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Four- and Five-Coordinate Nickel(II) Complexes of a Bidentate Arsenic-Antimony Ligand¹

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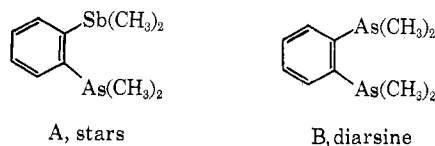
The preparation and characterization of the new chelating ligand dimethyl(*o*-dimethylarsinophenyl)stibine (stars) and some of its nickel(II) complexes are described. The ligand forms the stable four-coordinate, planar complex $[\text{Ni}(\text{stars})_2](\text{ClO}_4)_2$ and the five-coordinate, square-pyramidal complexes $[\text{Ni}(\text{stars})_2\text{X}]\text{X}$ and $[\text{Ni}(\text{stars})_2\text{X}][\text{B}(\text{C}_6\text{H}_5)_4]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$). The spectrochemical effect of the dimethylstibine donor group is slightly lower than that of the corresponding dimethylarsine group.

Introduction

In recent years numerous polydentate ligands that contain nitrogen, phosphorus, arsenic, or mixed combinations of these donor atoms have been prepared.³ Although triphenylstibine, $(\text{C}_6\text{H}_5)_3\text{Sb}$, has been used relatively often as a ligand with the second- and third-series metals^{4,5} and with first-row transition metal carbonyls⁶⁻⁹ and dithiolenes,¹⁰ there is still a paucity of stibine complexes of the first-row transition metals with normal oxidation states.¹¹ We became interested in stibine ligands as a result of our earlier investigations¹²⁻¹⁵ on the factors that stabilize pentacoordinate complexes. Those studies¹²⁻¹⁵ showed that easily polarized donor atoms such as P, As, S, and Se reduce the interelectronic repulsion parameters sufficiently to promote formation of low-spin, five-coordinate Co(II) and Ni(II) complexes. In the case of stibine ligands, the large antimony σ and π orbitals may be expected to overlap effectively with the orbitals of 4d and 5d transition metals, but they might be ineffective in bonding with 3d metals, owing to the disparity in size of the donor and acceptor orbitals.

For our initial studies on the coordination properties of organoantimony ligands with first-row transition

metals, we chose to synthesize the ligand dimethyl(*o*-dimethylarsinophenyl)stibine (A, stars). The structural similarity of stars to the familiar diarsine ligand B¹⁶⁻¹⁸ would permit direct comparisons of the



Sb-As and the As-As sets of donors. This paper reports the preparation and characterization of the ligand stars and of its Ni(II) complexes.

Experimental Section

The preparations of the nickel complexes and all the synthetic steps involving a dialkylantimony or -arsenic derivative were carried out in a dry nitrogen atmosphere unless stated otherwise.

Reagents.—Antimony trioxide and *o*-bromoaniline were obtained from Baker Chemical Co. and Pierce Chemical Co., respectively. Both were used without further purification. Reagent grade tetrahydrofuran (Baker) was dried over sodium wire for 24 hr, refluxed over calcium hydride, and then distilled under nitrogen from fresh calcium hydride. Nitromethane (Matheson Coleman and Bell) was stirred over fresh Linde 4A Molecular Sieves for 24 hr and filtered two times. "Anhydrous" diethyl ether was further dried over sodium wire. Reagent grade absolute ethanol, hexane, and dichloromethane were used without purification.

Preparation of the Ligand stars.—(1) *o*-Bromophenylstibonic acid (C) was prepared according to the procedure of Schmidt,¹⁹ except that glycerin was added to the yellow double salt in order to coagulate the suspension. The product was obtained in 25% yield, mp >300°. *Anal.* Calcd for $\text{C}_6\text{H}_5\text{BrO}_3\text{Sb}$: C, 21.9; H, 1.70. Found: C, 21.8; H, 1.84.

(2) *o*-Bromophenyldichlorostibine (D) was prepared in 78% yield by reduction of *o*-bromophenylstibonic acid (C) with SO_2 in concentrated hydrochloric acid, followed by recrystallization from carbon tetrachloride; mp 88–90°. *Anal.* Calcd for $\text{C}_6\text{H}_4\text{BrCl}_2\text{Sb}$: C, 20.7; H, 1.16. Found: C, 21.4; H, 0.94.

(3) *o*-Bromophenyldimethylstibine (E) was prepared as follows. Magnesium turnings (11.7 g, 0.483 g-atom) in 100 ml of dry diethyl ether were placed in a three-neck round-bottom flask that was equipped with a condenser, a pressure-equalizing dropping funnel, and a mechanical stirrer. Methyl iodide (68.1 g, 0.483 mol) in 50 ml of dry ether was placed in the dropping funnel and added over a period of 1 hr. The stirring was continued for 1 hr after addition. The resulting Grignard reagent was filtered through glass wool into a dropping funnel. The funnel was placed subsequently on a three-neck round-bottom flask which contained *o*-bromophenyldichlorostibine (80.2 g, 0.23 mol) in

(1) This paper is based, in part, on the dissertation submitted by B. R. Cook to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree.

(2) The Ohio State University postdoctorate fellow, 1968.

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(11) During the course of B. R. Cook's studies (1966–1969) with chelating stibine ligands, we learned that McAuliffe and Venanzi (C. A. McAuliffe, Ph.D. Thesis, Oxford University, 1967) had prepared Ni(II) and Co(II) complexes with the two rather rigid ligands $\text{Sb}(\text{o-C}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2)_2$ and $\text{Sb}(\text{o-C}_6\text{H}_4\text{As}(\text{C}_6\text{H}_5)_2)_2$, which contain antimony at the apex of a "tripod arrangement" of donor atoms. In such complexes the possibility exists that the antimony atom may be induced to bond to first-row metals because of the constrained trigonal geometry that is imposed by the steric requirements of these two ligands. Dr. McAuliffe joined our research effort on this problem in 1968 as a postdoctoral fellow.

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100 ml of dry ether. Addition of the methyl Grignard required 1 hr; the stirring and refluxing were continued for 1 additional hr. The solution was hydrolyzed with 250 ml of a saturated ammonium chloride solution, and the ether layer was separated and dried over sodium sulfate for 12 hr. The ether was removed with a stream of dry nitrogen and the product was distilled under vacuum; yield 45 g (64%); bp 80–82° (0.6 Torr). The proton nmr spectrum of the neat material shows a multiplet centered at τ 2.8, which is assigned to the phenyl protons, and a singlet at τ 9.12 due to the methyl protons. The relative intensities of the resonances correspond to four phenyl protons per six methyl protons, as expected for E.

(4) Dimethyl(*o*-dimethylarsinophenyl)stibine (A) was prepared as follows. Sodium dimethylarsenide was prepared as outlined by Feltham and Silversthorp,²⁰ except that stirring was continued for 3 hr after addition of the dimethylarsine to the sodium sand. The sodium dimethylarsenide in THF was filtered through glass wool into a dropping funnel. The funnel was placed on a three-neck round-bottom flask that contained *o*-bromophenyldimethylstibine (23.9 g, 0.078 mol) in 100 ml of dry ether. The sodium dimethylarsenide was added dropwise over a period of 1–2 hr, while the temperature was maintained at 0–10° with a Dry Ice–ligroin (bp 60–90°) bath. The mixture was stirred overnight, and then the THF was removed by distillation at atmospheric pressure. The flask was cooled and 400 ml of deaerated water was added to the residue. The lower layer was transferred in small portions *via* a dropping funnel into a microdistillation apparatus which was swept with nitrogen. The product was then vacuum distilled; bp 98–100° (0.6 Torr); yield 19 g (74%). The proton nmr spectrum of the neat material shows a multiplet at τ 2.75 that is assigned to the phenyl protons, a singlet at τ 8.89 due to the methyl protons on arsenic, and a singlet at τ 9.09 due to the methyl protons on antimony. The two methyl peaks have equal intensity and the total of the two methyl resonances has a relative intensity of 3 times the phenyl resonance, *i.e.*, 12:4 as expected for the ligand A.

Methyl Iodide Derivatives.—The mono(methyl iodide) derivative of dimethyl(*o*-dimethylarsinophenyl)stibine was isolated even though an excess of methyl iodide was added to approximately 1 g of dimethyl(*o*-dimethylarsinophenyl)stibine and the mixture was refluxed for 1 hr. The excess methyl iodide was evaporated under nitrogen, and the white precipitate was recrystallized from acetone. *Anal.* Calcd for C₁₁H₁₆AsISb: C, 27.8; H, 4.03. Found: C, 28.3; H, 3.80. The molar conductivity in nitromethane is 77 cm²/ohm mol, consistent with a uni-univalent electrolyte. The proton nmr spectrum of the compound in acetonitrile-*d*₃ shows the phenyl multiplet at τ 2.25 and singlets at τ 7.65 and 8.69 that are assigned to the methyl groups on arsenic and antimony, respectively.

The mono(methyl iodide) derivative of *o*-bromophenyldimethylstibine (E) was prepared in a similar manner except that an acetone–ethanol mixture was used for recrystallization. *Anal.* Calcd for C₈H₁₃BrISb: C, 24.0; H, 2.91. Found: C, 23.9; H, 2.68. The molar conductivity in nitromethane is 72 cm²/ohm mol. The proton nmr spectrum of the quaternary salt in dimethyl sulfoxide-*d*₆ shows the multiplet for the four phenyl protons at τ 2.32 and a singlet at τ 8.08 due to the nine methyl protons on antimony.

Preparation of Complexes. [Ni(stars)₂X]X (X = Cl, Br, I, NO₃).—The appropriate anhydrous nickel(II) salt (1.05 mmol) was dissolved with stirring in hot ethanol (30 ml). The hydrated salt was used in the case of nickel(II) nitrate. The solution was cooled to room temperature and 2.1 mmol of stars in 15 ml of ethanol was added. The resulting deep maroon solution was stirred for 30 min at room temperature. (Note: Warming the solution seemed to cause some decomposition.) The ethanolic solution was evaporated with nitrogen to less than half the original volume and deep maroon crystals were collected on a sintered-glass funnel. The product was recrystallized from a dichloromethane solution that contained a little hexane or ethanol. After evaporation of the dichloromethane, the crystals were collected, washed three or four times with anhydrous ether, and dried for 24 hr *in vacuo*.

[Ni(stars)₂Cl]B(C₆H₅)₄.—Sodium tetraphenylborate in ethanol (15 ml) was added to Ni(stars)₂Cl₂ in dichloromethane (15 ml). The red precipitate that formed immediately was collected, washed several times with cold ethanol and ether, and dried for 48 hr *in vacuo*.

[Ni(stars)₂NCS]B(C₆H₅)₄.—Anhydrous nickel(II) thiocyanate (1.05 mmol) was dissolved in hot ethanol (30 ml). The solution was cooled to room temperature and 1.05 mmol of sodium tetraphenylborate was added. Upon addition of 2.1 mmol of stars to the stirred solution, the solution became maroon and maroon crystals started to form. Stirring was continued for 30 min at room temperature, and the volume of ethanol was reduced with a stream of dry nitrogen. The crystals were collected, washed several times with cold ethanol, recrystallized from dichloromethane–hexane, and dried *in vacuo* for 24 hr.

Ni(stars)₂(ClO₄)₂.—Hydrated nickel(II) perchlorate (1.05 mmol) was dissolved in ethanol (10 ml) and stars (2.1 mmol) in ethanol was added to the well-stirred solution. A tan-pink precipitate formed immediately; however, stirring was continued for 30 min and then the precipitate was collected on a sintered-glass funnel and washed with cold ethanol. The complex was recrystallized from dichloromethane–hexane, washed with anhydrous ether several times, and dried for 24 hr *in vacuo*.

Spectra.—Electronic spectra of the compounds dissolved in a solvent were obtained with a Cary 14 spectrophotometer using 1-cm quartz cells. Solid-state spectra were obtained on the same instrument using the Nujol mull technique of Lee, *et al.*²¹ Infrared spectra were taken on a Perkin-Elmer 337 grating spectrophotometer in the form of Nujol mulls between potassium bromide plates.

Conductance.—The conductivity of approximately 10⁻³ M nitromethane solutions was measured at 23 ± 1° with an Industrial Instruments RC-16B conductivity bridge.

Magnetism.—Measurements on 20–25-mg samples were performed on a Faraday magnetic susceptibility balance. The measurements were taken at two different field strengths to check for ferromagnetic impurities; the reported values are an average of at least two determinations. All values have been corrected for the diamagnetic susceptibility of the ligand.²²

Nuclear Magnetic Resonance.—The spectra were obtained on a Varian A-60A spectrometer. Spectra of the pure liquids and of acetonitrile-*d*₃, dimethyl sulfoxide-*d*₆, and nitromethane-*d*₃ solutions were run with TMS as an internal standard.

Results and Discussion

Synthesis of the Ligand.—Dimethyl(*o*-dimethylarsinophenyl)stibine (stars) was prepared in a four-step synthesis and the overall yield is strongly dependent on the conditions used for the last three steps of the reaction sequence. The *o*-bromophenylstibonic acid (C) was reduced in 78% yield by bubbling sulfur dioxide into a concentrated HCl solution of C. This method gives a much higher yield than does reduction with stannous chloride, which has been used previously. In our hands SnCl₂ reduced C in only 35% yield. Treatment of *o*-bromophenyldichlorostibine (D) with methylmagnesium iodide gave *o*-bromophenyldimethylstibine (E) in 64% yield. The reverse order of addition of the reagents at this stage (*i.e.*, *o*-bromophenyldichlorostibine (D) to the Grignard solution) produced E in only 33% yield, together with extensive decomposition of D. The ligand dimethyl(*o*-dimethylarsinophenyl)stibine (A) was isolated in 74% yield by addition of sodium dimethylarsenide to *o*-bromophenyldimethylstibine, whereas the reverse order of addition gave the desired product in only 24% yield. The markedly lower yield in each of the last two steps of the synthesis, when the reverse order of addition of reagents is used, is due to decomposition of the organostibine compounds in the presence of an excess of the nucleophiles. The decomposition is evident by the formation of black solids. When the stibine was maintained in excess during these reactions, no black solids were observed and the yields were improved greatly.

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TABLE I
 ANALYTICAL DATA AND PHYSICAL PROPERTIES OF DIMETHYL(*o*-DIMETHYLARSINOPHENYL)STIBINE COMPLEXES OF Ni(II)

Compound	Color	Analysis ^a						A _M , ^d cm ² / ohm mol	Solid state (Nujol mulls)	Electronic absorption max, ν, cm ⁻¹		10 ³ χ _M ^{f,g} cgsu
		% C		% H		% X ^c				Soln ^f		
		Calcd	Found	Calcd	Found	Calcd	Found					
Ni(stars) ₂ Cl ₂ ^b	Brown	30.2	30.4	4.06	3.90			63	21,100	21,100 (864)	882	
[Ni(stars) ₂ Cl]B(C ₆ H ₅) ₄	Red-brown	49.0	49.3	4.86	4.97			66	21,000	21,000 (944)	970	
Ni(stars) ₂ Br ₂	Red-brown	27.2	27.5	3.65	3.79	18.1	18.3	75	20,500	20,600 (1210)	337	
Ni(stars) ₂ I ₂	Red-brown	24.6	24.8	3.30	3.12	25.9	26.3	84	20,000	20,300 (1240)	512	
Ni(stars) ₂ (NO ₃) ₂	Red-brown	28.3	28.7	3.80	3.90	3.30	3.33	85	21,800	21,900 (790)	337	
Ni(stars) ₂ (ClO ₄) ₂	Tan-pink	26.0	26.1	3.49	3.28	7.68	8.13	172	22,100	22,100 (1260)	512	
[Ni(stars) ₂ NCS]- B(C ₆ H ₅) ₄ ^g	Maroon	49.1	50.1	4.76	4.96	1.27	1.05	55	21,100	21,300 (819)	490	

^a Analyses were performed by P. Kovi, The Ohio State University, Galbraith Laboratories, Knoxville, Tenn., or M-H-W Laboratories, Garden City, Mich. ^b Stars is dimethyl(*o*-dimethylarsinophenyl)stibine, A. ^c X is the appropriate Cl, Br, I, N. ^d Conductivity values for approximately 10⁻³ M nitromethane solutions. ^e Magnetic susceptibility values are corrected for the diamagnetism of the ligand. These values are somewhat high for diamagnetic nickel(II) complexes even after considering the effect of TIP. ^f Extinction coefficients are given in parentheses. ^g The thiocyanate complex shows a single infrared band at 2072 cm⁻¹, which indicates nitrogen-bonded thiocyanate.

The proton nmr spectrum of A shows two sharp singlets at τ 8.89 and 9.09, in addition to the phenyl multiplet. The resonance at τ 9.09 is assigned to the methyl groups on antimony, as the methyl protons in *o*-bromophenyldimethylstibine are located at τ 9.12. The resonance at τ 8.89 is assigned to the methyl groups on arsenic, in excellent agreement with the value of τ 8.89 that we observed for the diarsine ligand, B. (A literature value for the methyl protons on B is τ 8.83.²⁰)

The methyl iodide derivative of A is a uni-univalent electrolyte in nitromethane even though the ligand was refluxed with excess methyl iodide. This result is consistent with the observations that diethyl(*o*-dimethylarsinophenyl)phosphine⁸ and the diarsine ligand B²³ add only one methyl iodide under these preparative conditions. The proton nmr spectrum of the quaternary salt of A shows two sharp singlets at τ 7.65 and 8.69 in an intensity ratio of 3:2. Analogously, the monomethiodide of *o*-phenylenebis(dimethylarsine) in acetonitrile-*d*₃ shows two sharp proton singlets at τ 7.65 and 8.66 in a ratio of 3:2. The coincidence of the peaks at τ 7.65 in the monomethiodides of A and B suggests that the dimethylarsino group of A is the site of quaternization, rather than the antimony group. The resonance position of both dimethylarsino groups in B shifts to lower values (shift 0.23 and 1.24 τ units) on formation of the monomethiodide, just as in the monomethiodide of A. The downfield shift of the dimethylstibine protons in A and of the second dimethylarsino protons in B is due to an inductive effect of the ortho quaternary arsenic group. The assignment of arsenic quaternization in A is also supported by the nmr spectrum of the methyl iodide salt of E, which shows one sharp methyl resonance at τ 8.08; that is a comparable shift of 1.04 τ units downfield from the methyl resonance of E. On the basis of the nmr spectrum of the monomethiodide of E, there should have been a peak close to τ 8.08 if antimony had been the site of quaternization in A. There is no peak between τ 7.65 and 8.69 in the spectrum of the methiodide of A.

Coordination Complexes of stars, A.—The bidentate ligand dimethyl(*o*-dimethylarsinophenyl)stibine (stars) forms five-coordinate complexes of the type Ni-

(stars)₂X⁺ (X = Cl, Br, I, NCS, NO₃), as well as the four-coordinate complex Ni(stars)₂²⁺. The properties and analytical data of the isolated nickel(II) complexes are given in Table I.

The complex [Ni(stars)₂](ClO₄)₂ has a symmetrical electronic absorption maximum at 22,100 cm⁻¹ (ε 1260) in nitromethane; in the solid state the band maximum occurs at the same position. It is diamagnetic in the solid state and is a bi-univalent electrolyte in a 10⁻³ M nitromethane solution. The infrared spectrum (Nujol mull) shows no splitting of the perchlorate frequencies at ~1100 or at 622 cm⁻¹; thus, the perchlorate ions retain their T_d symmetry and are not coordinated.²⁴ The [Ni(stars)₂](ClO₄)₂ complex is assigned a square-planar structure in which the stars ligand functions as a chelate.

The red-brown complexes Ni(stars)₂X₂ are all uni-univalent electrolytes in nitromethane and essentially diamagnetic (Table I). Each of the Ni(stars)₂X₂ compounds has an intense asymmetric absorption at ~20,000 cm⁻¹, in nitromethane solutions as well as in the solid state. The electronic spectrum of [Ni(stars)₂Cl]Cl is virtually identical with that of the diamagnetic, uni-univalent complex [Ni(stars)₂Cl]B(C₆H₅)₄. Thus, it is concluded that the Ni(stars)₂X₂ compounds (X = Cl, Br, and I) are five-coordinate [Ni(stars)₂X]X complexes. These five-coordinate stars complexes are analogous to the *o*-phenylenebis(dimethylarsine) complexes [Ni(diars)₂X]X reported recently by Preer and Gray.²⁵

In the case of the Ni(stars)₂(NO₃)₂ compound, one can anticipate four coordination possibilities: (1) a square-planar Ni(stars)₂²⁺ cation with ionic nitrates, (2) a five-coordinate Ni(stars)₂NO₃⁺ cation with one monodentate and one ionic nitrate, (3) a six-coordinate [Ni(stars)₂NO₃]NO₃ complex arising from one chelating nitrate, or (4) a six-coordinate Ni(stars)₂(NO₃)₂ complex involving two monodentate nitrate groups. An infrared spectrum of the solid has two strong absorptions at 1360 and 1318 cm⁻¹ and two medium-intensity frequencies at 1038 and 1033 cm⁻¹. These peaks are consistent with a monodentate nitrate;²⁶ however, Curtis and Curtis²⁷ have pointed out that it

(23) *o*-Phenylenebis(dimethylarsine)²⁰ was mixed with a large excess (1:20 ratio) of methyl iodide. The crystalline product was a uni-univalent conductor in nitromethane and had correct elemental analyses for C, H, and I.

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is impossible to assign infrared bands explicitly to the monodentate nitrate when an ionic nitrate is also present. We attach more significance to the uni-univalent conductance and the electronic spectral similarity with the halide complexes. Thus, we assign the formulation $[\text{Ni}(\text{stars})_2\text{NO}_3]\text{NO}_3$ to this complex, which implies a monodentate nitrate and a pentacoordinate cation.

These five-coordinate complexes of stars have electronic spectra (Figure 1) that are very similar to the

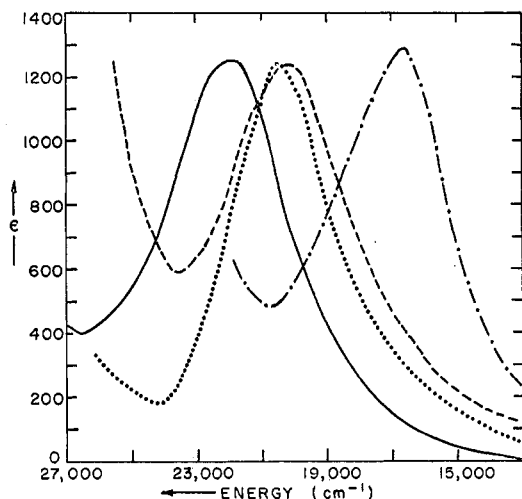


Figure 1.—The visible portions of the electronic absorption spectra: $[\text{Ni}(\text{stars})_2](\text{ClO}_4)_2$, ———; $[\text{Ni}(\text{stars})_2]\text{I}$, - - - - -; $[\text{Ni}(\text{diars})_2]\text{I}$, ·····; $\text{Ni}(\text{DSP})\text{I}_2$, - · - · - ·.

spectra of $[\text{Ni}(\text{SP})_2\text{X}]\text{X}$ and $\text{Ni}(\text{DSP})\text{X}_2$, where SP and DSP are (*o*-methylthiophenyl)diphenylphosphine and bis(*o*-methylthiophenyl)phenylphosphine, respectively.²⁸ The latter complex is known to have a square-pyramidal structure,²⁹ so square-pyramidal $\text{Ni}(\text{stars})_2\text{X}^+$ cations are proposed on the basis of the electronic spectra. The energy of the ${}^1\text{A}_1 \rightarrow {}^1\text{E}$ electronic transition ($d_{xz,yz} \rightarrow d_{x^2-y^2}$) in each of our $\text{Ni}(\text{stars})_2\text{X}^+$ complexes is almost identical with the corresponding peak in the square-pyramidal $\text{Ni}(\text{diars})_2\text{X}^+$ complexes.²⁵

A comparison of the ligand properties of antimony with those of arsenic and phosphorus was the primary impetus for this study. The electronic spectral maxima in Table I show that stars exerts a ligand field that is slightly lower than for the analogous diarsine, B. The lower field is more prominent in the square-planar complex $\text{Ni}(\text{stars})_2^{2+}$, where the absorption is $\sim 500 \text{ cm}^{-1}$ below that of $\text{Ni}(\text{diars})_2^{2+}$.²⁵

Conclusions.—This study shows that the bidentate antimony-arsenic ligand forms stable five-coordinate nickel(II) complexes and that the apparent spectrochemical effect of the phenyldimethylstibine group is slightly lower than for the corresponding arsine. The latter observation perhaps reflects the disparity in the size of the donor and acceptor orbitals.

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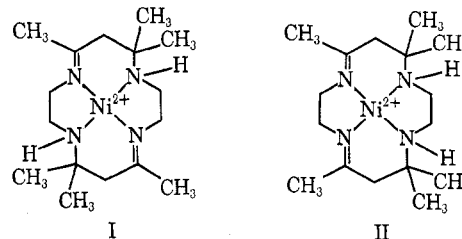
A Proton Magnetic Resonance Study of Some Tetraimine Complexes of Nickel

BY VIRGIL L. GOEDKEN AND DARYLE H. BUSCH*

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A series of salts of the nickel complexes with the isomeric tetraimine ligands 1,4,8,11-CT and 1,3,7,11-CT has been prepared and characterized and the pmr spectra of these species have been studied in detail. Selective deuteration facilitated the assignment of the various pmr resonances. The ligands are 14-membered macrocycles each having 4 imine donor atoms and 6 methyl substituents. Although the complexes are particularly resistant to attack by either strong acid or strong chelating agents, the chelate rings appear to undergo rapid flexing, thereby causing pairs of gem methyls to become equivalent.

The pmr spectra of a number of isomers of the diimine complexes derived from the condensation of ethylenediamine and acetone have been studied in detail.¹ These complexes exist as noninterconvertible isomeric forms which are related by the position of the imine functions which are located in either the 1(14) and 7 positions of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),7-dienickel(II) (structure I, $\text{Ni}(1,7\text{-CT})^{2+}$) or the 1 and 4 positions of 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),4-dienickel(II) (structure II, $\text{Ni}(1,4\text{-CT})^{2+}$).² The



$\text{Ni}(1,7\text{-CT})^{2+}$ species exists as interconvertible meso and *dl* isomers depending on the configuration of the two asymmetric nitrogen atoms, whereas the $\text{Ni}(1,4\text{-CT})^{2+}$ species has only been observed in the *dl* form.¹

Each of these complexes undergoes oxidative dehydrogenation of the ligand in concentrated nitric acid to

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