the National Science Foundation (Grant No. GP-5729).

(2) Presented at the Anniversary Meeting of The Chemical Society (London), Oxford, England, March 1966.

(3) Part I of this series: G. S. Benner, W. E. Hatfield, and D. W. Meek, *Inorg. Chem.*, **3**, 1544 (1964).

(4) Part II: G. Dyer and D. W. Meek, *ibid.*, **4**, 1398 (1965).

past few years.[3–10] The phosphine and arsine ligands form *diamagnetic* five-coordinate nickel(II) complexes,[3–8] whereas, recently, similar polydentate amine ligands have yielded paramagnetic five-coordinate nickel(II) complexes.[9–10]

Our previous investigations indicate that formation of diamagnetic, trigonal-bipyramidal nickel(II) complexes is determined more by the π-bonding nature of the donor atoms than by the symmetry or steric requirements of the ligands.[3,4] Since the extent of π bonding by the donor atoms surely is important in determining whether the singlet or triplet electronic state is the ground state for five-coordinate Ni(II), recently we have been investigating "mixed" ligands containing two different donor atoms of intermediate π-bonding character.

We reported that diamagnetic, five-coordinate nickel(II) complexes result from the tetradentate ligand tris(*o*-methylthiophenyl)phosphine, which contains three sulfur donor atoms.[4] We now report the preparation of the analogous selenium ligand, tris(*o*-methylselenophenyl)phosphine, $P(o\text{-}C_6H_4SeCH_3)_3$, and compare its nickel(II) complexes with those previously reported.

Experimental Section

Synthesis of Tris(*o*-methylselenophenyl)phospine.—Liquid *o*-bromoaniline (103.2 g, 0.6 mole) in a 3-l. beaker was treated with cold sulfuric acid (92.4 g of concentrated acid diluted with 120 ml of water). The amine sulfate slurry was diluted to 1200 ml with ice and water and diazotized by rapid addition of sodium nitrite (48 g, 0.63 mole, in 120 ml of water). The mixture was stirred for 30 min and filtered, and the filtrate was adjusted to pH 5 with saturated sodium acetate solution. Ice (900 g) was then added, and potassium selenocyanate solution (75 g, 0.52 mole, in 700 ml of water) was added dropwise over a period of 30 min with stirring. The mixture was stirred for an additional 30 min at 0°, and the precipitate of crude $o\text{-}BrC_6H_4SeCN$ (107 g, 0.41 mole, 79% yield based on KSeCN) was collected on a large filter paper, washed well with water, and then dried in a vacuum desiccator for 6 hr over P_4O_{10}. The $o\text{-}BrC_6H_4SeCN$ was heated in 450 ml of refluxing ethanol with excess iodomethane (100 g, 0.7 mole), and then potassium hydroxide (46.0 g, 0.82 mole, in 630 ml of ethanol) was added over a period of 1 hr. The mixture was refluxed for 1 hr more; then about 300 ml of liquid was distilled to remove excess iodomethane. The remaining solution, which contained some solid potassium iodide, was poured into 5 l. of water and extracted with ether (1200 ml in portions). The ether phase was dried over calcium chloride, filtered, and concentrated to a boiling point of 80° under nitrogen at 1 atm. The remainder of the liquid, which was fractionated *in vacuo*, gave 56 g (0.224 mole, 55% yield) of *o*-bromoselenoanisole as a pale yellow liquid, bp 125–130° (0.5 mm).

Anal. Calcd for C_7H_7BrSe: C, 33.63; H, 2.82; Br, 31.96; Se, 31.58. Found: C, 33.85; H, 2.98; Br, 31.78; Se, 31.22.

To a solution of *o*-bromoselenoanisole (50 g, 0.20 mole) in dry ether (250 ml) at 0° was added dropwise a solution of 1-butyllithium (0.20 mole in 125 ml of hexane) with stirring under nitrogen. The solution was stirred 30 min after complete addition; then phosphorus trichloride (9.6 g, 0.07 mole) in dry ether (125 ml) was added over a period of 1 hr at 0°. The mixture, containing a beige precipitate in a yellow solution, was stirred 1 hr more and was then hydrolyzed with aqueous 0.2 *N* hydrochloric acid (150 ml). The ether layer was separated, dried with calcium chloride, filtered, and concentrated to 150 ml under nitrogen. After standing at 0° under nitrogen for 48 hr, colorless crystals of tris(*o*-methylselenophenyl)phosphine (2.6 g, 0.0048 mole, 7.2%) were collected. A sample which was recrystallized from dichloromethane and ethanol melted at 159–161°. *Anal.* Calcd for $C_{21}H_{21}PSe_3$: C, 46.60; H, 3.91; P, 5.72; Se, 43.76. Found: C, 46.85; H, 4.02; P, 5.69; Se, 43.13.

Preparation of the Complexes: $[Ni(TSeP)X](ClO_4)$ (X = Br, Cl, NCS).—The ligand (0.27 g, 0.5 mmole) in warm dichloromethane (5 ml) was treated with a mixture of the appropriate nickel salt[11] (0.5 mmole) and nickel perchlorate hexahydrate (0.183 g, 0.5 mmole) in hot ethanol (25 ml). The resulting deep blue solution was boiled for a few minutes and concentrated slightly to remove dichloromethane; at this point glistening blue-black crystals separated. These crystals were collected on a sintered-glass funnel after the mixture had cooled to 30°, and they were recrystallized by dissolving in dichloromethane (15–25 ml), adding 25 ml of ethanol, and then boiling off the dichloromethane (yields 72, 74, and 71%, respectively).

$[Ni(TSeP)I]ClO_4$.—The ligand (0.27 g, 0.5 mmole) in 10 ml of warm dichloromethane was treated with a mixture of nickel iodide (0.25 mmole) and nickel perchlorate (0.25 mmole) in 2.5 ml of absolute ethanol. Petroleum ether (20 ml, bp 60–100°) was added slowly with stirring. Intensely green crystals were collected, washed with petroleum ether, and recrystallized from 4 ml of boiling dichloromethane (yield 47%).

$[Ni(TSeP)CH_3(CH_2)_4C(CH_2O)_3P](ClO_4)_2$.—To a warm solution of nickel perchlorate (0.183 g, 0.5 mmole) in ethanol (10 ml) was added a solution of the "cage phosphite,"[12] $CH_3(CH_2)_4C(CH_2O)_3P$ (0.1 g, 0.5 mmole), in 5 ml of dichloromethane, followed by a solution of TSeP (0.27 g, 0.5 mmole, in 10 ml of dichloromethane). The resulting intensely violet solution was concentrated to 10 ml and allowed to cool; the complex separated as an oil. Methanol (4 ml) and tetrahydrofuran (8 ml) were added, and the mixture was boiled for 1 min with stirring. When the solution had cooled, small purple crystals were collected and washed with tetrahydrofuran. The complex was recrystallized by dissolving it in a mixture of boiling dichloromethane (50 ml) and methanol (15 ml), filtering the solution, concentrating it to 30 ml, and adding 30 ml of tetrahydrofuran. The solution was not disturbed during crystallization; after 24 hr, violet crystals (yield 0.28 g, 56%) were collected, washed with tetrahydrofuran, and dried.

$[Ni(TSeP)_2](ClO_4)_2$.—The ligand (0.27 g, 0.5 mmole) in 5 ml of warm dichloromethane was treated with $[Ni(H_2O)_6](ClO_4)_2$ (0.366 g, 1 mmole) in hot ethanol (25 ml). The resulting brown solution yielded purple-brown crystals, which were washed by decantation with ethanol and then collected (yield 0.3 g, 45%). This complex was not sufficiently soluble for recrystallization, but it was analytically pure as obtained.

Spectral and Conductance Measurements.—These were obtained as described previously.[4]

Magnetic Measurements.—Magnetic moments were determined using a Faraday magnetic susceptibility balance which was constructed recently in this laboratory.[13] The observed susceptibility values were corrected for the diamagnetism of the ligands.[14] The sample (*ca.* 20 mg) in a light quartz boat was

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

(6) G. Booth and J. Chatt, *ibid.*, 3238 (1965).

(7) G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 415 (1960).

(8) G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965), and references cited therein.

(9) (a) M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966); (b) M. Ciampolini and N. Nardi, *ibid.*, **5**, 41 (1966).

(10) Z. Dori and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 1394 (1966).

(11) Nickel iodide and nickel thiocyanate were used as concentrated ethanolic solutions (approximately 1 *M*) prepared by mixing stoichiometric amounts of nickel nitrate with sodium iodide or sodium thiocyanate in ethanol and filtering off the sodium nitrate.

(12) The authors thank Professor J. G. Verkade of Iowa State University for a sample of this phosphite.

(13) The authors gratefully acknowledge the National Science Foundation research instrument grant (GP-1719) which permitted construction of the magnetic susceptibility balance.

(14) 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.

suspended on a quartz fiber from the torsion beam of a Cahn gram electrobalance in a static helium atmosphere maintained at 285 mm. The magnetic field was controlled with a water-cooled Varian 4-in. electromagnet equipped with constant-gradient-field pole caps and mounted on rails so that it could be moved back for the "out-of-field" readings and forward to a fixed stop position for "in-field" readings.

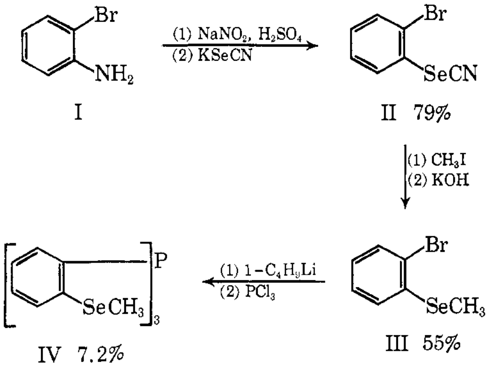
Discussion

Preparation of the Ligand.—Relatively little work has been reported previously concerning selenium ligands and their complexes. A synthetic route, which may be applied to the preparation of a number of aryl polydentate ligands containing *o*-selenium donor groups, is now described.

The synthesis of the new tetradentate ligand, tris(*o*-methylselenophenyl)phosphine is outlined in Scheme I. The first stage consists of treating the diazo solution from *o*-bromoaniline with selenocyanate ion. Such a reaction was described in 1913 for the preparation of *o*-$NO_2C_6H_4SeCN$,[15] and a slight improvement in procedure was reported by Develotte in 1950.[16] The crude *o*-BrC_6H_4SeCN decomposes gradually at room temperature; however, when used within 24 hr, it gave a 55% yield of *o*-bromoselenoanisole, a stable, pale yellow liquid with only a mild odor. The procedure for this conversion of an aryl selenocyanate to a selenoanisole was based upon a Japanese report of 1936.[17] The rather low yield of 7.2% in the final stage is probably due to attack of selenium–carbon bonds by 1-butyllithium;[18] certainly foul-smelling by-products, which caused a headache, were formed. In spite of several attempts, the yield of ligand was not improved by carrying out the reactions at −78°, nor by using tetrahydrofuran as solvent, nor by using tetramethylethylenediamine as a catalyst during the reaction with 1-butyllithium.[19] The pure tris(*o*-methylselenophenyl) phosphine forms colorless, odorless crystals, which are stable to air and water.

SCHEME I

SYNTHESIS OF TRIS(*o*-METHYLSELENOPHENYL)PHOSPHINE



Complexes.—An intensely blue color develops immediately when an ethanol solution of a nickel(II) salt is added to a dichloromethane solution of tris(*o*-methylselenophenyl)phosphine. The complexes separate as intensely blue crystals. The properties and analytical data for the complexes are listed in Table I.

All of the tris(*o*-methylselenophenyl)phosphine complexes are diamagnetic. The molar conductance values indicate that the complexes $[Ni(TSeP)X](ClO_4)$ (where X = I, Br, Cl, or NCS) are uni-univalent electrolytes in nitromethane, and $[Ni(TSeP)L](ClO_4)_2$ (where L = the "cage phosphite" $CH_3(CH_2)_4C(CH_2O)_3P$) is a di-univalent electrolyte. The properties of the TSeP complexes closely resemble those of the corresponding complexes of tris(*o*-methylthiophenyl)phosphine, TSP, except that, whereas the complexes of the sulfur ligand were decomposed by methanol or ethanol,[4] those of the selenium ligand are stable in these solvents. This may indicate that they are less labile or that they have higher stability constants than the TSP complexes.

The extremely intensely green to blue colors of the complexes, due to strong absorption bands about 16,000 cm^{-1}, appear to be characteristic of diamagnetic five-coordinate nickel(II) compounds. A trigonal-bipyramidal structure is indicated for these complexes by a comparison of the electronic absorption spectra of corresponding TSeP, TSP, and QAS[20] bromide complexes (Figure 1). There are clearly two ligand-field bands with shapes, energy positions, and intensities characteristic of the trigonal-bipyramidal structure.[3,4] As with the QAS and TSP complexes,[4] the electronic transitions are assigned to the two ${}^1A_1 \rightarrow {}^1E(D)$ transitions.

Within the TSeP series, the two ligand-field absorption bands move to higher energy in the order: $I < Br < Cl < NCS < CH_3(CH_2)_4C(CH_2O)_3P$. This series is expected on the basis of the spectrochemical series of ligands observed in four- and six-coordinate nickel complexes. By comparing the energies of the bands in corresponding TSeP, TSP, and QAS complexes (Figure 1), one may conclude that the spectrochemical series for the donor groups is $R_2Se < R_2S < R_3As$. The order Se < S has not been established previously, owing to the scarcity of complexes with selenium ligands, but it might have been predicted from a consideration of the corresponding elements in groups V (where As < P) and VII (where Br < Cl).

A different order is found when the intensities of the first spectral bands of the complexes of the selenium, sulfur, and arsenic ligands are compared (Figure 1). In all cases the intensities are very high, and the order of increasing intensity is S < Se < As. A probable reason for the high-intensity electronic absorptions observed in diamagnetic, trigonal-bipyramidal complexes is that the equatorial $d_{x^2-y^2}$ and d_{xy} orbitals of the metal can overlap strongly with orbitals of e symmetry on the three equatorial ligand atoms (Figure 2). The more polarizable these equatorial ligand atoms are, the more covalent will be the ligand–metal bond, *i.e.*, the more mixing of ligand and metal orbitals there will be, making the formal d–d transition of the metal ion

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[15] H. Bauer, *Ber.*, **46**, 92 (1913).

[16] J. Develotte, *Ann. Chim.* (Paris), **5**, 218 (1950).

[17] S. Keimatsu and I. Satoda, *J. Pharm. Soc. Japan*, **56**, 703 (1936); *Chem. Abstr.*, **31**, 2589⁸ (1937).

[18] H. Gilman and F. J. Webb, *J. Am. Chem. Soc.*, **71**, 4062 (1949).

[19] G. G. Eberhardt and W. A. Butte, *J. Org. Chem.*, **29**, 2928 (1964).

[20] QAS is tris(*o*-diphenylarsinophenyl)arsine, $As(o\text{-}C_6H_4As(C_6H_5)_2)_3$, prepared by Dr. L. M. Venanzi and co-workers.

TABLE I

PROPERTIES AND ANALYTICAL DATA FOR THE NICKEL(II)–TRIS(*o*-METHYLSELENOPHENYL)PHOSPHINE COMPLEXES[a]

Compound	Color	Dec pt, °C	Λ_M,[b] cm²/ohm mole	—Electronic absorption maxima,[c]
$[Ni(TSeP)I]ClO_4$	Intense green	229	88	14,815 (1362), 19,230 sh (272),
$[Ni(TSeP)Br]ClO_4$	Intense blue-green	232[e]	89	14,925 (1697), 20,200 (198),
$[Ni(TSeP)Cl]ClO_4$	Intense blue	232[e]	88	15,150 (1860), 20,300 (220),
$[Ni(TSeP)NCS]ClO_4$	Intense blue	251–253	80	15,875 (2585), 20,410 (693),
$[Ni(TSeP)CH_3(CH_2)_4C(CH_2O)_3P](ClO_4)_2$	Intense violet	173[e]	163	18,570 (2306), 25,640 (660),
$[Ni(TSeP)_2](ClO_4)_2$	Brown-purple	201–204	174	14,225 (267), 22,220 (2150),

[a] All of the complexes are diamagnetic, are not hygroscopic, and appear to be stable in air. [b] For approximately 10^{-3} *M* nitromethane solutions at 25°. A uni-univalent electrolyte will have a value in the range 80–95 and a di-univalent electrolyte will have a value in

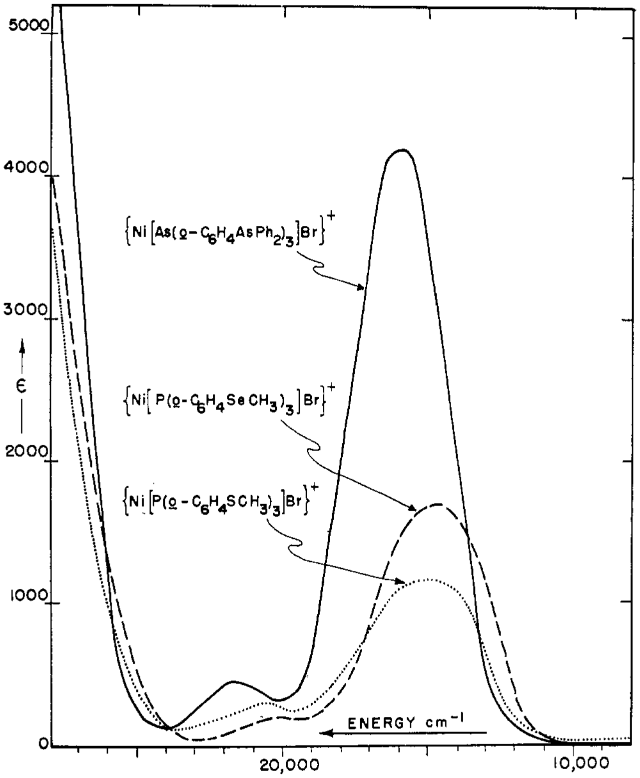

Figure 1.—Electronic absorption spectra of the five-coordinate complexes (———) $[NiAs(o-C_6H_4AsPh_2)_3Br]^+$, (– – – –) $[NiP(o-C_6H_4SeCH_3)_3Br]$, and (· · · ·) $[NiP(o-C_6H_4SCH_3)_3Br]^+$.

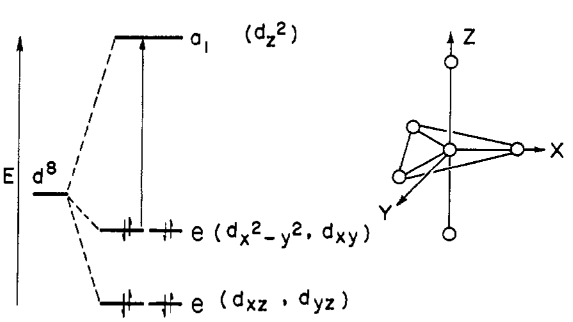

Figure 2.—d-Orbital splitting diagram for C_{3v} five-coordinate complexes. The $d_{x^2-y^2}$ and d_{xy} metal orbitals are closest to the three equatorial ligand atoms; thus, the arrow represents the first electronic transition and the one most sensitive to the ligand field created by donor atoms at the equatorial positions.

less forbidden. The observed intensity trend S (ϵ ~1100) < Se (ϵ ~1700) < As (ϵ ~4000) would indicate that selenium forms more covalent bonds than sulfur, in accord with its larger size and greater polarizability. Increased covalent bonding may also explain the fact that the TSeP complexes are more stable in organic solvents than analogous TSP complexes. The arsenic–nickel bonds in QAS complexes produce a considerably more intense absorption; also changing the metal ion in $[Ni(QAS)Br](ClO_4)$ to the palladium(II) ion results in another large increase in intensity; ϵ is *ca.* 8700 for the corresponding spectral band of $[Pd(QAS)Br](ClO_4)$.[21] This may be correlated with the well-known fact that palladium(II) forms more covalent complexes than nickel(II).

Other workers have compared the electron-donating properties of similar sulfur and selenium compounds by a variety of different methods. A kinetic study of the formation of sulfonium and selenonium salts showed that selenides exhibit considerably greater nucleophilic character than the analogous sulfides.[22] Also, intermolecular hydrogen-bonding studies have shown that selenium esters are more basic than the sulfur isologs.[23] Vapor-phase measurements have shown that dialkyl selenide adducts of trimethylgallium are more stable than the corresponding dialkyl sulfide adducts.[24] These considerations, when extended to transition metal complexes, tend to support our proposal that the nickel–selenium bond in these trigonal-bipyramidal complexes involves greater metal electron delocalization than in the analogous nickel–sulfur bond.

The diamagnetism of all the tris(methylselenophenyl)phosphine complexes is of particular interest since Ciampolini and Nardi have recently reported that nickel(II) forms paramagnetic, trigonal-bipyramidal complexes with the tetradentate nitrogen ligand $N[CH_2CH_2N(CH_3)_2]_3$.[9b] The energy-level diagram constructed by Ciampolini[9a] is reproduced in Figure 3, and the crossover between a paramagnetic and diamagnetic ground state occurs at a ligand field corresponding to five equal point dipoles of 8.5 D. at 2.0 A from the nickel atom. The visible spectra of bis(N-methylsalicylaldimino)nickel(II) was fitted to the diagram, assuming dipoles of about 5.2 D. If crystal-field arguments can be applied to the diamagnetic complexes, then the ligand atoms sulfur, selenium,

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[21] G. Dyer and L. M. Venanzi, *J. Chem. Soc.*, 2771 (1965).

[22] J. Gosselck and H. Barth, *Z. Naturforsch.*, **16b**, 280 (1961).

[23] J. Gosselck and J. Meinrenken, *Angew. Chem. Intern. Ed. Engl.*, **2**, 663 (1963).

[24] G. E. Coates, *J. Chem. Soc.*, 2003 (1951).

	Analyses,[d] %							
	C		H		P		Other	
$E_{\max}$, cm^{-1} (ϵ)	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
27,030 sh (4360), 34,720 (11,640)	30.52	30.35	2.56	2.52	3.76	3.93	28.68	28.38 (Se)
32,050 sh (6700), 36,850 (18,350)	32.37	32.43	2.71	2.87	3.97	4.04	30.40	30.63 (Se)
32,360 sh (5620)	34.32	35.27	2.88	2.80	4.21	4.26	9.65	10.20 (Cl)
30,770 sh (5440), 36,830 (11,030)	34.88	35.08	2.79	2.90	4.10	4.26		
31,800 sh (5230), 37,900 (15,700)	35.92	35.38	3.82	3.67	6.18	6.37		
27,625 (12,820), 33,300 sh (16,300)	37.64	37.78	3.16	3.30	4.62	4.65	5.29	5.43 (Cl)

the range 160–190. [c] Dichloromethane solutions; sh, shoulder. [d] Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. [e] Decomposes explosively.

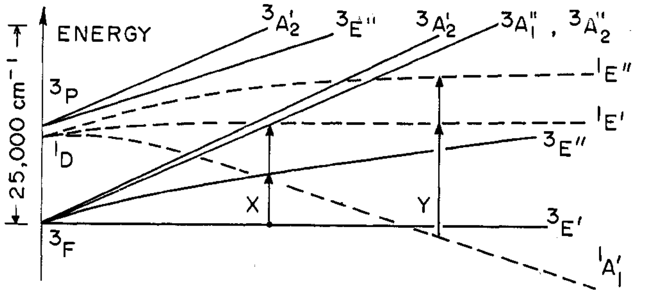

Figure 3.—A portion of the energy-level diagram for a d^8 ion. Arrows (X) represent the two transitions in bis(N-methylsalicylaldimino)nickel(II) at 7500 and 14,400 cm^{-1}, and arrows (Y) represent the two transitions in diamagnetic [Ni(TSeP)Br]ClO$_4$ at 14,925 and 20,200 cm^{-1}.

arsenic, and phosphorus must have considerably larger effective dipole moments. Livingstone[25] has pointed out that the effective dipole moments of polarizable ligand atoms can be increased considerably above the permanent dipole value because of an additional induced dipole moment, which is directly proportional to the polarizability. The spectra of the series of TSP and TSeP complexes can be fitted to the energy-level diagram (Figure 3) with remarkable agreement and indicate an apparent dipole moment equivalent to 9.05 D. for [Ni(TSeP)Br]ClO$_4$. This is beyond the crossover point and consistent with the observed diamagnetism. However, the agreement between the spectrum of [Ni(TSeP)Br]ClO$_4$ and Ciampolini's energy diagram[9a] may be entirely fortuitous since the diamagnetic complexes should be described in terms of molecular orbitals, especially in view of the high extinction coefficients for the electronic transitions.

Conclusion.—Using the tetradentate ligand P(*o*-C$_6$H$_4$SeCH$_3$)$_3$, we have obtained a series of diamagnetic, trigonal-bipyramidal nickel(II) complexes, in which the three selenium atoms are located at equatorial positions of the trigonal-bipyramidal structure. Detailed comparisons of their electronic absorption spectra with those of corresponding nickel(II) compounds previously reported with three equatorial sulfur, arsenic, or phosphorus atoms indicate that the spectrochemical series for the donor groups is R$_2$Se < R$_2$S < R$_3$As < R$_3$P. The intensity of the spectral band corresponding to the $d_{x^2-y^2}$, $d_{xy} \rightarrow d_{z^2}$ transition is consistently greater for the selenium complexes than for the sulfur complexes, but less than for the arsenic or phosphorus complexes. This may be interpreted in terms of increasing electron delocalization in the order S < Se < As $\sim$ P between the (equatorial) $d_{x^2-y^2}$ and d_{xy} orbitals of the metal and orbitals of e symmetry on the ligand atoms at equatorial positions of the trigonal bipyramid. Other evidence is cited to indicate that selenide donors should be more polarized on coordination with metals than sulfides, thus supporting the correlation between the spectral band intensities and increased metal electron delocalization, *i.e.*, covalent bonding.

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(25) S. E. Livingstone, *Quart. Rev.* (London), **19**, 386 (1965).