except for $[Ph_3Bi(DMSO)]_2O(ClO_4)_2$ and $[Ph_3Bi(pyO)]_2O(ClO_4)_2$.

Molar conductances for $\sim10^{-3}$ *M* solutions of these complexes in nitromethane and dichloromethane are shown in Table III. Λ_M values in nitromethane correspond to those for 1:2 electrolytes.[32] For a 10^{-3} *M* solution of a 1:1 electrolyte such as tetraethylammonium perchlorate, in dichloromethane, we observed a Λ_M value of 22.8 $ohm^{-1}\ cm^2\ mol^{-1}$ at 25°. Therefore, with the exceptions of $[Ph_3Bi(DMSO)]_2O(ClO_4)_2$ and $[Ph_3Bi(pyO)]_2O(ClO_4)_2$, these complexes also behave as 1:2 electrolytes in dichloromethane. Since the molar conductance of $[Ph_3Bi(OClO_3)]_2O$ in dichloromethane is $\sim1.4\ ohm^{-1}\ cm^2\ mol^{-1}$, the lower Λ_M values for $[Ph_3Bi(DMSO)]_2O(ClO_4)_2$ and $[Ph_3Bi(pyO)]_2O(ClO_4)_2$ indicate the following equilibrium in solution

$$[Ph_3BiL]_2O(ClO_4)_2 \rightleftharpoons [Ph_3Bi(OClO_3)]_2O + 2L \qquad (3)$$

In accordance with the proposed equilibrium there was a marked increase in the conductances upon adding free ligand to the dichloromethane solutions of $[Ph_3Bi(DMSO)]_2O(ClO_4)_2$ and $[Ph_3Bi(pyO)]_2O(ClO_4)_2$. The infrared data for the two complexes, in solution, are also consistent with the proposed dissociation. Conductance of $[Ph_3Bi(Ph_3AsO)_2](BF_4)_2$ in dichloromethane was found to decrease with time and this can be attributed to the decomposition of the complex into Ph_3BiF_2[2] and Ph_3AsOBF_3[6] as shown in eq 1.

Registry No. $[Ph_3Bi(OClO_3)]_2O$, 38496-61-6; Ph_3BiCl_2, 28719-54-2; $[Ph_3Bi(DMSO)_2](ClO_4)_2$, 38467-44-6; $[Ph_3Bi(DMSO\text{-}d_6)_2](ClO_4)_2$, 38467-45-7; $[Ph_3Bi(pyO)_2](ClO_4)_2$, 38467-46-8; $[Ph_3Bi(Ph_3PO)_2](ClO_4)_2$, 38467-47-9; $[Ph_3Bi(Ph_3PO)_2](PF_6)_2$, 38467-48-0; $[Ph_3Bi(Ph_3AsO)_2](ClO_4)_2$, 38467-49-1; $[Ph_3Bi(Ph_3AsO)_2](BF_4)_2$, 38467-50-4; $[Ph_3Bi(Ph_3AsO)_2](BF_4)_2 \cdot C_3H_6O$, 38467-51-5; $[Ph_3Bi(Ph_3AsO)_2](PF_6)_2$, 38467-52-6; $[Ph_3Bi(Ph_3AsO)_2](PF_6)_2 \cdot C_3H_6O$, 38467-53-7; $[Ph_3Bi(Ph_3AsO)_2](PF_6)_2 \cdot C_5H_{10}O$, 38566-47-1; $[2[Ph_3Bi(Ph_3AsO)_2](PF_6)_2 \cdot C_5H_8O_2$, 38531-33-8; $[Ph_3Bi(DMSO)]_2O(ClO_4)_2$, 38566-48-2; $[Ph_3Bi(DMSO\text{-}d_6)]_2O(ClO_4)_2$, 38531-34-9; $[Ph_3Bi(pyO)]_2O(ClO_4)_2$, 38566-49-3; $[Ph_3Bi(Ph_3PO)]_2O(ClO_4)_2$, 38566-44-8; $[Ph_3Bi(Ph_3AsO)]_2O(ClO_4)_2$, 38566-45-9; $[Ph_3Bi(Ph_3AsO)_2](NO_3)_2$, 38566-46-0.

Table III. Molar Conductances[a] for $Ph_3BiL_2X_2$ and $(Ph_3BiL)_2OX_2$ Complexes

Compd	Λ_M, $ohm^{-1}\ cm^2\ mol^{-1}$	
	CH_3NO_2	CH_2Cl_2
$[Ph_3Bi(DMSO)_2](ClO_4)_2$	150	*b*
$[Ph_3Bi(pyO)_2](ClO_4)_2$	150	*b*
$[Ph_3Bi(Ph_3PO)_2](ClO_4)_2$	177	38
$[Ph_3Bi(Ph_3PO)_2](PF_6)_2$	184	44
$[Ph_3Bi(Ph_3AsO)_2](ClO_4)_2$	182	41
$[Ph_3Bi(Ph_3AsO)_2](BF_4)_2$	170	52
$[Ph_3Bi(Ph_3AsO)_2](PF_6)_2$	188	36
$[Ph_3Bi(DMSO)]_2O(ClO_4)_2$	162	12[c]
$[Ph_3Bi(pyO)]_2O(ClO_4)_2$	162	22[c]
$[Ph_3Bi(Ph_3PO)]_2O(ClO_4)_2$	163	41
$[Ph_3Bi(Ph_3AsO)]_2O(ClO_4)_2$	161	56

[a] At $\sim1 \times 10^{-3}$ *M* and 25°. [b] Not sufficiently soluble. [c] Conductance increased upon adding free ligand.

Acknowledgments. Thanks are due to The National Research Council of Canada for financial support.

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Notes

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Preparation and Chemistry of Sodium Bis(borane)dimethylarsenide(1−)

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Recent papers from this laboratory described studies of the reactions of B_2H_6 with $LiP(CH_3)_2$,[1] and with mono- and di-*N*-alkyl-substituted lithium amides, LiNHR and $LiNR_2$.[2] In addition we have described the reaction of amine hydrochlorides with $Na(CH_3)_2N(BH_3)_2$[3] and $Li(CH_3)_2P(BH_3)_2$[4] to form chain compounds with NBNB and NBPB backbones, respectively. This article represents an extension of this work to the formation and characterization of the arsenic–boron compound $Na(CH_3)_2As(BH_3)_2$ and its conversion to $(CH_3)_3N\text{-}BH_2\text{-}As(CH_3)_2\text{-}BH_3$.

Experimental Section

General Data. Standard high-vacuum and inert-atmosphere techniques[5] were employed for all manipulations. Boron-11 and proton nmr spectra were obtained using a Varian HA-100 spectrometer operating at 32.1 and 100 MHz, respectively. Boron chemical shifts are expressed in ppm relative to $(C_2H_5)_2O \cdot BF_3$. Infrared spectra were obtained with a Perkin-Elmer 337 spectrophotometer. Mass spectra were produced by a Hitachi-Perkin RMU-6E double-focusing spectrometer.

Pure dry solvents were stored over $LiAlH_4$ in evacuated bulbs and, when needed, were condensed directly into the reaction vessel. Dimethylarsine was prepared by the procedure of Feltham and Silverthorn,[6] modified slightly for vacuum-line application. Sodium dimethylarsenide was formed by the reaction of $(CH_3)_2AsH$ with finely divided sodium in benzene at 25°.[7]

For analysis arsenic was determined by the quantitative recovery of $(CH_3)_2AsH$ following acid hydrolysis. Boron, nitrogen, and hydrolytic hydrogen were determined by standard methods.

Preparation of $Na(CH_3)_2As(BH_3)_2$. In a typical reaction a 2.0-

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[1] L. D. Schwartz and P. C. Keller, *Inorg. Chem.*, 10, 645 (1971).

[2] L. D. Schwartz and P. C. Keller, *J. Amer. Chem. Soc.*, 94, 3015 (1972).

[3] P. C. Keller, *Inorg. Chem.*, 10, 2256 (1971).

[4] L. D. Schwartz and P. C. Keller, *Inorg. Chem.*, 11, 1934 (1972).

[5] D. F. Shriver, "The Manipulation of Air-sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

[6] R. D. Feltham and W. Silverthorn, *Inorg. Syn.*, 10, 159 (1967).

[7] The $(CH_3)_2AsH$–Na reaction outlined in ref 6 used tetrahydrofuran as the solvent. In this work we have found that benzene containing a trace of tetrahydrofuran is a more convenient reaction medium if actual isolation of $NaAs(CH_3)_2$ is desired.

mmol sample of $NaAs(CH_3)_2$ in 2 ml of diethyl ether was treated with 3.0 mmol of B_2H_6 for 40 min at 25°. Separation of volatile products resulted in the recovery of 0.9 mmol of B_2H_6, implying 2.1-mmol consumption. The involatile solid–liquid residue was taken up in fresh diethyl ether, filtered, and reevaporated to produce a clear colorless oil. Dissolution in dioxane and evaporation gave a colorless solid which was kept under dynamic vacuum for 12 hr to remove the last traces of solvent. *Anal.* Calcd for $Na(CH_3)_2As(BH_3)_2 \cdot 0.5C_4H_8O_2$[8] (mmol/g): B, 10.0; H_2 (hydrolytic), 30.0; $(CH_3)_2AsH$, 5.00. Found: B, 10.0; H_2 (hydrolytic), 30.0; $(CH_3)_2AsH$, 4.97. Colorless hygroscopic crystals appeared, which were soluble in acetone, ethanol, methanol, and water; slightly soluble in diethyl ether and dioxane; and insoluble in benzene and toluene. Boron-11 nmr (D_2O): quartet, 33.6 ppm, $J_{BH} = 88$ Hz. Proton nmr (D_2O): singlet, τ 9.29, intensity 1; quartet (1:1:1:1), τ 9.64, $J_{BH} = 88$ Hz, intensity 1. Ir (KBr, bands not assigned to dioxane) in cm^{-1} (relative intensity): 2980 (w), 2960 (w, sh), 2920 (w), 2340 (vs), 2280 (s, sh), 1420 (w), 1160 (w), 1080 (s, sh), 1055 (vs), 1020 (m, sh), 500 (vw). As indicated by the boron-11 nmr spectrum a D_2O solution of $Na(CH_3)_2As(BH_3)_2$ showed only 15% hydrolysis after 4 months at room temperature. Hydrogen isotope exchange between BH_3 groups and the solvent did not occur.

Reaction of $Na(CH_3)_2As(BH_3)_2$ with B_2H_6 and B_2D_6. Treatment of an ether solution of $Na(CH_3)_2As(BH_3)_2$ with diborane results only in the recovery of starting materials. To test the possibility of hydrogen isotope exchange 0.15 mmol of B_2D_6 was allowed to interact with 0.054 g (0.27 mmol) of $Na(CH_3)_2As(BH_3)_2 \cdot 0.5C_4H_8O_2$ in 2 ml of diethyl ether for 1 hr. The infrared spectrum of the recovered diborane clearly indicated isotope exchange had occurred; this was complemented by the appearance of new bands at 1740, 1725, and 1690 cm^{-1} in the spectrum (KBr) of the solid residue.

Preparation of $(CH_3)_3N\text{-}BH_2\text{-}As(CH_3)_2\text{-}BH_3$. A 0.287-g (1.43-mmol) sample of $Na(CH_3)_2As(BH_3)_2 \cdot 0.5C_4H_8O_2$ was allowed to react with 0.168 g (1.75 mmol) of $[(CH_3)_3NH]Cl$ in 5 ml of monoglyme in an evacuated reaction bulb at 50° for 18 hr. At the end of this time 1.35 mmol of hydrogen had been produced. After evaporation of the solvent while the vessel was kept at 0°, the involatile colorless residue was extraced with benzene and filtered. The filtrate was evaporated and sublimed at 40° to a 0° cold finger to yield 0.193 g of colorless solid product. *Anal.* Calcd for $(CH_3)_3NBH_2As(CH_3)_2BH_3$ (mmol/g): $(CH_3)_3N$, 5.24; B, 10.5; H_2 (hydrolytic), 26.2; $(CH_3)_2AsH$, 5.25. Found: $(CH_3)_3N$, 4.71; B, 10.3; H_2 (hydrolytic), 24.9; $(CH_3)_2AsH$, 4.98. Colorless crystals unaffected by brief exposure to air, mp 70–71°, appeared; they were soluble in benzene, glyme ethers, dioxane, and acetone; and insoluble in water. Boron-11 nmr (C_6H_6): quartet, 31.7 ppm, $J = 93$ Hz; triplet, 5.9 ppm, $J = 110$ Hz, equal intensity. Proton nmr (C_6H_6): Singlet, τ 7.93, intensity 3; singlet, τ 8.93, intensity 2. Ir (KBr) in cm^{-1} (relative intensity): 2980 (m, sh), 2950 (m), 2900 (w), 2420 (vs), 2380 (vs), 2340 (s), 2260 (w), 1480 (s), 1460 (s), 1410 (m), 1258 (m), 1180 (m), 1150 (s), 1120 (s), 1090 (s), 1045 (s), 985 (m), 895 (w), 875 (m, sh), 860 (m), 750 (w), 675 (vw), 665 (vw), 615 (w), 485 (m). The mass spectrum is characteristic of the assigned structure, showing no peaks higher than the parent ion at *m/e* 191. Pyrolysis of a sample of $(CH_3)_3NBH_2As(CH_3)_2BH_3$ in a sealed, evacuated tube at 140° for 2 hr resulted in approximately 50% decomposition. Work-up of the products gave undecomposed starting material, $(CH_3)_3NBH_3$, and $[(CH_3)_2AsBH_2]_3$. The first two were identified by their infrared, mass, and boron-11 nmr spectra; the latter was identified by its mass spectrum and by comparison of its boron-11 nmr spectrum with that of an authentic sample (triplet, 30.0 ppm, $J = 107$ Hz) prepared by the method of Stone and Burg.[9]

Results and Discussion

The reaction of $NaAs(CH_3)_2$ with B_2H_6 parallels that of $LiP(CH_3)_2$[1] in quantitatively forming the bis(borane) adduct $Na(CH_3)_2As(BH_3)_2$. The behavior of the phosphorus and arsenic bases contrasts with that of mono- and di-*N*-alkyl-substituted lithium amides toward B_2H_6, which has been shown in most cases to proceed according to eq 1,[2]

$$3LiNR_2 + 2B_2H_6 \rightarrow B(NR_2)_3 + 3LiBH_4 \qquad (1)$$

followed by reaction of $B(NR_2)_3$ with more diborane leading ultimately to formation of a μ-aminodiborane. We feel the basic cause of this difference is the inability of phosphorus and arsenic to form dative $p\pi\text{-}p\pi$ bonds to boron of sufficient strength to stabilize species like $B[As(CH_3)_2]_3$, $[(CH_3)_2As]_2BH$, or monomeric $(CH_3)_2AsBH_2$. As a result, only σ-bonded borane adducts form.

Table I. Boron-11 Nmr Parameters of Group V Bis(borane) Salts

Compound	Solvent	$\delta(BH_3)$, ppm	J_{BH}, Hz
$Na(CH_3)_2N(BH_3)_2$[a]	Monoglyme	11.2	90
$Li(CH_3)_2P(BH_3)_2$[b]	D_2O	34.5	88
$Na(CH_3)_2As(BH_3)_2$	D_2O	33.6	88

[a] Reference 3. [b] Reference 1.

Table II. Boron-11 Nmr Parameters of N-B-(N, P, or As)-B Compounds

Compound	$\delta(BH_3)$, ppm	J_{BH}, Hz	$\delta(BH_2)$, ppm	J_{BH}, Hz
$(CH_3)_3N\text{-}BH_2\text{-}N(CH_3)_2\text{-}BH_3$[a]	11.7	95	−3.5	108
$(CH_3)_3N\text{-}BH_2\text{-}P(CH_3)_2\text{-}BH_3$[b]	35.2	93	6.2	*c*
$(CH_3)_3N\text{-}BH_2\text{-}As(CH_3)_2\text{-}BH_3$	31.7	93	5.9	110

[a] G. A. Hahn and R. Schaeffer, *J. Amer. Chem. Soc.*, 86, 1503 (1964). [b] Reference 4. [c] J_{BH} indeterminate owing to line broadening and coupling to phosphorus-31.

The chemical and physical properties of $Na(CH_3)_2As(BH_3)_2$ and $Li(CH_3)_2P(BH_3)_2$[1] are similar. Neither compound loses a hydride ion to B_2H_6, although this reaction occurs readily with the nitrogen analog (eq 2). A

$$(CH_3)_2N(BH_3)_2^- + B_2H_6 \leftrightarrows \mu\text{-}(CH_3)_2NB_2H_5 + B_2H_7^- \qquad (2)$$

prohibitively acute B-As-B angle probably blocks formation of μ-$(CH_3)_2AsB_2H_5$ by this process;[10] however, an equilibrium like reaction 2, shifted well to the left, may account for the hydrogen exchange with B_2D_6. Table I compares the boron-11 nmr parameters of the known nitrogen, phosphorus, and arsenic bis(borane) salts. The coupling constants are nearly identical, but the similar chemical shifts of the phosphorus and arsenic compounds are widely separated from the nitrogen analog.

Treatment of $Na(CH_3)_2As(BH_3)_2$ with $[(CH_3)_3NH]Cl$ (eq 3) produces the sublimable solid $(CH_3)_3N\text{-}BH_2\text{-}$

$$Na(CH_3)_2As(BH_3)_2 + (CH_3)_3NHCl \rightarrow (CH_3)_3N\text{-}BH_2\text{-}As(CH_3)_2\text{-}BH_3 + H_2 + NaCl \qquad (3)$$

$As(CH_3)_2\text{-}BH_3$ in good yield. This type of reaction has been previously exploited to synthesize compounds with N-B-N-B[3] and N-B-P-B[4] backbones. The boron-11 nmr parameters of $(CH_3)_3N\text{-}BH_2\text{-}As(CH_3)_2\text{-}BH_3$ are compared with those of the analogous nitrogen and phosphorus compounds in Table II. Again it is interesting to note the upfield shift occurring when boron bonds to phosphorus or arsenic rather than nitrogen.

Pyrolysis of $(CH_3)_3N\text{-}BH_2\text{-}As(CH_3)_2\text{-}BH_3$ occurs in agreement with eq 4. The phosphorus and nitrogen analogs

$$(CH_3)_3N\text{-}BH_2\text{-}As(CH_3)_2\text{-}BH_3 \rightarrow (CH_3)_3NBH_3 + {}^1/_3[(CH_3)_2AsBH_2]_3 \qquad (4)$$

in Table II pyrolyze in a similar fashion giving $(CH_3)_3NBH_3$

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(8) Dioxane of crystallization could be quantitatively removed by warming the solid at 65° under vacuum for 10 hr.

(9) F. G. A. Stone and A. B. Burg, *J. Amer. Chem. Soc.*, 76, 386 (1954).

(10) The B-P-B angle in the unknown μ-$(CH_3)_2PB_2H_5$ was estimated in ref 4 to be about 60°. Because of the greater B-As distance, the B-As-B angle in μ-$(CH_3)_2AsB_2H_5$ would be significantly smaller.

and $[(CH_3)_2PBH_2]_3$[4] or $[(CH_3)_2NBH_2]_2$,[11] respectively.

Registry No. B_2H_6, 19287-45-7; $NaAs(CH_3)_2$, 13787-40-1; $Na(CH_3)_2As(BH_3)_2 \cdot {}^1/_2C_4H_8O_2$, 37956-01-7; $[(CH_3)_3NH]Cl$, 593-81-7; $(CH_3)_3NBH_2As(CH_3)_2BH_3$, 37954-24-8.

Acknowledgment. This work was supported by a National Aeronautics and Space Administration traineeship held by L. D. S. and by a grant from the National Science Foundation. This support is gratefully acknowledged.

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Far-Infrared Spectra of Some Nickel(II) and -(IV) Complexes of 2,6-Diacetylpyridine Dioxime

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Several recent studies have dealt with the effect of oxidation state changes on the far-infrared spectra of transition metal complexes.[1-3] These studies have dealt with the numerous low formal oxidation states stabilized by 2,2′-bipyridine and 1,10-phenanthroline.

Recently, Baucom and Drago have reported the synthesis and characterization of Ni(II) and Ni(IV) complexes derived from 2,6-diacetylpyridine dioxime ($DAPDH_2$) shown in Figure 1.[4] The ligand forms a bis chelate and is bonded through the iminoxy and pyridine nitrogens as indicated. The Ni(IV) complex appears to be one of the few authentic examples of Ni in this high oxidation state. We report in this paper a far-infrared spectroscopic investigation of $[Ni(DAPDH_2)_2](ClO_4)_2$, $Na_2[Ni(DAPD)_2]$, and $[Ni(DAPD)_2]$. Due to the complicated nature of the spectra in the 600-100-cm^{-1} region, the metal isotope technique was used to identify the metal-ligand stretching vibrations.[5-7] The Ni-N_1 and Ni-N_2 stretches (see Figure 1 for subscripts) were found to be sensitive to both the charge on the ligand and the oxidation state of Ni.

Experimental Section

The ligand 2,6-diacetylpyridine dioxime and the natural-abundance Ni complexes $[Ni(DAPDH_2)_2](ClO_4)_2$, $Na_2[Ni(DAPD)_2]$, and $[Ni(DAPD)_2]$ were prepared as described by Baucom and Drago.[4] All of the solvents used in the preparation of $Na_2[Ni(DAPD)_2]$ were anhydrous and deoxygenated, and the reactions were carried out in a nitrogen atmosphere. $[Ni(DAPD)_2]$ was prepared both by method A, which consists of the oxidation of $[Ni(DAPD)_2]^{2-}$ by $(NH_4)_2S_2O_8$ in aqueous NH_3-acetone solution, and by method B, which consists of the oxidation of $[Ni(DAPDH_2)_2](ClO_4)_2$ by addition of bromine and pyridine to the perchlorate salt dissolved in methanol-acetonitrile. Both methods gave products whose ir spectra were identical.

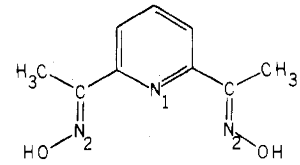

Figure 1. Structure of 2,6-diacetylpyridine dioxime.

Anal. Calcd for $[Ni(DAPDH_2)_2](ClO_4)_2$: C, 33.57; H, 3.45; N, 13.04. Found: C, 33.49; H, 3.27; N, 12.99. Calcd for $[Ni(DAPD)_2]$: C, 49.05; H, 4.12; N, 19.03. Found: C, 48.87; H, 4.07; N, 18.91.

Isotopically pure (minimum isotopic purity >98%) complexes were prepared from ^{58}Ni and ^{62}Ni metal (Oak Ridge National Laboratory). Weighed amounts of the respective metal isotopes (≃10 mg) were dissolved in minimum volumes of 70% $HClO_4$. The resulting solutions were evaporated to dryness, small volumes of water (<1 ml) added and again evaporated to dryness. The resulting $[^{58}Ni(H_2O)_6](ClO_4)_2$ and $[^{62}Ni(H_2O)_6](ClO_4)_2$ were dissolved in minimum volumes of acetone and $DAPDH_2$ added in 2:1 mole ratios; $[^{58}Ni(DAPDH_2)_2](ClO_4)_2$ and the ^{62}Ni analog were isolated as previously described for the natural-abundance complexes. Portions of isotopic $[Ni(DAPDH_2)_2](ClO_4)_2$ were converted to $Na_2[Ni(DAPD)_2]$ and $[Ni(DAPD)_2]$; the Ni(IV) complex ($[Ni(DAPD)_2]$) was prepared by method B. In all cases, the spectra of the isotopically substituted complexes were checked against the spectra of the natural-abundance complexes.

The infrared spectra were recorded on Beckman IR-12 (600-400 cm^{-1}) and Hitachi-Perkin Elmer FIS-3 (400-100 cm^{-1}) spectrophotometers. The spectra were recorded as Nujol mulls on CsI and polyethylene plates at scanning speeds of 1-2 cm^{-1}/min. The reproducibility was checked by multiple scans over the frequency range of interest: the average error in frequency was ±0.5 cm^{-1}.

Results and Discussion

Far-infrared spectra (600-100 cm^{-1}) for $[Ni(DAPDH_2)_2](ClO_4)_2$, $Na_2[Ni(DAPD)_2]$, and $[Ni(DAPD)_2]$ are shown in Figure 2. Observed frequencies and isotopic shifts for $[^{58}Ni(DAPDH_2)_2](ClO_4)_2$, $Na_2[^{58}Ni(DAPD)_2]$, $[^{58}Ni(DAPD)_2]$, and their respective ^{62}Ni analogs are listed in Table I.

Although three ir-active stretching bands ($2\ B_2 + E$) are expected from the symmetry (D_{2d}) of the cation, the only isotope-sensitive bands observed for $[Ni(DAPDH_2)_2](ClO_4)_2$ are at 235 and 229 cm^{-1} (Table I). It is not possible to identify the Ni-N_1 and Ni-N_2 stretching vibrations on the basis of available data. However, the spectral evidence does indicate that the Ni-N_1 and Ni-N_2 bonds are quite similar as evidenced by the narrow frequency range. The observed frequencies for Ni-N_1 and Ni-N_2 stretches are in the general range previously assigned for Ni-N(pyridine) type stretches. For example, Clark and Williams assigned the Ni-N(pyridine) stretches at 236 and 233 cm^{-1} in *trans*-$Ni(py)_4Cl_2$ and *trans*-$Ni(py)_4(NCS)_2$, respectively.[8,9]

Previous investigations on the effect of deprotonation upon metal-nitrogen stretching vibrations have been made by Watt and coworkers. They have shown that small shifts to higher frequency generally accompany deprotonation. For example, deprotonation of $Ni(gly)_2$ to $[Ni(gly\text{-}H)_2]^{2-}$ results in a shift of ≃50 cm^{-1} in the Ni-N(glycine) stretch;[10] this shift is, however, unusually large. Typically, deprotonation results in much smaller shifts; *e.g.*, deprotonation of Ni(β-ala)$_2$ results in a shift of only ≃15 cm^{-1}.[10] Other systems show similar small shifts (0-10 cm^{-1}) to higher frequency upon deprotonation.[11,12] These results would indicate that

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