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Trigonal-Bipyramidal Nickel(II) Complexes of Tris(3-dimethylarsinopropyl)stibine

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Trigonal-bipyramidal complexes $[Ni(ligand)X]B(C_6H_5)_4$ *(*$X = Cl, Br, I, NCS, NO_3, CN$*) of the new flexible, quadridentate stibine ligand* $Sb[CH_2CH_2CH_2As(CH_3)_2]_3$ *were prepared and characterized by analyses and by spectral, magnetic, and conductivity measurements. Electronic spectra of three series of trigonal-bipyramidal complexes of the ligands* $D[CH_2CH_2CH_2As(CH_3)_2]_3$ *(*$D = P, As, Sb$*) show that the normal spectrochemical series* $P > As > Sb$ *is obtained for the cyanide and chloride complexes, in contrast to the anomalous spectrochemical order* $P > As < Sb$ *that was observed by Higginson, McAuliffe, and Venanzi*[8] *with the rigid o-phenylene ligands* $(o\text{–}Ph_2L\text{–}C_6H_4)_3L'$ *(*$L =$ *P and As;* $L' = P$*, As, and Sb). The present study with* $Sb[CH_2CH_2CH_2As(CH_3)_2]_3$ *provides confirmatory evidence for a compression effect in the nickel(II) complexes of the rigid ligand* $Sb(o\text{–}C_6H_4LPh_2)_3$*.*

Introduction

Previous papers from this laboratory[1-4] and other laboratories[5-8] have described the characterization of several series of five-coordinate complexes that are formed with «tripod-like» tetradentate ligands containing different donor atoms. The trigonalbipyramidal-nickel(II) complexes of $D[CH_2CH_2CH_2As(CH_3)_2]_3$ ($D = P$, As) are especially interesting since the flexible aliphatic linkages in the ligands allow the metal ion to adopt its preferred coordination number and geometry when surrounded by the soft arsenic and phosphorus donor atoms.

We now report the synthesis of the similar tetradentate ligand, $Sb[CH_2CH_2CH_2As(CH_3)_2]_3$, and the syntheses and characterization of its five-coordinate $[Ni(ligand)X]^+$ complexes. In addition to the electronic spectral comparisons among the three series of trigonal-bipyramidal nickel(II) complexes, the antimony ligand provides some rare examples of $Ni^{II}\text{–}SbR_3$ coordination complexes.

Experimental Section

Preparation of Tris(3–dimethylarsinopropyl)stibine, $Sb[CH_2CH_2CH_2As(CH_3)_2]_3$. The ligand was prepared from antimony trichloride and 3–chloropropyldimethylarsine in a procedure similar to that used in the synthesis of $P[CH_2CH_2CH_2As(CH_3)_2]_3$.[1] As the antimony ligand is a heavy oil at room temperature, it was dissolved in ethanol to give a solution of known concentration; aliquots of this solution were used in the following syntheses.

$[Ni(ligand)X][B(C_6H_5)_4]$ ($X = Cl, Br, I, NCS, NO_3$). An ethanol solution of $Sb[CH_2CH_2CH_2As(CH_3)_2]_3$ (1.0 g, 1.8 mmoles) was added to 20 ml of a warm ethanol solution containing the appropriate nickel(II) salt (2.0 mmoles) and sodium tetraphenylborate (0.66 g, 2.0 mmoles). An immediate intense blue-black color developed and a precipitate formed. The mixture was stirred for an additional 15 min; then the solid was collected on a filter and recrystallized from a dichloromethane-ethanol mixture. Yields, ~70%.

$[Ni(ligand)CN][B(C_6H_5)_4]$. This complex was prepared by a metathesis between $[Ni(ligand)Cl][B(C_6H_5)_4]$ and sodium cyanide (1:1.1 molar ratio) in boiling ethanol.

Spectral, Conductance and Magnetic Measurements. These characterization measurements were obtained as previously reported.[9]

Results and Discussion

Intense blue solutions are formed when nickel(II) salts and tris(3–dimethylarsinopropyl)stibine are combined in ethanol; addition of a large non-coordinating anion such as $B(C_6H_5)_4^-$ results in precipitation of the complexes $[Ni(ligand)X]B(C_6H_5)_4$ ($X = Cl$, Br, I, NCS, NO_3). The cyano complex was prepared by metathesis from $[Ni(ligand)Cl]B(C_6H_5)_4$ by using a slight excess of sodium cyanide. If a large excess of cyanide ion is used, the $[Ni(ligand)CN]^+$ complex is destroyed and $[Ni(CN)_4]^{2-}$ is formed.

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Table I. Physical Properties and Analytical Data for the Nickel(II) Complexes of $Sb[CH_2H_2CH_2As(CH_3)_2]_3$

Compound	Color	$10^6\chi_M$[a]	Λ_M[b]	Analyses %C Calcd.	Analyses %C Found	Analyses %H Calcd.	Analyses %H Found	% Other Calcd.	% Other Found
$[NiLCl]B(C_6H_5)_4$	Violet	63	74.2	47.95	47.01	5.74	5.57		
$[NiLBr]B(C_6H_5)_4$	Blue	34	69.0	45.88	45.30	5.49	5.29		
$[NiLI]B(C_6H_5)_4$	Green-black	19	71.4	43.86	43.17	5.25	5.40	11.90[c]	11.47
$[NiL(NCS)]B(C_6H_5)_4$	Blue	27	76.2	48.10	48.06	5.61	5.39	1.40[d]	1.48
$[NiL(NO_3)]B(C_6H_5)_4$	Blue	36	68.3	46.71	46.09	5.59	5.38	1.40[d]	1.50
$[NiL(CN)]B(C_6H_5)_4$	Deep red	44	79.3	49.69	49.53	5.80	5.73	1.45[d]	1.43

[a] χ_M is the corrected molar susceptibility in c.g.s. units; *i.e.* all of the complexes are diamagnetic with small T.I.P. contributions. [b] Molar conductance values on freshly prepared $1\text{x}10^{-3}M$ solutions in nitromethane. These values are appropriate for uni-univalent electrolytes in nitromethane. [c] Halogen analysis. [d] Nitrogen analysis.

Table II. Electronic Spectral Data for the Nickel(II) Complexes of $Sb[CH_2CH_2CH_2As(CH_3)_2]_3$

Compound	Absorption Maxima, cm^{-1} Solution[a, b]	Absorption Maxima, cm^{-1} Nujol mull, 298°K[c]	Absorption Maxima, cm^{-1} Nujol mull, 77°K[c]
$[NiLCl]B(C_6H_5)_4$	16,400 (1,800)	16,400, 13,800 sh[d]	17,000, 13,700 sh[d]
$[NiLBr]B(C_6H_5)_4$	16,130 (1,695)	16,100, 13,800 sh	15,900, 13,200 sh
$[NiLI]B(C_6H_5)_4$	15,950 (1,420)	16,000[e], 13,900 sh	15,900
$[NiL(NCS)]B(C_6H_5)_4$	17,790 (1,990)	17,800, 15,400 sh	18,100
$[NiL(NO_3)]B(C_6H_5)_4$	18,590 (2,310)[f]	18,850, 16,950 sh	
$[NiL(CN)]B(C_6H_5)_4$	21,300 (3,580)	21,300	

[a] *In* dichloromethane. [b] Molar extinction coefficients are given in parentheses. [c] Transmission spectrum of the finely ground solid complex suspended in Nujol on filter paper; E_{max} values are ±50 cm^{-1}. [d] Sh, shoulder on the side of a more intense absorption band. [e] A broad band with an ill-defined maximum. [f] In acetonitrile.

The complexes that were isolated, together with their analytical data and physical properties, are listed in Table I. All of these complexes are diamagnetic and are uni-univalent electrolytes in nitromethane. Their electronic spetra are all very similar to each other and are virtually identical in both the solid state and in solution (Table II, Figure 1); thus, the structure of the $[Ni(ligand)X]^+$ cations in the solid state is retained in solution.

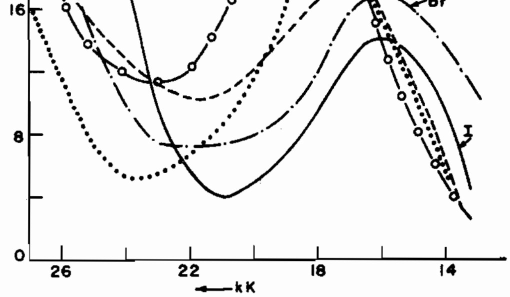

Figure 1. The visible region of the electronic absorption spectra of the $[Ni(SbAs_3)X]B(C_6H_5)_4$ complexes (X=I,——; Br,—·—·—·—·—; Cl, - - - - -; NCS, · · · · ·; NO_3—o—o—o) in dichloromethane solutions. The $P[CH_2CH_2CH_2As(CH_3)_2]_3$ complex has been shown by X-ray crystallography to be a regular trigonal bipyramid.[11]

The electronic spectra exhibit a strong, asymmetric absorption in the range 16,000-22,000 cm^{-1} (ε ~1500-3500) with a weak shoulder on the low-energy side of the band. The transmission spectra of the solids show this shoulder better, especially at 77°K. The spectra of the $SbAs_3$ complexes are very similar to those of the corresponding $AsAs_3$[2] and PAs_3[1] complexes and are characteristic of diamagnetic trigonal-bipyramidal nickel(II) complexes.[1-4,6,10] On the basis of the spectral similarity (Figure 1) and an X-ray structure determination of $[Ni(PAs_3)CN]ClO_4$,[11] which has a C_{3v} arrangement of donor atoms around the nickel ion, it is concluded that these five-coordinate $SbAs_3$ complexes are also trigonal bipyramids. The general structural representation is given in Figure 2. The absorption maxima (Table II) produce a normal spectrochemical series in the $[NiLX]^+$ complexes, as a result of changing the fifth donor, *i.e.*,

$$I < Br < Cl < {-}NCS < NO_3 < CN.$$

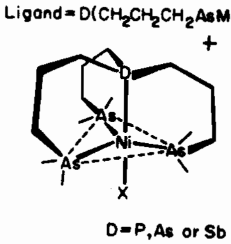

Figure 2. The structural representation of the trigonal-bipyramidal (C_{3v} microsymmetry or C_3 symmetry over-all[11]) $[Ni(ligand)X]^+$ cations, where the three quadridentate ligands are $D[CH_2CH_2CH_2As(CH_3)_2]_3$ (D=P,As,Sb).

(10) G. Dyer and L.M. Venanzi, *J. Chem. Soc.*, 2771 (1965).
(11) D.L. Stevenson and L.F. Dahl, *J. Am. Chem. Soc.*, *89*, 3424 (1967).

In order to compare the ligand field strength of the apical donor atom in the $D[CH_2CH_2CH_2As(CH_3)_2]_3$ ligands (D = P, As, Sb), the electronic absorption maxima of some $[Ni(ligand)X]^+$ complexes (X=Cl, Br, I, CN are listed in Table III. It can be seen that for the cyano and chloro complexes, the apparent ligand field strength is clearly:

$$P > As > Sb$$

This spectrochemical series is the same as that obtained for monodentate R_3P, R_3As, and R_3Sb ligands.[12] In the case of the bromide complex, As≅Sb; the iodide complexes give a reversal in the spectrochemical position of arsenic and antimony, *i.e.*,

$$P > As < Sb$$

Note that the intensity of the $^1A_1 \rightarrow {}^1E$ transition decreases regularly as the two axial donors are changed to produce the two series

$$CN > Cl > Br > I$$

and

$$P > As > Sb.$$

An *anomalous* apparent ligand field affect has also been observed by Higginson, McAuliffe, and Venanzi,[8] who studied the complexes $[M\{(o\text{-}Ph_2L\text{-}C_6H_4)_3\text{-}L'\}X]^+$ (L=P and As; L′=P, As, and Sb; M=Ni, Pd, and Pt). As the apex atom L′ was varied, the shift of the $^1A_1 \rightarrow {}^1E$ $[(e_2)^4(e_1)^4 \rightarrow (e_2)^4(e_1)^3(a_1)^1]$ transition gave the spectrochemical order:

$$P > As < Sb.$$

Table III. A Comparison of Absorption Maxima for the $[NiLX]^+$ Complexes of the Tetradentate Ligands $D[CH_2CH_2CH_2As(CH_3)_2]_3$, D=P, As, Sb [a]

X	E_{max}, cm^{-1} PAs_3 [b]	 $AsAs_3$ [b]	 $SbAs_3$ [b]
I	16,670 (1760) [c]	15,670 (1560) [c]	15,950 (1420) [c]
Br	17,210 (2140)	16,050 (1847)	16,130 (1695)
Cl	17,790 (2330)	16,560 (1975)	16,400 (1800)
CN	22,880 (4540)	21,740 (3803)	21,300 (3580)

[a] All of the spectra were obtained on dichloromethane solutions. [b] The tetradentate ligand abbreviations correspond to the sets of donor atoms; in each case, the atom listed first is the apex atom of the ligand. [c] Molar extinction coefficients are given in parentheses.

The out-of-sequence position[12] of antimony in the $[M\{(o\text{-}Ph_2L\text{-}C_6H_4)_3L'\}X]^+$ complexes was attributed[8] to a compression of the apical bond caused by chelation of the rigid «tripod-like» ligand. This compression effect becomes more important as the size of L′ increases, *i.e.* with antimony, the compression apparently more than compensates for the normal decreasing ligand field strength of P>As>Sb.[12]

Our tetradentate ligand $Sb[CH_2CH_2CH_2As(CH_3)_2]_3$, which has a flexible three-carbon connecting chain between the apex antimony and arsenic donor atoms, is an ideal model with which to test the «compression effect». Since the length of the six-member chelate ring pushes the arsenic atoms 0.19 Å below the nickel atom in the structure of $[Ni(PAs_3)CN]ClO_4$,[11] the longer antimony-nickel bond[13] should cause the arsenic atoms to be more nearly coplanar with the nickel atom in the trigonal-bipyramidal $[Ni(SbAs_3)X]^+$ complexes. Since little structural distortion is expected as a result of using the flexible $Sb[CH_2CH_2CH_2As(CH_3)_2]_3$ ligand, the observed spectrochemical series, *i.e.* P>As>Sb, in the chloride and cyanide complexes is in agreement with the trend obtained with monodentate ligands.[12] In the case of the iodide complex the reversal of the apparent ligand field effect of arsenic and antimony may be attributed to the nephelauxetic effect, as discussed previously,[2] or to a steric effect with the largest anion, or to a combination of these two possibilities.

The infrared spectrum of the $[Ni(SbAs_3)CN]B(C_6H_5)_4$ complex exhibits one sharp C≡N absorption at 2101 cm^{-1}. The thiocyanate complex exhibits a strong C≡N absorption at 2090 cm^{-1} in the solid state and at 2093 cm^{-1} ($\nu_{1/2} = 36.0$ cm^{-1}, $A = 9.34 \times 10^4$ M^{-1} cm^{-2}) in dichloromethane, indicative of N-bonding in the solid state and in solution.[14]

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(12) The spectrochemical series for monodentate R_3P, R_3As, and R_3Sb ligands is: P>As>Sb. [P.L. Goggin, R.J. Knight, L. Sindellari, and L.M. Venanzi, submitted for publication]

(13) The nickel-antimony bond distance is estimated to be ~2.49 Å, since the average bond lengths in the antimony compounds SbX_3 (X=Cl, Br, CH_3) are 0.28 Å longer than those in the corresponding phosphorus compounds [L E. Sutton, *Tables of Interatomic Distances*, Chem. Soc. London), 1958 and Supplement, 1965].

(14) D.W. Meek, P.E. Nicpon, and V.I. Meek, *J. Am. Chem. Soc.*, *92*, 5351 (1970), and references cited therein.