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Trigonal-Bipyramidal Nickel(II) Complexes Containing Sulfur Ligand Atoms[1]

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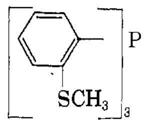
A new tetradentate ligand, tris(*o*-methylthiophenyl)phosphine, $P(o\text{-}C_6H_4SCH_3)_3$ (TSP, I), forms a series of crystalline, intensely-colored, trigonal-bipyramidal nickel(II) complexes containing the species $[Ni(TSP)X]^+$ (X = I, Br, Cl, or NCS) or $[Ni(TSP)L]^{2+}$ (L = thiourea, triphenylphosphine, or methyldiphenylphosphine). The two lowest energy electronic absorption bands in the visible and ultraviolet spectra have been assigned to the two $^1A_1 \rightarrow {}^1E(D)$ transitions. Under similar conditions, the analogous arsine compound, tris(*o*-methylthiophenyl)arsine, $As(o\text{-}C_6H_4SCH_3)_3$ (TSA), did not react with nickel(II) salts.

Introduction

Recently several definitive five-coordinate nickel(II) complexes have been obtained using polydentate ligands containing phosphorus(III) or arsenic(III) donor atoms. Dyer, Hartley, and Venanzi[2] prepared two series of trigonal-bipyramidal complexes with the ligands tris(*o*-diphenylarsinophenyl)arsine (QAS) and tris(*o*-diphenylphosphinophenyl)phosphine (QP). Since the electronic absorption spectra of the nickel(II) complexes are very similar to the spectrum of $[Pt(QAS)I][B(C_6H_5)_4]$, which exhibits a trigonal-bipyramidal structure,[3] the same structure has been assigned to the nickel(II) complexes. Venanzi[5] proposed that the trigonal symmetry of the rigid aryl ligands QAS and QP imposed the same symmetry upon the metal ion in the d^8 complexes. However, Benner, Hatfield, and Meek have demonstrated that the flexible aliphatic ligands $P[CH_2CH_2CH_2As(CH_3)_2]_3$ (TAP)[4] and $As[CH_2CH_2CH_2As(CH_3)_2]_3$[5] also form trigonal-bipyramidal complexes with nickel(II). In fact, an X-ray investigation has shown that the structure of $[Ni(TAP)CN]^+$ is a very symmetrical trigonal bipyramid around the Ni(II) ion.[6] X-Ray analysis showed that $[Ni(tas)Br_2]$ (where tas = $CH_3As[CH_2CH_2CH_2As(CH_3)_2]_2$ is five-coordinate in the solid,[7] and Harris, Nyholm, and Phillips[8] have reported that nickel(II) complexes with *o*-bis(dimethylarsino)benzene are five-coordinate in solution.

It is interesting to note that five-coordinate complexes of d^8 transition metal ions usually contain ligand atoms capable of extensive π bonding. Since thioethers generally form less stable complexes than the corresponding phosphines and arsines,[9,10] we prepared the tetradentate ligands tris(*o*-methylthiophenyl)phosphine (TSP, I) and tris(*o*-methylthiophenyl)arsine (TSA) to determine if π bonding in the sulfur–metal bonds would be sufficient to promote formation of trigonal-bipyramidal complexes analogous to those obtained with the QAS and QP ligands. The coordinating properties of the ligands TSP and TSA with several different transition metals are being investigated. This paper reports the results obtained with nickel(II).



TSP, I

Experimental

Synthesis of Tris(*o*-methylthiophenyl)phosphine.—Reaction of *o*-mercaptoaniline with sodium and iodomethane, as described by Livingstone,[11] gave *o*-aminothioanisole in 87% yield. This compound was converted to *o*-bromothioanisole in 57% yield by the method of Brand and Stallman.[12] A solution of *o*-bromothioanisole (77 g.) in ether (400 ml.) was treated with an equimolar quantity of *n*-butyllithium in hexane (250 ml. of a 1.5 *N* solution) during 2 hr. at 0° under a nitrogen atmosphere. A slight excess over the theoretical quantity of phosphorus trichloride (22 g. in 250 ml. of ether) was added during 3 hr., and then the reaction mixture was hydrolyzed with 250 ml. of 0.2 *N* hydrochloric acid. The white precipitate was washed thoroughly with water, ethanol, and ether (yield 45 g., 89%). The compound was recrystallized from 1-butanol.

Synthesis of Tris(*o*-methylthiophenyl)arsine.—The above procedure was used, except that arsenic trichloride was substituted for phosphorus trichloride in the final stage (yield 87%).

Preparation of the Complexes[13]: $[Ni(TSP)X](ClO_4)$ (X = I, Br, Cl, NCS).—The ligand (1 g.) in hot 1-butanol (50 ml.) was added to a mixture of the appropriate nickel salt[14] (1 g.) and nickel perchlorate hexahydrate, $Ni(ClO_4)_2 \cdot 6H_2O$, (1 g.) in hot 1-butanol (50 ml.). A very intense blue color developed immediately. When the mixture was boiled for a few minutes, crystals separated; these were collected on a sintered glass funnel after the mixture had cooled to 50–60° (yields 92, 92, 88, 81%, respectively). The complexes were recrystallized by dissolving

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[1] The authors gratefully acknowledge that this research was supported by a grant (DA-ARO-D-31-124-G500) from the U. S. Army Research Office (Durham).

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[13] In all cases except where mole quantities are specified, a slight to considerable excess of nickel salts may be used. Usually 0.0025 mole (1 g.) of ligand was used for each preparation with approximately 0.005 mole (100% excess) of nickel(II) compounds.

[14] Nickel iodide and nickel thiocyanate were used as concentrated ethanolic solutions (approximately 1 *M*) prepared by mixing ethanolic nickel nitrate and sodium iodide or thiocyanate and filtering off the sodium nitrate.

the appropriate compound in dichloromethane (25–50 ml.), adding 1-butanol (50 ml.), and concentrating the solution to 50 ml.

[Ni(TSP)$_2$](ClO$_4$)$_2$.—Hot 2% 1-butanol solutions of the ligand and Ni(ClO$_4$)$_2$·6H$_2$O were mixed; a brown complex crystallized after a few minutes (yield 88%).

[Ni(TSP)L](ClO$_4$)$_2$ (L = P(C$_6$H$_5$)$_3$, P(C$_6$H$_5$)$_2$CH$_3$).—Nickel perchlorate hexahydrate (2 g.) and the appropriate tertiary phosphine (1 g.) in hot 1-butanol (50 ml.) were added to the ligand (1 g.) in hot 1-butanol (50 ml.). The purple complexes (yields 65 and 74%) were recrystallized by dissolving in dichloromethane (100 ml.) containing 0.5 g. of the appropriate tertiary phosphine to repress dissociation, adding 1-butanol (70 ml.), and concentrating the solution to 80 ml.

[Ni(TSP)(tu)](ClO$_4$)$_2$.—This complex was prepared by the above procedure, but using thiourea (0.5 g.) instead of the tertiary phosphine. The black, crystalline complex (yield 82%) was insoluble in dichloromethane, but soluble in acetone to give a deep blue solution.

[Ni(TSP)(etu)$_2$](ClO$_4$)$_2$.—A solution of the ligand (1 g.) and ethylenethiourea (0.75 g.) in warm (85°) 1-butanol (100 ml.) was added to a cool (35°) solution of Ni(ClO$_4$)$_2$·6H$_2$O (1.5 g.) in 100 ml. of 1-butanol. A blue solution formed immediately and subsequently a red precipitate formed. When the mixture had cooled to 40°, the red crystals were collected, washed with warm (70°) 1-butanol, and dried (yield 63%). The compound was recrystallized by dissolving in warm acetone (150 ml.), adding chlorobenzene (150 ml.), and concentrating the solution to 150 ml. at 35° under reduced pressure.

[Ni(TSP)(C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$](ClO$_4$)$_2$.—A hot 1-butanol solution of 1 g. of Ni(ClO$_4$)$_2$·6H$_2$O was added to 95 ml. of a hot 1-butanol solution containing 1 g. of TSP and 1 g. of (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$. An olive-brown, microcrystalline precipitate was isolated from the mixture (yield 84%).

[Ni(TSP)Br$_2$].—Nickel bromide trihydrate, NiBr$_2$·3H$_2$O (0.9 g., 0.0033 mole) in acetone (60 ml.) was added slowly to a refluxing solution of the ligand (1.2 g., 0.0030 mole) in acetone (150 ml.). After refluxing for 1 hr., the mixture was cooled and the green crystals were collected (yield 65%).

[Ni(TSP)Br]$_2$[NiBr$_4$].—Hot solutions of nickel bromide trihydrate (3 g., 0.010 mole) in ethanol (10 ml.) and the ligand (1.2 g., 0.003 mole) in 150 ml. of acetone were mixed. Dark blue crystals separated from the solution after a few minutes (yield 80%).

Analyses.—The compounds were dried by heating at 56° and 1 mm. pressure for 24 hr. before analysis. Arsenic and phosphorus were determined by colorimetric methods described elsewhere,[2] and nitrogen analyses were obtained using a Coleman Model 29 analyzer. Carbon, hydrogen, sulfur, and halogen microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Spectra.—Infrared spectra were obtained with a Perkin-Elmer Model 337 grating spectrophotometer using Nujol mulls between KBr 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 use of Nujol mulls supported on filter paper.[15]

Magnetic Measurements.—Magnetic moments were determined by the Gouy method at room temperature using Hg[Co(NCS)$_4$] as the standard. The observed values were corrected for the diamagnetism of the ligands.[16]

Conductance Measurements.—The measurements were performed with an Industrial Instruments Model RC-16B conductivity bridge on approximately 10^{-3} *M* nitromethane solutions.

TABLE I

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

Compound	Color	Dec. pt., °C.	Λ_M,[b] cm.²/ohm *M*	E_{max}, cm.$^{-1}$ (ϵ) Visible spectra bands[c]		Analyses C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	S, % Calcd.	S, % Found	As or P, % Calcd.	As or P, % Found	Halogen, % Calcd.	Halogen, % Found
TSA	Colorless	164–166	0.7			56.74	56.83	4.76	4.78	21.64	21.48	16.85	16.50		
TSP	Colorless	174–176	0.5			62.97	62.92	5.28	5.43	24.02	24.14	7.73	7.48		
[Ni(TSP)1](ClO$_4$)	Dark green	222–225	90	19,500 sh (250[d])	15,060 (1100)	36.79	37.01	3.09	3.20	14.03	13.75	4.52	4.58		
[Ni(TSP)Br](ClO$_4$)	Dark blue	230–233	91	20, 750 (278)	15,150 (1170)	39.49	39.56	3.31	3.40	15.06	14.85	4.85	4.95		
[Ni(TSP)Cl](ClO$_4$)	Dark blue	241–242	99	20,960 (303)	15,390 (1260)	42.45	42.73	3.56	3.57	16.19	15.97	5.21	5.30	11.93	12.03
[Ni(TSP)(NCS)](ClO$_4$)	Dark blue	215–217	96	20,830 (900)	16,100 (1840)	42.84	42.96	3.43	3.64	20.79	21.07	5.02	5.08	5.75	5.80
[Ni(TSP)(etu)$_2$](ClO$_4$)$_2$	Red[e]	155–157	188	23,600 sh (371)	16,700 (915)	37.60	37.42	3.86	4.00	18.59	18.44	3.59	3.55		
[Ni(TSP)(tu)](ClO$_4$)$_2$	Blue-black	227–228	185	24,100 sh (1015)	16,850 (2470)	35.98	36.21	3.43	3.59	17.47	17.66	4.22	4.24	9.66	9.91
[Ni(TSP)(P(C$_6$H$_5$)$_3$)](ClO$_4$)$_2$	Purple	224–226	196	25,510 (14,000)	18,180 (1170)	50.89	50.74	3.94	3.75	10.45	10.31	6.73	6.82	7.70	7.83
[Ni(TSP)(P(C$_6$H$_5$)$_2$CH$_3$)](ClO$_4$)$_2$	Purple	219–221	180	26,800 (12,400)	18,500 (960)	47.57	47.44	3.99	4.03	11.21	11.50			8.26	8.48
[Ni(TSP)$_2$](ClO$_4$)$_2$	Brown	222–224	181	26,310 (9800)	21,650 (3540)	47.65	47.96	4.00	4.25	18.17	18.14	5.85	5.85	6.70	6.90
[Ni(TSP)((C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$)](ClO$_4$)$_2$	Brown	235–238	166	*f*	*f*	53.42	53.40	4.30	4.42	9.10	9.29	8.79	8.81	6.72	6.59
[Ni(TSP)Br$_2$]	Green	243–244	60[g]	*h*	*h*	40.74	40.48	3.42	3.52	15.54	15.40	5.00	4.93	25.82	25.63
[Ni(TSP)Br]$_2$[NiBr$_4$]	Dark blue	236–239	160	20,750 (555)	15,150 (2370)	34.63	34.32	2.91	3.05	13.21	12.88	4.25	4.33	32.91	32.73

[a] All of the complexes except [Ni(TSP)Br$_2$] and [Ni(TSP)Br]$_2$[NiBr$_4$] are diamagnetic. μ_{eff} = 3.2 B.M. for [Ni(TSP)Br$_2$] and 4.1 B.M. for the [NiBr$_4$]$^{2-}$ ion in the [Ni(TSP)Br]$_2$[NiBr$_4$] complex. For the calculations the cation [Ni(TSP)Br]$^+$ was assumed to be diamagnetic, as in [Ni(TSP)Br]ClO$_4$. [b] For approximately 10^{-3} *M* nitromethane solutions at 25°. [c] Dichloromethane solutions, except ethylenethiourea and thiourea complexes, for which nitromethane was used; sh, shoulder. [d] The extinction coefficient of the Gaussian curve under this shoulder is estimated at 250. [e] This red compound dissolved to produce a blue solution; its solid spectrum is shown in Figure 2D. [f] The visible solution spectrum in nitromethane consisted of a broad intense band extending into the ultraviolet with barely perceptible shoulders. The more informative solid spectrum is shown in Figure 2E. [g] The nitromethane solution was an intense blue color, indicating formation of trigonal-bipyramidal [Ni(TSP)Br]$^+$ species. [h] The compound decomposes in dichloromethane or nitromethane; the solid spectrum shows bands at 11,100 (broad) and 14,600 cm.$^{-1}$ (sh).

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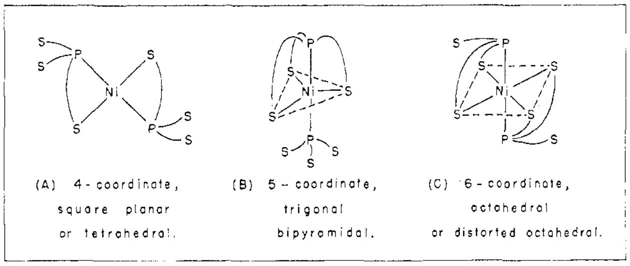
(16) N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 403.

Discussion

The properties and analytical data for the nickel(II) complexes of tris(*o*-methylthiophenyl)phosphine are listed in Table I. The corresponding arsenic ligand tris(*o*-methylthiophenyl)arsine shows no reaction with nickel salts, whereas the phosphorus ligand gives immediate intensely colorful reactions. The same difference in behavior toward nickel(II) is noted with triphenylarsine and triphenylphosphine. Triphenylarsine does not react, whereas triphenylphosphine gives distorted tetrahedral complexes, *e.g.*, $[Ni(P(C_6H_5)_3)_2Br_2]$.[17] However, some polydentate arsenic chelating ligands form relatively stable complexes with nickel(II).[2,7,8]

The complexes $[Ni(TSP)X](ClO_4)$, where X = I, Br, Cl, or NCS, are all diamagnetic and 1:1 electrolytes in nitromethane. The extremely intense ($\epsilon > 10^3$ for the lowest energy electronic absorption band) green to blue colors of the complexes indicate that the structures do not possess a center of symmetry. That all four donor atoms of the tetradentate ligand are coordinated and that the compounds have trigonal-bipyramidal structures is indicated by the visible and ultraviolet solution spectra, which clearly show two ligand-field bands with shapes, energy positions, and intensities characteristic of this structure.[2,4,18] Since the spectra of the solid complexes exhibit the same band contours and λ_{max} as are obtained in solution, the trigonal-bipyramidal structure is preserved also in the solid state.

An attempt to prepare [Ni(TSP)Br]Br by adding nickel bromide to the ligand in acetone gave a green compound, probably a distorted tetrahedral $[Ni(TSP)Br_2]$ with two sulfur atoms of the tetradentate ligand uncoordinated. Its magnetic moment is 3.2 B.M., and its solid spectrum (showing a broad absorption maximum at 11,100 cm.$^{-1}$ with a marked shoulder at 14,600 cm.$^{-1}$) resembles that of $[Ni(P(C_6H_5)_3)_2Br_2]$. The latter complex exhibits reflectance maxima at 10,700 and 16,900 cm.$^{-1}$.[19] In nitromethane, the $[Ni(TSP)Br_2]$ complex gives an intense blue solution, presumably due to a bromide dissociation and subsequent formation of the five-coordinate $[Ni(TSP)Br]^+$ species. Excess nickel bromide in acetone causes precipitation of the $[Ni(TSP)Br]_2[NiBr_4]$ complex, the solid spectrum of which shows a low-energy band at 7050 cm.$^{-1}$, characteristic of the tetrahedral $[NiBr_4]^{2-}$ ion,[20] as well as a more intense band at 15,150 cm.$^{-1}$, due to the trigonal-bipyramidal $[Ni(TSP)Br]^+$ ion. These results are to be contrasted with those obtained with the aryl tetraarsine ligand, QAS,[2] where the five-coordinate [Ni(QAS)Br]Br was readily obtained with no tendency for the free bromide ion to coordinate even in the solid state, and where a tetrabromonickelate(II) derivative was not obtained even in the presence of a large excess of nickel bromide.



(A) 4-coordinate, square planar or tetrahedral.
(B) 5-coordinate, trigonal bipyramidal.
(C) 6-coordinate, octahedral or distorted octahedral.

Figure 1.—Various possible structures for the $[Ni(TSP)_2]^{2+}$ ion.

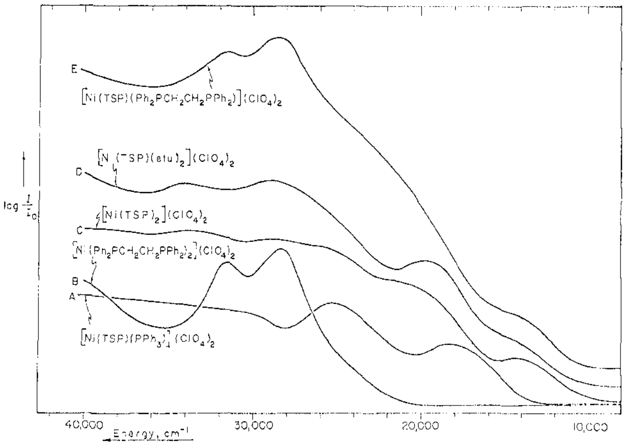


Figure 2.—Solid state electronic spectra of the nickel(II)-tris(*o*-methylthiophenyl)phosphine complexes.

The QAS ligand also gave complexes with nickel nitrate or perchlorate containing one coordinated nitrato or perchlorato group. In contrast, tris(*o*-methylthiophenyl)phosphine gives no complex with nickel nitrate, whereas the sparingly soluble diamagnetic $[Ni(TSP)_2](ClO_4)_2$ complex crystallizes rapidly from nickel perchlorate solutions. It is highly improbable that all eight potential donor atoms in this compound are coordinated to nickel. Several possible structures are represented in Figure 1. The diamagnetic character of the compound eliminates cubic, tetrahedral, or regular octahedral stereochemistries. The solid (Figure 2C) and solution spectra (Table I) show bands at 14,200, 21,500, and 26,300 cm.$^{-1}$. These energies might result from a distorted octahedral arrangement of ligand atoms, with a strong and directional ligand field produced by the two phosphorus atoms. The bands are broader than usual, perhaps indicating the considerable distortion from a regular octahedral structure which must exist in a d^8 diamagnetic complex. For comparison, the solid spectrum of a square-planar complex, $[Ni((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2](ClO_4)_2$, is shown in Figure 2A; the lowest energy band occurs at 28,500 cm.$^{-1}$, about twice the energy of the first band of $[Ni(TSP)_2](ClO_4)_2$. If the compound had a trigonal-bipyramidal structure as in Figure 1B, the solid spectrum should closely resemble that of $[Ni(TSP)(P(C_6H_5)_3)](ClO_4)_2$. However, the spectrum of the latter (Figure 2B) is quite different. A distorted octahedral structure is therefore assigned to the compound. As further evidence, the complex

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(17) L. M. Venanzi, *J. Chem. Soc.*, 719 (1958).

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$\{Ni[C_6H_5P(o\text{-}C_6H_4SCH_3)_2]_2\}(ClO_4)_2$ was prepared.[21] The absorption spectrum of the solid compound is similar to that of $[Ni(TSP)_2](ClO_4)_2$.

Five-coordinate complexes of the type $[Ni(TSP)L](ClO_4)_2$, where L is a neutral ligand such a triphenylphosphine, methyldiphenylphosphine, or thiourea, were obtained from the reaction between nickel perchlorate and TSP in the presence of excess of the ligand L. Attempts to prepare the corresponding triphenylarsine, dibenzyl sulfide, pyridine, and triphenylphosphine oxide complexes gave only $[Ni(TSP)_2](ClO_4)_2$. When ethylenethiourea was used, a red diamagnetic complex $[Ni(TSP)(etu)_2](ClO_4)_2$ crystallized from the intense blue solution. The red complex dissolves in various solvents to give a blue solution, indicating formation of the trigonal-bipyramidal $[Ni(TSP)(etu)]^{2+}$ species, but it always crystallizes from the solution in the red form with two coordinated ethylenethiourea molecules. The spectrum of the solid, with three broad bands (Figure 2D), is similar to that of $[Ni(TSP)_2](ClO_4)_2$ (Figure 2C), indicative of a six-coordinate structure in the solid state. However, the spectrum of the blue solution is typical of a trigonal-bipyramidal complex.

By the use of the bidentate phosphine ligand $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, the diamagnetic compound $[Ni(TSP)((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)](ClO_4)_2$ was obtained. The spectrum of the solid compound (Figure 2E) indicates a distorted octahedral structure for this complex also, *i.e.*, all the donor atoms of the tetradentate and bidentate ligands appear to be coordinated.

The above complexes are obtained readily in a very pure state. Most are destroyed when warmed with water or methanol, and some with ethanol, but all appear to be stable in 1-butanol. The complexes which are 1:1 electrolytes are very soluble in dichloromethane, whereas the 2:1 electrolytes are only sparingly soluble.

The infrared spectrum of the thiocyanato complex shows a very strong band at 2090 cm.$^{-1}$ (C≡N stretch) and a medium band at 858 cm.$^{-1}$, confirming coordination through the nitrogen atom.[22] The N—H stretching frequencies and the C=S band in the spectrum of the thiourea complex confirm that coordination occurs through sulfur.[23,24] All of the perchlorate complexes showed intense infrared bands at 1100 (broad) and 625 cm.$^{-1}$ (sharp). Neither of these bands was split, indicating that perchlorato coordination did not occur in the solid state.[25,26]

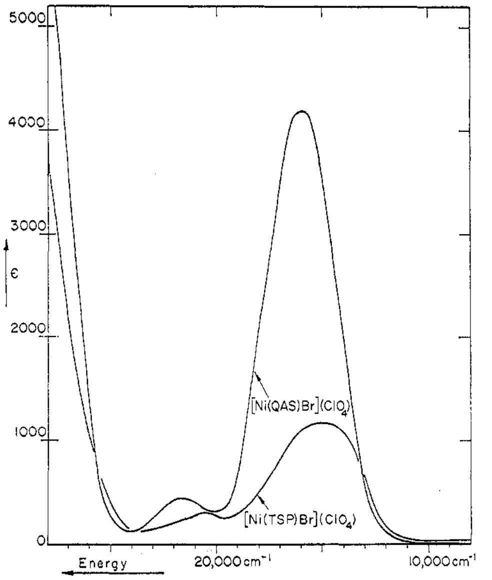

Figure 3.—Electronic absorption spectra of two trigonal-bipyramidal nickel(II) complexes in dichloromethane solution.

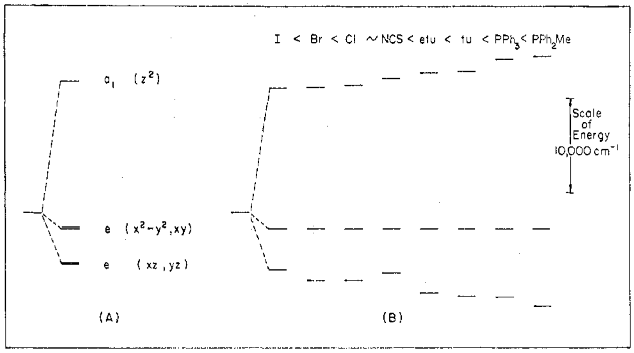

Figure 4.—d-Orbital energy-level splittings in trigonal-bipyramidal complexes.

The trigonal-bipyramidal complexes $[Ni(TSP)X]ClO_4$ or $[Ni(TSP)L](ClO_4)_2$ exhibit characteristic electronic absorption spectra. Two bands, which are assigned as ligand field bands, move to higher energy in the order: $X \text{ or } L = I < Br < Cl \sim NCS < etu < tu < P(C_6H_5)_3 < P(C_6H_5)_2CH_3$. This is exactly the behavior expected from the spectrochemical series. The similarity of the spectra of corresponding TSP and QAS complexes is illustrated in Figure 3. As with the QAS complexes,[2,18,27] the bands are assigned to the two $^1A_1 \rightarrow {}^1E(D)$ transitions, which correspond to electronic transitions from the two e levels to the a_1 level (Figure 4A). Thus, the energies of the two bands permit the d-orbital energy-level splittings in the complexes to be compared directly (Figure 4B). The relative energies happen to coincide remarkably well with those calculated by Basolo and Pearson[28] using a crystal field model for a d^1 system.

The lower-energy band in each spectrum is Gaussian in shape, indicating that the nickel ion is surrounded by a symmetrical trigonal field. (Deviation from C_{3v} symmetry would resolve the degeneracy of the $d_{x^2-y^2}$ and d_{xy} orbitals, which lie in the equatorial plane, and would result in a broad non-Gaussian band in the visible spectrum). The intensity of the lower-energy band varies only slightly (ϵ 915–2470) with a change of the ligand in the fifth (axial) position. The intensity of

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[21] The authors wish to thank M. Workman for supplying a sample of the tridentate ligand, $C_6H_5P(o\text{-}C_6H_4SCH_3)_2$.

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this band (due to transitions between the $d_{x^2-y^2}$, d_{xy} orbitals and the d_{z^2} orbital) may reflect the extent of metal-to-ligand π back bonding between the $d_{x^2-y^2}$, d_{xy} orbitals of the metal and the empty d orbitals of the sulfur. If this is so, the π-bonding character of the Ni–S bond appears to remain approximately constant throughout this series and to be substantially less than that of the Ni–As bond in the corresponding QAS complexes (Figure 3).

The intensity of the higher-energy band varies rather systematically whenever the fifth ligand is Cl, Br, I, NCS, etu, and tu (ϵ 250–1015), but it is considerably greater whenever L = $P(C_6H_5)_3$ or $P(C_6H_5)_2CH_3$ ($\epsilon \sim 12{,}000$). The data suggest that the higher-energy band may be sensitive to the π-bonding nature of the two ligands in the apical positions of the trigonal bipyramid. Further studies are in progress to test these observations.

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Thiocyanatocarbonyl Complexes of Manganese(I)[1]

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A series of thiocyanatocarbonyl complexes of manganese(I) was prepared by reaction of thiocyanatopentacarbonylmanganese(I) with neutral ligands L, where L is an amine, phosphine, arsine, or stibine, and/or by metathesis involving analogous chloro or bromo complexes and potassium thiocyanate. The infrared spectra suggest that the tetracarbonyls, $Mn(CO)_4L(SCN)$, are sulfur-bonded in the solid phase and chloroform solutions, whereas the *trans* and *cis* tricarbonyls, $Mn(CO)_3L_2(CNS)$, are nitrogen-bonded, the apparent exceptions being *cis*-$Mn(CO)_3[As(C_6H_5)_3]_2SCN$ and *cis*-$Mn(CO)_3[Sb(C_6H_5)_3]_2SCN$. A possible explanation of these modes of manganese–thiocyanate attachment is offered in terms of $Mn{=}C{=}O$ π bonding. Some unusual spectral features of the nitrogen-bonded *cis* tricarbonyls are also presented and interpreted on the basis of the proposed bonding hypothesis. It is suggested that steric factors play a major role in stabilizing manganese–sulfur linkage in the *cis* tricarbonyls containing triphenylarsine and -stibine. Finally, metal–thiocyanate bonding in six-coordinate manganese(I) carbonyls is compared with that in four-coordinate palladium(II) complexes.

Introduction

Recently, we have reported the synthesis of thiocyanatopentacarbonylmanganese(I),[3] which represents the first simple thiocyanato metal carbonyl. Infrared spectral studies on this complex suggested that equilibria between the linkage isomers are established in several solvents and that the S- and N-bonded species prevail in the solid phase and acetonitrile, respectively. Because of a facile interconversion of the two linkage forms of $Mn(CO)_5CNS$,[4] it was of interest to investigate the effect of partial replacement of the carbonyl groups by various neutral ligands on the mode of manganese–thiocyanate attachment in the resultant derivatives.

That the nature of other ligands in a complex can strikingly influence the bonding of a coordinated thiocyanate has been clearly demonstrated for palladium(II) and platinum(II) square-planar compounds by Turco and Pecile[5] and, more recently, by Burmeister and Basolo.[6] The latter authors suggest that a delicate balance of both electronic and steric factors is responsible for the observed variations in the mode of metal–thiocyanate attachment.

Unlike the four-coordinate complexes above, "octahedral" thiocyanato compounds have not yet been systematically studied with respect to the bonding. This may be due, at least in part, to a greater stereochemical complexity of six-coordinate compounds. Indeed, a thorough study of metal–thiocyanate bonding requires synthesis of a number of representative complexes and a complete knowledge of their structures. Such information is frequently not available.

The above difficulty could be conceivably avoided in the investigation of thiocyanatomanganese(I) carbonyl complexes. By analogy with the halogenopentacarbonyls, $Mn(CO)_5CNS$ is expected to undergo substitution reactions with a variety of neutral[7] and negatively-charged[8] ligands. For $Mn(CO)_5X$ (X = Cl, Br, I), these reactions are generally highly stereospecific, and the structures of the products can be often elucidated by infrared spectroscopy. Therefore, derivatives of $Mn(CO)_5CNS$ offer a systematic approach to the study of various effects that the nature and position of different ligands in the complex exert on the mode of manganese–thiocyanate attachment.

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[2] Based on the Ph.D. thesis submitted by M. F. F. to The Ohio State University, Aug. 1964.

[3] M. F. Farona and A. Wojcicki, *Inorg. Chem.*, **4**, 857 (1965).

[4] The symbols NCS and SCN designate N- and S-bonding, respectively; CNS denotes that either the bonding is not known or both isomers are present in equilibrium.

[5] A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

[6] J. L. Burmeister and F. Basolo, *Inorg. Chem.*, **3**, 1587 (1964).

[7] R. J. Angelici, F. Basolo, and A. J. Poë, *J. Am. Chem. Soc.*, **85**, 2215 (1963), and references therein.

[8] E. W. Abel and I. S. Butler, *J. Chem. Soc.*, 434 (1964); also, R. J. Angelici, *Inorg. Chem.*, **3**, 1099 (1964).