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Syntheses and Phosphorus-31 NMR Studies of Five-Coordinate Nickel(II) Complexes of the New Ligand Tris(*o*-(dimethylarsino)phenyl)phosphine

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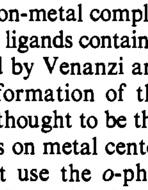
A series of low-spin, five-coordinate nickel(II) complexes of the new tripod ligand tris(*o*-(dimethylarsino)phenyl)phosphine, Ptas, have been synthesized and characterized by elemental analyses, infrared and electronic absorption spectroscopy, and $^{31}P\{^1H\}$ NMR spectroscopy. All of the complexes possess trigonal-bipyramidal coordination geometries in which the Ptas ligand occupies one apical and the three equatorial positions; the monodentate fifth ligand occupies the apical position trans to the phosphorus atom. Phosphorus-31 NMR spectroscopy provides a sensitive method for determining the effect of the fifth ligand on the chemical shift of the apex phosphorus atom and the mode of bonding for the ambidentate thiocyanato ligand.

Introduction

Considerable interest in the syntheses, properties, and reactions of five-coordinate transition-metal complexes[2,3] has resulted since the tripodlike tetradentate ligands containing group V (15[29]) donor atoms were first reported by Venanzi and co-workers.[4] One of the factors involved in formation of the trigonal-bipyramidal coordination geometry is thought to be the geometrical constraint imposed by tripod ligands on metal centers, particularly by rigid tetradentate ligands that use the *o*-phenylene connection. A low-spin d^8 electronic configuration (e.g., Co(I), Ni(II)) appears to be another factor that favors a trigonal-bipyramidal geometry with the heavier donor atoms of group V (e.g., P, As, Sb). Generally, tripod ligands occupy one axial and three equatorial sites in trigonal-bipyramidal complexes, with a monodentate ligand occupying the remaining axial site:

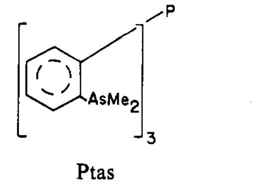


L′ = N, P, As, Sb, Bi
L = group V or VI donor groups
X = neutral or anionic ligands

The spectrochemical and stereochemical properties of five-coordinate complexes containing tripodal tetradentate ligands can be varied by substitution of either the apical, equatorial, or monodentate ligand groups. A previous study had shown that a change of the apical atom of the tetradentate ligand in the complexes $[Ni(QL)X][BPh_4]$ (where QL is $(o\text{-}Ph_2PC_6H_4)_3P$, $(o\text{-}Ph_2PC_6H_4)_3As$, and $(o\text{-}Ph_2PC_6H_4)_3Sb$ and X is Cl and I) gave an anomalous spectrochemical order: P > As < Sb.[6] This effect was attributed to compression of the apical metal–ligand bond caused by the tight *o*-phenylene connecting linkage. A series of related ligands, Qas,[7] Sbtas,[8] and Bitas,[9] which contains *o*-dimethylarsino donor groups, also form five-coordinate nickel(II) complexes. Both arsenic and antimony analogues form trigonal-bipyramidal complexes, whereas the bismuth analogue forms square-pyramidal complexes.

Both stereochemical and spectrochemical properties reflect the nature of axial and equatorial donor groups in trigonal-bipyramidal complexes. Tetradentate ligands such as $P(\sim\sim D)_3$, containing different sets of donor atoms D, can be studied by ^{31}P NMR spectroscopy. Recent studies in this laboratory[10] on the complexes $[M(PP_3)L]X$ (where M is Co(I) and Ni(II) and PP_3 is tris(2-(diphenylphosphino)ethyl)phosphine) revealed large coordination chemical shifts ($\Delta(P)$ = 160–200 ppm) for the apical phosphine; the magnitude of $\Delta(P)$ was a function of the trans ligand, L. The chemical shifts of both apical and equatorial phosphorus groups were sensitive to variations of L.[10] The observed Δ order I > Br > Cl is opposite to that predicted on the basis of electronegativity of the halides.

As part of a continuing ^{31}P NMR study of the nature of trans influences in trigonal-bipyramidal complexes, we have synthesized the new ligand tris(*o*-(dimethylarsino)phenyl)phosphine, Ptas, and



Ptas

a series of its complexes, $[Ni(Ptas)L](AsF_6)_n$, where $n = 2$ for neutral and $n = 1$ for anionic ligands L. We report herein the synthesis and results of ^1H and ^{31}P NMR and electronic spectroscopic studies on these complexes.

Experimental Section

Reagents and Chemicals. Reagent grade chemicals were used as received unless stated otherwise. Phosphorus trichloride, triethylphosphine, *n*-butyllithium, 2,2-dimethoxypropane, and sodium thiocyanate were obtained from Aldrich Chemical Co. Sodium thiocyanate-^{15}N (99 atom %) was obtained from MSD Isotopes. Trimethyl phosphite was obtained from Strem Chemical Co.; triphenylphosphine (Carlisle Chemical Co.) was recrystallized from ethanol, dried, and stored under nitrogen. Nickel nitrate hexahydrate, potassium cyanide, and potassium iodide were obtained from Baker Chemical Co. Anhydrous nickel bromide and lithium hexafluoroarsenate were obtained from Alfa Inorganics. Nickel chloride hexahydrate and nickel perchlorate hexahydrate were obtained from MCB Manufacturing Chemists and G. Frederick Smith Chemical Co.,

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respectively. Organic solvents were purified by standard methods, and petroleum ether (35–60 °C) from MCB Manufacturing Chemists was purified as described in the literature.[11]

Instrumentation. Fourier-mode, broad-band proton-decoupled ^{31}P NMR spectra were obtained by use of a Bruker HX-90 spectrometer operating at 36.43 MHz. Trimethyl phosphate and deuterated acetone were sealed in a coaxial insert suited for 10-mm tubes and used for the secondary external reference (δ 1.59 relative to 85% H_3PO_4 standard) and deuterium lock, respectively. Positive chemical shifts are downfield from the standard. Proton NMR spectra were obtained with an IBM NR-80 spectrometer operating at 80 MHz and referenced to internal Me_4Si.

Infrared spectra of solid complexes in KBr pellets were recorded with a Perkin-Elmer 283 B grating spectrometer from 4000 to 200 cm^{-1} and were calibrated with use of polystyrene film. All complexes exhibited strong, sharp bands in the regions 690–695 and 392–395 cm^{-1}, characteristic of an ionic hexafluoroarsenate counterion. Infrared bands for the presence of the Ptas ligand in the nickel coordination complexes were readily assigned.

Electronic spectra were obtained on $\sim 2 \times 10^{-4}$ M solutions of the complexes in dichloromethane in 1.00-cm quartz cuvettes with a Beckman DU-7 spectrophotometer. Chemical analyses were performed by MHW Laboratories,[12] and mass spectral analysis of Ptas was obtained with a Finnigan 4021 mass spectrometer.[13]

Synthesis of Ptas. The new tetradentate ligand tris(*o*-(dimethylarsino)phenyl)phosphine was synthesized by a procedure similar to that used for Qas, tris(*o*-(dimethylarsino)phenyl)arsine.[7,14] The starting material, *o*-bromophenyldimethylarsine, was prepared as described previously.[7,14] To 1.55 M *n*-BuLi (46.2 mL, 0.072 mol) in hexane under an atmosphere of dry N_2 was added petroleum ether (100 mL). To this solution was added freshly distilled (*o*-bromophenyl)dimethylarsine (18.7 g, 0.072 mol) in petroleum ether (50 mL) dropwise over a 0.5-h period. The reaction was sufficiently exothermic to cause the solution to reflux; after the addition was complete, refluxing was continued for an additional 1.5 h. The resultant solution was cooled to room temperature, and then PCl_3 (2.09 mL, 0.0239 mol) in hexane was added over 1.5 h, followed by refluxing for 2 h. The reaction was quenched with a deareated saturated aqueous NH_4Cl solution. The resulting pale yellow solid was separated and dissolved under N_2 in CH_2Cl_2, which was then dried with anhydrous $MgSO_4$. After removal of the $MgSO_4$ by filtration under N_2, the solvent was removed by controlled vacuum distillation, which also removed lower molecular weight products and unreacted starting material. The solid residue that remained was recrystallized from degassed 1:1 MeOH/EtOH under N_2 and dried in vacuo. The pale yellow, air-sensitive crystals melt at 121 °C and have a mass spectral parent ion of 574; yield 2.1 g (15%). Anal. Calcd for $C_{24}H_{30}As_3P$: C, 50.20; H, 5.27; P, 5.39. Found: C, 50.37; H, 5.31; P, 5.45.

Syntheses of Nickel Complexes. Schlenk apparatus and oxygen-free, dry N_2 were used in the syntheses of all complexes. Decomposition points of the complexes exceed 320 °C. Satisfactory C, H, and X microanalyses were obtained for all of the complexes reported; the data are included as supplementary material.

[NiCl(Ptas)]AsF$_6$. To a 100-mL flask flushed with N_2 containing $NiCl_2{\cdot}6H_2O$ (0.166 g, 0.70 mmol), $LiAsF_6$ (0.16 g, 0.80 mmol), and 1:1 MeOH/EtOH (25 mL) was added Ptas (0.40 g, 0.70 mmol) in CH_2Cl_2 (10 mL). A dark purple solution formed immediately. After the solution was stirred for 10 h, CH_2Cl_2 was partially removed by vacuum distillation, and the resultant purple microcrystals were collected on a frit and dried in vacuo; yield 0.52 g (87%).

[NiBr(Ptas)]AsF$_6$. A procedure analogous to that for the synthesis of the chloro complex was used except that anhydrous $NiBr_2$ was used as the starting material; yield 0.52 g (82%).

[NiI(Ptas)]AsF$_6$. To a 50-mL flask was added $Ni(NO_3)_2{\cdot}6H_2O$ (0.050 g, 0.20 mmol), KI (0.033 g, 0.20 mmol), $LiAsF_6$ (0.078 g, 0.40 mmol), and MeOH (10 mL); the resultant mixture was filtered to remove KNO_3. To the clear green solution was added Ptas (0.12 g, 0.20 mmol) in CH_2Cl_2 (10 mL); immediately, an intense blue-black solution formed. This solution was stirred overnight, and black crystals formed. These were collected and dried in vacuo; yield 0.114 g (0.12 mmol, 60%).

[Ni(CN)(Ptas)]AsF$_6$. The cyano complex was prepared by a procedure similar to that for the iodo complex. Infrared spectral analysis[15] of the microcrystalline product indicated the presence of the cyano group by ν(CN) at 2108 cm^{-1}; yield 0.078 g (29%).

[Ni(Ptas)P(OMe)$_3$](AsF$_6$)$_2$. To a 50-mL Schlenk flask under a N_2 atmosphere were added $Ni(NO_3)_2{\cdot}6H_2O$ (0.071 g, 0.25 mmol) and $LiAsF_6$ (0.14 g, 0.74 mmol) in MeOH (12 mL); then a solution[16] of Ptas (0.14 g, 0.25 mmol) in CH_2Cl_2 (5 mL) was added. An intense purple solution formed immediately. $P(OMe)_3$ (0.30 mL, 0.25 mmol) was added by syringe, and the solution became orange. The resulting solution was stirred overnight at room temperature, and then part of the CH_2Cl_2 was removed. The resultant air-stable, microcrystalline orange crystals were collected on a frit; yield 0.21 g (74%).

[Ni(NO$_3$)(Ptas)]AsF$_6$. To a 50-mL flask were added $Ni(NO_3)_2{\cdot}6H_2O$ (0.12 g, 0.41 mmol), 2,2-dimethoxypropane (0.50 mL, 4.0 mmol), $LiAsF_6$ (0.18 g, 0.90 mmol), and MeOH (15 mL) under N_2. After the solution was stirred at 20 °C for 12 h, Ptas (0.23 g, 0.40 mmol) in CH_2Cl_2 (5 mL) was added. The resulting blue-black solution was stirred for 6 h followed by partial removal of solvent. The resulting blue-black crystals were collected and dried in vacuo. An infrared spectrum indicated the presence of coordinated nitrate; yield 0.28 g (79%).

[Ni(Ptas)PPh$_3$](AsF$_6$)$_2$. To a solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (0.073 g, 0.20 mmol), $LiAsF_6$ (0.098 g, 0.50 mmol), and PPh_3 (0.066 g, 0.25 mmol) in 1:1 MeOH/EtOH (15 mL) was added a solution of Ptas (0.12 g, 0.20 mmol) in CH_2Cl_2 (5 mL). After the mixture was stirred for 12 h, crimson microcrystals were collected; yield 0.21 g (80%).

[Ni(Ptas)PEt$_3$](AsF$_6$)$_2$. A solution of [NiCl(Ptas)]AsF_6 (0.15 g, 0.18 mmol) and $LiAsF_6$ (0.034 g, 0.18 mmol) in 1:1 MeOH/EtOH was prepared. To this resulting slurry was added PEt_3 (0.026 mL, 0.18 mmol) via a syringe; the color of the solution changed quickly from blue-black to orange-red. After the mixture was stirred for 12 h, red crystals were collected and dried in vacuo; yield 0.17 g (82%).

[Ni(CNS)(Ptas)]AsF$_6$. Complexes of this formula were obtained by two methods. To a 50-mL flask were added $Ni(ClO_4){\cdot}6H_2O$ (0.096 g, 0.26 mmol), NaSCN (0.024 g, 0.30 mmol), $LiAsF_6$ (0.078 g, 0.40 mmol), and 1:1 MeOH/EtOH (20 mL). To this solution was added Ptas (0.15 g) in CH_2Cl_2 (5 mL). The resulting mixture was stirred for 12 h, and then dark purple microcrystals were collected and dried in vacuo; yield 0.17 g (76%). The second preparative method used the metathetical reaction of NaSCN with [Ni(NO$_3$)(Ptas)]AsF_6. To a solution of [Ni(NO$_3$)(Ptas)]AsF_6 (0.14 g, 0.16 mmol) and $LiAsF_6$ (0.031 g, 0.16 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added a solution of NaSCN (0.016 g, 0.20 mmol in MeOH (5 mL). After the solution was stirred at 0 °C for 12 h and the solvent partially removed, purple microcrystals were obtained and dried in vacuo; yield 0.086 g (62%). The infrared spectrum showed two partially separated absorption bands at 2105 and 2085 cm^{-1} in the solid product from the second procedure; these two peaks indicated the presence of both S- and N-bonded thiocyanato linkage isomers, respectively. The product isolated from the first method exhibited only one broad infrared band in this region, although areas of the ^{31}P NMR resonances indicated that both preparations yielded nearly 50:50 mixtures of the two linkage isomers.

Results and Discussion

Synthetic Procedures. Considerable difficulty was encountered in the synthesis of the ligand Ptas, resulting in yields of ca. 15% compared to ca. 45% for Qas using a similar procedure.[7] Use of petroleum ether (35–60 °C), which had been purified with a sulfuric acid wash and distillation from sodium,[11] gave the best yield. The pale yellow, crystalline solid is moderately air-sensitive; thus, the solid and solutions of Ptas need to be handled under nitrogen, whereas the Ni(II)–Ptas complexes appear to be stable in air for long periods of time, both as solids and in solution.

Methods similar to those previously reported for synthesis of five-coordinate complexes were used for preparation of the new complexes [NiL(Ptas)]$(AsF_6)_n$, where L is Cl^-, Br^-, I^-, NO_3^-, CNS^-, PPh_3, PEt_3, and $P(OMe)_3$. Normal infrared bands for the nonbonded counterion AsF_6^-, at ca. 693 and 394 cm^{-1}, were observed for all complexes.

The thiocyanate complex was prepared by two different routes because the ^1H and ^{31}P NMR spectra showed two distinct methyl and phosphorus environments, indicating a mixture. The potential presence of an aquo ligand[9,17] was eliminated on the basis of (i)

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(16) When a 1:1 MeOH/EtOH solvent mixture was used in the synthesis, a mixture of four complexes, [Ni(Ptas){$P(OMe)_n(OEt)_{3-n}$}]$(AsF_6)_2$, was formed due to solvent–P–OMe interchange as evidenced by the ^{31}P NMR spectra of the product.

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Table I. Absorption Maxima for Electronic Spectra of $[NiL(Ptas)](AsF_6)_n$ Complexes[a]

L	λ_{max}, nm (absorbance)	10^4[complex], M	abs max, 10^3 cm^{-1} (ϵ_{max}, M^{-1} cm^{-1})
Cl^-	541.0 (0.4821)	1.91	18.5 (2520)
	360 (0.130)		27.8 sh ($\gtrsim$400)
Br^-	554.0 (0.455)	1.82	18.1 (2500)
	<300		23.5 sh ($\gtrsim$200)
			33.3
I^-	587.5 (0.3454)	1.81	17.0 (1910)
	431.2 (0.0892)		23.2 (490)
	343.5 (0.8134)		29.1 (4490)
	<310		>32.2
CN^-	413.0 (0.880)	2.41	24.2 (3700)
	292.7 (0.8445) sh		34.2 sh (3500)
	<240		42.1 (>10 000)
$P(OMe)_3$	429.0 (0.362)	1.55	23.3 (2340)
	302.5 (0.441) sh		33.1 sh (2850)
	<250		>40.0
NO_3^-	540.5 (0.519)	2.13	18.5 (2440)
	270.0 (3.134)		23.5 sh (390)
			37.0 (14 700)
PPh_3	522.0 (0.3422)	1.52	19.2 (2250)
	354.8 (1.373)		28.2 (9010)
PEt_3	474.8 (0.360)	1.61	21.1 (2240)
	306.2 (1.046) sh		32.7 (6500)
	260.0 (3.225) sh		38.5 (20 000)
	240.5 (4.249)		41.5 (26 400)
CNS	mixture (N and S bonded)		unresolved

[a] UV–vis spectra were taken on ca. 2×10^{-4} M solutions of the complexes in dichloromethane with use of 1.00-cm cells; sh = shoulder.

metathesis of $[Ni(NO_3)(Ptas)]AsF_6$ with NaSCN under anhydrous conditions, (ii) absence of absorptions due to water in the infrared spectra, and (iii) absence of a signal for an aquo ligand in the ^1H NMR spectrum. Satisfactory microanalysis of $[Ni(CNS)(Ptas)]AsF_6$ indicated that the stoichiometric amount of thiocyanate was present, and the infrared spectrum revealed absorptions at 2105 and 2085 cm^{-1}, which are assigned to both S- and N-bonded thiocyanate. The lower energy band corresponds to the C–N stretch reported[7] for the N-bonded isomer of $[Ni(NCS)(Qas)]SCN$ at 2097 cm^{-1}.

An O-bound nitrato ligand in $[Ni(NO_3)(Ptas)]AsF_6$ is indicated by infrared bands at 1480, 1255, and 990 cm^{-1}, which are assigned[15] to $\nu(N{=}O)$, $\nu_a(NO_2)$, and $\nu_s(NO_2)$, respectively. Similar bands at 1490, 1256, and 976 cm^{-1} were reported[7] for the nitrato group in $[Ni(NO_3)(Qas)]BPh_4$. The infrared band at 2108 cm^{-1} observed for $[Ni(CN)(Ptas)]AsF_6$ is assigned to $\nu(CN)$. Infrared bands at 1010 and 1040 cm^{-1} ($P(OMe)_3$), 1091 cm^{-1} (PPh_3), and 1046 cm^{-1} (PEt_3) indicate the presence of the monodentate phosphorus ligands in their respective complexes.

Electronic Spectra. Ultraviolet and visible spectroscopy on these nickel–Ptas complexes yielded the absorption peaks given in Table I; the λ_{max} and ϵ values are characteristic[2,18] of trigonal-bipyramidal nickel(II) complexes containing tripodlike tetradentate ligands. The position of the lowest energy absorption band is ascribed to the transition $(e'')^4(e')^4 \rightarrow (e'')^4(e')^3(a_1')^1$, and it is very sensitive to the nature of the fifth ligand.[18,19] The asymmetric nature of this band for the bromo and chloro complexes is attributed to the Jahn–Teller effect in the excited state. Changing X from I^- to CN^- causes a blue shift of 7.2×10^3 cm^{-1}; the spectral data produce the spectrochemical series

$$I < Br < Cl \approx NO_3 < PPh_3 < PEt_3 < P(OMe)_3 < CN$$

On the basis of electronic spectra, Ptas exerts a stronger ligand field than PTAS, tris(*o*-(diphenylarsino)phenyl)phosphine. For example, the first d $\leftrightarrow$ d bands for the chloro (18.5×10^3 vs. 16.4×10^3 cm^{-1}) and iodo complexes (17.0×10^3 vs. 15.2×10^3 cm^{-1}) are blue shifted compared to those of the PTAS complexes. The spectral shift is consistent with the greater donor properties of $-AsMe_2$ groups compared to $-AsPh_2$, which is expected from both electronic and steric effects.[20] Also, the first d $\leftrightarrow$ d bands of $[NiL(Ptas)]AsF_6$ ($L = Cl^-, Br^-, I^-, NCS^-, NO_3^-$) occur at slighly higher energies than those of $[NiL(Qas)]BF_4$[7] (Qas = $As(o\text{-}C_6H_4AsMe_2)_3$) in agreement with the normal spectrochemical order, P > As > Sb, observed for complexes of monodentate ligands[21] (all bands in units of 10^3 cm^{-1}):

L	Ptas	Qas[7]
NO_3	18.5	18.3
NCS		18.0
Cl	18.5	17.8
Br	18.1	17.3
I	17.0	16.6

Proton and ^{31}P NMR Spectra. The ^1H and $^{31}P\{^1H\}$ NMR spectra of Ptas and the series of complexes $[NiL(Ptas)](AsF_6)_n$ (where $n = 1$ for L = Cl, Br, I, CN, CNS, and NO_3 and $n = 2$ for PPh_3, PEt_3, and $P(OMe)_3$) were obtained in dichloromethane and are given in Table II. A single $^{31}P\{^1H\}$ resonance was observed at −20.2 ppm for the free ligand Ptas, and the proton resonance for the methyl groups was observed at 1.11 ppm. Corresponding methyl proton resonances for Qas,[7] Sbtas,[8] and Bitas[9] have been reported at 1.15 ($CDCl_3$), 1.20 ($CDCl_3$), and 1.1 ($CDCl_3$), respectively. The resonance signals of the methyl protons shift downfield about 1 ppm on coordination of the tetradentate ligand to Ni(II). Methyl resonances of the dispositive complexes (containing neutral phosphine monodentate ligands) are shifted ca. 0.2 ppm further downfield than those of the monopositive complexes (containing anionic fifth ligands). Observation of only one methyl $\delta(^1H)$ signal for all of the complexes, other than $[Ni(CNS)(Ptas)]AsF_6$, supports the expected trigonal-bipyramidal geometry. Observation of two proton resonances at 1.81 and 1.85 ppm for the thiocyanate complex suggested the presence of a mixture of thiocyanato and isothiocyanato linkage isomers.

The Ni(II) complexes gave simple ^{31}P NMR spectra; downfield shifts of the phosphorus resonances on coordination to metal centers are treated quantitatively as coordination chemical shifts, Δ, defined as $\delta(P_{coord}) - \delta(P_{free\ ligand})$.[22] Values of Δ varied from 113 to 174 ppm for Ni–Ptas complexes, demonstrating the sensitivity of the apical phosphorus δ(Pa) to the influence of the trans ligands. The trans-influence order as determined by the ability of the monodentate ligand to deshield the apical phosphorus atom is

$$I^- > P(OMe)_3 \approx CN^- > Br^- > PEt_3 \approx SCN^- \approx PPh_3 > \mathit{N}CS^- > NO_3^-$$

The range of coordination chemical shifts is not as large as those reported for corresponding Co(I) and Ni(II) trigonal-bipyramidal complexes containing the tetradentate ligand tris(2-(diphenylphosphino)ethyl)phosphine, PP_3.[10] The difference may be due to the more rigid backbone of the *o*-phenylene group in Ptas compared to an ethylene backbone in PP_3.

The rather large downfield Δ's result in part from incorporation of a phosphorus atom as part of a five-membered chelate ring with the increased deshielding designated as Δ_R.[23] The larger deshielding values of Δ_R are characteristic of five-membered chelate rings, whereas four- and six-membered chelate rings exhibit smaller shielding values.[24] In addition $\delta(P_a)$ increases nearly

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Table II. NMR Data[a] for $[NiL(Ptas)](AsF_6)_n$ Complexes

compd	$\delta(^{31}P_2)$[b]	$\delta(^{31}P_1)$	$\Delta(P_2)$,[c] ppm	$^2J_{P_2P_1}$, Hz	$\delta(CH)$[d]
$[NiI(Ptas)]AsF_6$	153.82		174.03		1.85
$[Ni(Ptas)(P(OMe)_3)](AsF_6)_2$[e]	138.95	128.72	159.16	391.9	2.03
$[Ni(CN)(Ptas)]AsF_6$	138.70		158.91		1.83
$[NiBr(Ptas)]AsF_6$	134.68		154.89		1.81
$[Ni(Ptas)(PEt_3)](AsF_6)_2$[f]	130.44	30.96	150.65	200.2	1.99
$[Ni(SCN)(Ptas)]AsF_6$[g]	129.15		149.36		1.85 or 1.81[h]
$[NiCl(Ptas)]AsF_6$	120.64		140.85		1.77
$[Ni(Ptas)(PPh_3)](AsF_6)_2$	118.80	34.73	139.01	205.1	2.06
$[Ni(NCS)(Ptas)]AsF_6$[g]	111.53		131.74		1.85 or 1.81[h]
$[Ni(NO_3)(Ptas)]AsF_6$	93.13		113.34		1.90

[a] Relative to Me_4Si for ^1H NMR and 85% H_3PO_4 for ^{31}P NMR, with downfield shifts recorded as positive. [b] P_2 is defined to be the apical phosphorus atom of Ptas, and P_1 is the phosphorus atom of a monodentate ligand, which is located trans to P_2 along the trigonal-bipyramidal axis. [c] Coordination chemical shifts, $\Delta(P_2)$, are computed from $\delta(P_2) - \delta(P_{free})$, where $\delta(P_{Ptas}) = \delta(P_{free}) = -20.2$. [d] The aromatic protons of the ligand Ptas were generally found between 7.5 and 8.4 ppm. The solvent was CD_2Cl_2. The free ligand Ptas gives $\delta(CH_3) = 1.11$. [e] Trimethyl phosphite protons were observed at 4.41 ppm wtih $^3J_{P_1H} = 9.44$ Hz and $^5J_{P_2H} = 2.10$ Hz for the X part of the ABX pattern. [f] Unresolved multiplets in the proton spectra were observed for the methylene and methyl protons at 2.5 and 3.6 ppm, respectively. [g] Chemical shifts are reported for a mixture of the linkage isomers with the S-bonded isomer being further downfield than the N-bonded isomer. See text for discussion. [h] Assignment uncertain.

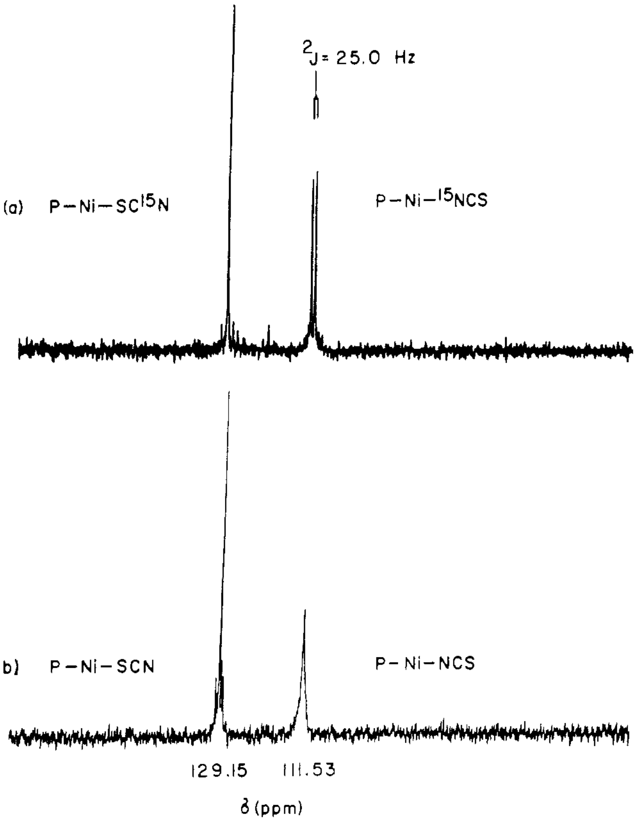

Figure 1. $^{31}P\{^1H\}$ NMR spectra of (a) $[Ni(C^{15}NS)(Ptas)]AsF_6$ and (b) $[Ni(C^{14}NS)(Ptas)]AsF_6$, which indicate the presence of a ca. 50:50 mixture of thiocyanato and isothiocyanato linkage isomers.

additively with the number of chelating five-membered rings to which P_a is attached.[10]

Two phosphorus-31 NMR peaks are observed for $[Ni(CNS)(Ptas)]AsF_6$; the two peaks are attributed to approximately a 50:50 mixture of both S- and N-bonded thiocyanato linkage isomers. The assignment of the two peaks is based on the fact that the higher field peak is broad at room temperature,[25] but it sharpened as the temperature was decreased. This broadening is ascribed to scalar coupling of phosphorus-31 with the quadrupolar nitrogen-14 nucleus.[26] This assignment was supported by the synthesis of the ^{15}N-labeled NCS complexes. Figure 1 shows that one of the ^{31}P NMR peaks is split into a doublet ($^2J_{PNi^{15}N} = 25.0$ Hz) due to the ^{15}N ($I = {}^1/_2$) nucleus; thus, this resonance is assigned to the N-bonded isomer.

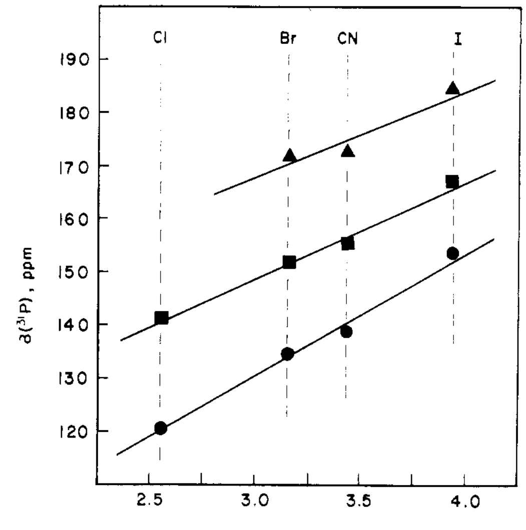

Figure 2. Plot of $^{31}P\{^1H\}$ chemical shifts of $[CoX(PP_3)]$[10] (triangles), $[NiX(PP_3)]AsF_6$[10] (squares), and $[NiX(Ptas)]AsF_6$ (circles) with the "*Q*" parameter reported[27,28] for X in the three series of compounds. Regression analyses of the three series of complexes resulted in $\delta = 16.2Q_X + 119.4$ ($r = 0.961$), $\delta = 18.1Q_X + 94.5$ ($r = 0.997$), and $\delta = 22.9\ Q_X + 61.9$ ($r = 0.996$), respectively.

On the basis of the magnitude of the shift of the ^{31}P resonance, the trans influence of a phosphorus fifth ligand is $P(OMe)_3 > PEt_3 > PPh_3$. A difference of ~10 ppm occurs between each pair of adjacent ligands. There is a significant decrease in the electronegativity of the phosphorus atom between $P(OMe)_3$ and PEt_3, and there is a significant increase in the cone angle between PEt_3 and PPh_3.

An intriguing situation is evident in the trans-influence order of $I^- > Br^- > Cl^-$; this same sequence was observed previously with Ni(II)– and Co(I)–PP_3 complexes.[10] At first, this order appears anomalous since the trend is opposite to that predicted on the basis of electronegativity values of the halides. However, the trend is consistent with the nephelauxetic series in which larger (more polarizable) anions establish a larger effect than expected.

Although little theoretical justification is currently available, the "*Q*" parameter, which has been used to correct for the "ortho" effect on chemical shifts,[27] forms a linear correlation with the phosphorus chemical shifts of these complexes and with those of

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the PP_3 complexes (Figure 2). The semiempirical parameter Q is an approximation to the paramagnetic contribution (second term) in Ramsey's shielding equation.[28] It is assumed that the first ionization potential of the variable substituent, I, should be roughly proportional to the mean excitation energy ΔE, which is not known. The use of a correction factor P/r^3, where P is the polarizability of the bonded atom and r is the interatomic distance, results in the relationship $Q = P/Ir^3$.[27,28]

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Registry No. $[NiCl(Ptas)]AsF_6$, 101348-53-2; $[NiBr(Ptas)]AsF_6$, 101348-55-4; $[NiI(Ptas)]AsF_6$, 101348-57-6; $[Ni(CN)(Ptas)]AsF_6$, 101374-88-3; $[Ni\{P(OMe)_3\}(Ptas)](AsF_6)_2$, 101375-11-5; $[Ni(NO_3)(Ptas)]AsF_6$, 101375-13-7; $[Ni(PPh_3)(Ptas)](AsF_6)_2$, 101348-59-8; $[Ni(PEt_3)(Ptas)](AsF_6)_2$, 101348-61-2; $[Ni(NCS)(Ptas)]AsF_6$, 101348-63-4; $[Ni(SCN)(Ptas)]AsF_6$, 101348-65-6; Ptas, 101348-66-7; PCl_3, 7719-12-2; P, 7723-14-0; (*o*-bromophenyl)dimethylarsine, 4457-88-9.

Supplementary Material Available: A listing of analytical data for $[NiX(Ptas)][AsF_6]_{1,2}$ complexes (1 page). Ordering information is given on any current masthead page.

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(29) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Selenium-77 NMR and Raman Study of $S_xSe_{4-x}^{2+}$ Cations and Crystal Structure of $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$ Containing a Disordered Mixture of $S_xSe_{4-x}^{2+}$ Cations[1]

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The series of "square-planar" cations $S_xSe_{4-x}^{2+}$ (x = 0–3) has been characterized by Raman and ^{77}Se NMR spectroscopy. Chemical shifts range from 587 to 729 ppm with respect to saturated aqueous H_2SeO_3, and the ^{77}Se–^{77}Se coupling constant in SSe_3^{2+} is 336 Hz. The mean ^{77}Se T_1 value is 0.38 s. The structure of $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$ has been determined by X-ray crystallography (monoclinic, space group $B2_1/c$, a = 15.267 (3) Å, b = 13.440 (4) Å, c = 16.437 (6) Å, β = 91.59 (2)°, Z = 4, and R = 0.078 for 3670 observed reflections). Occupational disorder, anion–cation interactions, and the geometry of the $Sb_4F_{17}^-$ anion in this compound are discussed.

Introduction

The species S_4^{2+}, Se_4^{2+}, and Te_4^{2+} were among the first of the polyatomic cations of the chalcogens to be characterized by conductometric and cryoscopic measurements nearly 20 years ago.[3] The square-planar geometry of these cations has since been established by X-ray crystallography.[4-6] Similarly, the mixed cations $Te_xSe_{4-x}^{2+}$ (x = 0–4) have been characterized by ^{77}Se and ^{125}Te NMR studies,[7,8] and the X-ray crystal structures of $(Te_2Se_2)(Sb_3F_{14})(SbF_6)$ and $(Te_{3.0}Se_{1.0})(Sb_3F_{14})(SbF_6)$ have recently been determined.[9] In this investigation we have prepared for the first time the analogous cations $S_xSe_{4-x}^{2+}$. The Se-containing members of this series (x = 0–3) have been characterized in SO_2 solution by ^{77}Se NMR spectroscopy (^{77}Se: spin $^1/_2$, 7.50% natural abundance, 5.26×10^{-4} relative receptivity to ^1H), and the X-ray crystal structure of $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$ has shown this compound to contain a mixture of square-planar $S_xSe_{4-x}^{2+}$ cations along with the novel $Sb_4F_{17}^-$ anion. Although several mixed Te/Se cations and two Te/S cations have been reported,[10-12] this is the

Table I. Crystal Data and Details of X-ray Intensity Measurements and Structure Refinement for $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$

syst	monoclinic
$a \times b \times c$, Å	15.267 (3) × 13.440 (4) × 16.437 (6)
β, deg	91.59 (2)
V, Å^3	3371 (2)
space group	$B2_1/c$
Z/D_c, g cm^{-3}/temp, °C	4/3.68/22
μ, cm^{-1}	84.8
no. of reflns used in cell detn (2θ range, deg)	15 (19–30)
radiation	Mo K$\bar{\alpha}$ (λ = 0.71069 Å), graphite monochromated
max 2θ, deg/scan type	55/θ–2θ
scan range	Kα_1 − 1.0° to Kα_2 + 1.0°
scan rates, deg min^{-1}	6.0–29.3 (dependent on prescan)
std reflns (no./interval)	2/48
quadrants collcd	$h,k,\pm l$
no. of data collcd (incl stds and B-centered reflcns)	8803
abs cor (ABSORB)	A^*: 2.51–3.88
cryst dimens, cm	{0,1,0}: 0.0065 (1,0,1): 0.0135 (0,0,−1): 0.0085 (1,0,0): 0.0085
no. of nonzero data	3670
no. of data with $F > 6\sigma(F)$	2912
R factors	
6σ: R_1 (R_2)	0.0631 (0.0690)
all: R_1 (R_2)	0.0776 (0.0893)
max shift/error (las cycle), %	12
weighting scheme: $w^{-1} = \sigma(F)^2 + GF^2$	G = 0.0088

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