Acid-Catalyzed Decomposition of 1-Adamantyl *tert*-Butyl Ether. A 0.112-g sample of 1-adamantyl *tert*-butyl ether was allowed to stand for 53 hr at 25.0° within 10 ml of *tert*-butyl alcohol containing 0.05 *M* HCl. Evaporation to dryness gave 0.082 g (100%) of white solid whose pmr and ir spectra indicated it to be 1-adamantanol.

Product Studies. A 0.43-g portion of 1-adamantyl *p*-toluenesulfonate was solvolyzed in 25 ml of the appropriate solvent. After completion of reaction, the solution was partitioned between water and hexane. The hexane fraction was dried over anhydrous $MgSO_4$ and evaporated to dryness to give the solvolysis product, which was identified by comparison of ir and pmr spectra with those of appropriate authentic samples. The data are summarized in Table VIII.

Kinetic Procedures. At suitable time intervals, 2-ml aliquots were removed from 25 ml of bulk solution. For runs in dry alcohols, 25 ml of temperature-equilibrated solvent was added to slightly in excess of 0.4 g of 1-adamantyl *p*-toluenesulfonate. For runs in aqueous organic solvents, all prepared on a volume-to-volume basis, the rate at which the substrate passed into solution was frequently low compared to the reaction rate and, therefore, the substrate was dissolved in the organic phase and an appropriate volume of water added immediately prior to the start of the kinetic run. Also, for some runs carried out in aqueous–organic solvents, the concentration of 1-adamantyl *p*-toluenesulfonate was halved.

Aliquots were quenched by drowning in 20 ml of acetone, neutral to resorcinol blue (Lacmoid) indicator, and cooled within a solid CO_2– acetone or ice–salt bath, and the acid which had developed was titrated against a standardized solution of sodium methoxide in methanol. For runs in the presence of pyridine or quaternary ammonium salts, the appropriate concentration of additive was introduced into the solvent prior to its addition to the substrate. Infinity titers were estimated by removing aliquots into 10 ml of 60% ethanol, allowing them to stand for several hours prior to addition of 20 ml of acetone and titration as indicated above. For each run, a mean value of two infinity determinations was taken. For several of the faster kinetic runs, true infinity titers were also obtained by direct addition to neutral acetone and these closely agreed with the infinity titers estimated by the above technique.

With the exception of the *tert*-butyl alcohol runs, first-order rate coefficients were obtained from a statistical computation of the slope of a plot of log $[(\text{titer})_{t=\infty} - (\text{titer})_{t=t}]$ against time. For the *tert*-butyl alcohol runs, integrated rate coefficients were determined on a point-by-point basis, as in example D of Table IX, and an initial value was obtained by statistical extrapolation of a plot of these coefficients against extent of reaction to zero extent of reaction. In the four illustrative runs which appear in Table IX, the first-order rate coefficients reported for each point are the integrated first-order rate coefficients with respect to 1-adamantyl *p*-toluenesulfonate.

Electronic Structures of Low-Spin, Square-Pyramidal Complexes of Nickel(II)

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Abstract: Detailed electronic spectral measurements at 300 and 77°K have been carried out on square-pyramidal complexes of the type $[Ni(diars)_2X]^z$ (diars = *o*-phenylenebisdimethylarsine; X = Cl, Br, I, CNS, CN, thiourea, NO_2, As). Assignment of the ligand-field bands leads to a d-level ordering $xy < xz, yz < z^2 \ll x^2 - y^2$. Central to this interpretation is identification of the main absorption band as the symmetry-allowed ${}^1A_1 \rightarrow {}^1E$ $(xz, yz \rightarrow x^2 - y^2)$ transition. The assignment was facilitated by the low-temperature measurements, and by comparison with electronic spectral results on the four-coordinate $[Ni(diars)_2]^{2+}$ complex. Comparison of the ligand-field spectra for $[Ni(diars)_2X]^+$ (X = Cl, Br, I) with those for analogous trigonal-bipyramidal complexes shows large differences. At low temperatures, there are three bands in the square-pyramidal cases, whereas two bands are resolved in the trigonal bipyramids. These results and other electronic spectral criteria are presented which provide a means of distinguishing between the square-pyramidal and trigonal-bipyramidal geometries in the d^8 low-spin electronic configuration. The charge-transfer region of the spectra of the four- and five-coordinate complexes is complicated by intraligand diarsine absorption.

It has been known for some time that the bisdiarsine complexes of M(II) (M = Ni, Pd, Pt) readily form adducts of higher coordination number with various simple ligands (X).[3,4] The pioneering work of Nyholm on the transition metal complexes of diarsine included conductivity and spectrophotometric evidence which indicated that these adducts are five coordinate in solution. Since that time, additional evidence has been provided by Peloso and coworkers, who were able to determine formation constants and thermodynamic parameters for a wide range of the $[M(diars)_2X]^z$ (M = Ni(II), Pd(II), Pt(II)) species.[5] The suggestion that these five-coordinate complexes are square pyramidal[4] has received strong support from the determination of the crystal and molecular structure of the once very puzzling compound[6] now known[7] to be $[Ni(diars)(triars)](ClO_4)_2$. The complex ion is composed of a nearly regular square pyramid of As atoms about the central nickel atom. Although a significant number of low-spin d^8 square-pyramidal structures have been determined by X-ray methods,[8–12] and some electronic

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spectra have been measured, there have been insufficient data on which to formulate a detailed electronic structural model. The $[\mathrm{Ni(diars)_2X}]^z$ complexes are particularly attractive for study because variations in axial bonding interactions can be made in a systematic way.

We report in this paper the electronic absorption spectra of a series of five-coordinate complexes of the type $[\mathrm{Ni(diars)_2X}]^z$, and the four-coordinate species $[\mathrm{Ni(diars)_2}]^{2+}$, in solution at 300°K and in frozen solutions which form clear, rigid glasses at 77°K. The increased resolution achieved at low temperature has proved important in facilitating assignment of the ligand-field spectra. The temperature dependence of the spectra has also furnished evidence concerning the symmetry-allowed or -forbidden character of the bands. Based on the spectral results, a discussion is presented of the electronic structures of the square-pyramidal complexes.

Experimental Section

Reagents. All metal salts were reagent grade and were used without further purification. The ligand *o*-phenylenebisdimethylarsine (diarsine) was prepared and purified by the method of Feltham, *et al.*[13]

$[\mathrm{Ni(diars)_2X}]\mathrm{X}$ (X = Cl, Br, I). These compounds were prepared according to the method of Nyholm[14] and recrystallized from ethanol. $[\mathrm{Ni(diars)_2}](\mathrm{ClO_4})_2$ was prepared by the method of Harris, *et al.*,[3] and recrystallized from a mixture of acetonitrile and ethanol. $[\mathrm{Ni(diars)(triars)}](\mathrm{ClO_4})_2$ was prepared using the nickel(II)-catalyzed conversion of diars to triars described by Nyholm, *et al.*[6,7] All samples were analyzed for C, H, and As (Galbraith Microanalytical Laboratory, Knoxville, Tenn.) and characterized by visible absorption spectral measurements.

$[\mathrm{Ni(diars)_2X}]\mathrm{ClO_4}$ (X = Cl, Br, I, NCS). These compounds were prepared by a modification of Nyholm's method.[3] This modification was suggested by the method used by Meek and coworkers[15] to prepare complexes of the type $[\mathrm{NiLX}]\mathrm{ClO_4}$, where L is a tetradentate "tripod" ligand and X is Cl, Br, I, CN, or NCS. The method consists of mixing equimolar amounts of $\mathrm{Ni(ClO_4)_2 \cdot 6H_2O}$ and $\mathrm{NiX_2}$ in ethanol and adding a stoichiometric amount of diarsine in ethanol to produce the solid $[\mathrm{Ni(diars)_2X}]\mathrm{ClO_4}$. The products were recrystallized from dichloromethane or methanol. All samples were analyzed for C, H, and As, and the results found to be in excellent agreement with calculated percentages.

$[\mathrm{Ni(diars)_2CN}]\mathrm{ClO_4}$. This compound was first prepared in an unusual reaction involving $[\mathrm{Ni(diars)_2}](\mathrm{ClO_4})_2$ and tetracyanoethylene (TCNE) in ethanol. $[\mathrm{Ni(diars)_2}](\mathrm{ClO_4})_2$ (0.035 g) was mixed with ethanol (35 ml), in which it is very slightly soluble, and TCNE (0.035 g) was added. Upon heating on the steam bath, a red solution was formed. The solution was filtered, and after reducing the volume of solution or addition of ethyl ether, a red solid precipitated. This material was impure, but recrystallization from methanol afforded dark crystals of the compound. The solid exhibits a single, sharp C≡N stretching frequency at 2101 $\mathrm{cm^{-1}}$. In acetonitrile solution the band appears at 2109 $\mathrm{cm^{-1}}$. *Anal.* Calcd for $[\mathrm{Ni(diars)_2CN}]\mathrm{ClO_4}$: C, 33.35; H, 4.26; As, 39.62. Found: C, 33.31; H, 4.35; As, 39.34.

$[\mathrm{Ni(diars)_2(thiourea)}](\mathrm{ClO_4})_2$. $[\mathrm{Ni(diars)_2}](\mathrm{ClO_4})_2$ was mixed with ethanol containing a large excess of thiourea. A red solid was formed after warming a few minutes on the steam bath. The solid was filtered off and washed repeatedly with cold ethanol, in which it is sparingly soluble. This complex is extensively dissociated in ethanol solution to $[\mathrm{Ni(diars)_2}]^{2+}$ and thiourea. Addition of an excess of thiourea to the ethanol solution is necessary to suppress dissociation. *Anal.* Calcd for $[\mathrm{Ni(diars)_2(thiourea)}](\mathrm{ClO_4})_2$: C, 27.84; H, 4.01; As, 33.08. Found: C, 27.74; H, 3.93; As, 33.33.

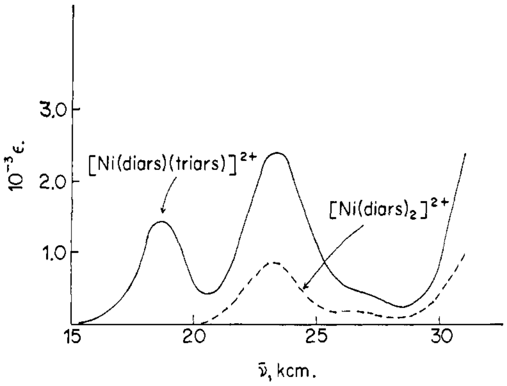

Figure 1. Electronic spectra of $[\mathrm{Ni(diars)_2}](\mathrm{ClO_4})_2$ in 2-methyltetrahydrofuran–methanol and $[\mathrm{Ni(diars)(triars)}](\mathrm{ClO_4})_2$ in 2-methyltetrahydrofuran–ethanol–propionitrile at 77°K.

Physical Measurements. All ultraviolet and visible spectral measurements were made on the Cary Model 14CMRI spectrophotometer. Measurement of spectra at 77°K was carried out as previously described.[16] Measurements in the visible region were made using Pyrex square cells prepared from square tubing obtained from Wilmad Glass Co. For the ultraviolet region, quartz cells of a similar type were used. In this case, however, the cells were made by molding round quartz tubing on a square, solid molybdenum form. The advantage of these cells over fused or cemented quartz square cells is that they show much less tendency to induce crack formation in unstable rigid glasses at 77°K. A number of measurements were carried out using commercial Suprasil square cells, and these results agree well with those taken using the tubing cells. Repeated measurements have been carried out using these cells, and reproducibility is good. Base-line measurements using solvent alone at 300 and 77°K were used to correct measured spectra. Solutions for spectral measurements were prepared using the 2:1 mixture of 2-methyltetrahydrofuran and methanol, propionitrile, or ethanol, as described earlier.[17] A 2:1 mixture of ethanol and ethyl ether was found to form a transparent, crack-free glass on a certain percentage of trials, and this glass was used for a number of measurements. Propionitrile (Eastman White Label) was purified according to a published method.[18]

Molar extinction coefficients at 77°K have been corrected for volume contraction using correction factors given earlier.[17] The contraction of the 2:1 ethanol–ethyl ether mixture at 77°K is 20%, as determined by cooling a measured volume of solvent in a graduated tube.

Infrared spectra of Nujol mulls were measured on a Perkin-Elmer Model 225 grating spectrophotometer between potassium bromide plates. Solution infrared spectra in spectroquality acetonitrile or dichloromethane (Matheson Coleman and Bell) were obtained using 1.00-mm cells with calcium fluoride windows.

Results and Discussion

$[\mathrm{Ni(diars)_2}](\mathrm{ClO_4})_2$ and $[\mathrm{Ni(diars)(triars)}](\mathrm{ClO_4})_2$. These two compounds contain only arsenic donor atoms, and form a logical starting point for a discussion of the electronic spectra presented here. An X-ray structural study of $[\mathrm{Ni(diars)(triars)}](\mathrm{ClO_4})_2$ has shown that this compound is five coordinate, with an essentially regular, square-pyramidal structure.[7] The nickel atom is raised slightly above the plane of the four arsenic atoms. The visible absorption spectrum of the solid in a Nujol mull is the same as the solution spectrum, both at room temperature and 77°K, indicating that

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Table I. Electronic Spectra of $[Ni(diars)_2](ClO_4)_2$ and $[Ni(diars)(triars)](ClO_4)_2$[a]

	Solvent mixture[b]			50% C_2H_5OH	98% C_2H_5OH	98% CH_2Cl_2
$^1A_{1g}$ →	300°K	77°K	C_2H_5CN	50% CH_3CN	2% CH_3CN	2% CH_3CN
$[Ni(diars)_2](ClO_4)_2$						
^1E_g	22,600 (440)	23,200 (880)	22,600 (1140)	22,675 (840)	22,725 (715)	22,600 (330)
$^1A_{2g}$		26,250 (sh 195)				
Charge-Transfer and Intraligand Transitions						
	30,870 (sh 2880)	31,665 (sh 1580)			30,830 (sh 2300)	30,040 (4500)
	33,650 (sh 8640)		34,600 (sh 15,800)	34,405 (sh 15,000)	33,615 (sh 10,400)	33,005 (sh 11,200)
		36,000 (17,800)				35,555 (sh 18,000)
	37,365 (28,500)	38,735 (27,200)	38,550 (25,600)	38,460 (25,200)	*c*	38,740 (25,600)
$[Ni(diars)(triars)](ClO_4)_2$ in 2-Methyltetrahydrofuran–Methanol						
$^1B_1$	18,555 (765)	18,620 (1150)				
^1E	23,040 (1490)	23,365 (2380)				
$^1A_2$		26,850 (sh 385)				
Charge-Transfer and Intraligand Transitions						
		30,650 (sh 1150)				
	34,525 (7680)					
	37,810 (11,400)	37,960 (14,700)				

[a] $\bar{\nu}$, cm^{-1} (ϵ, l. mol^{-1} cm^{-1}). [b] Solvent mixture is 4:1:1 2-methyltetrahydrofuran–ethanol–propionitrile. [c] Not measured.

the structure of the complex in the solid persists in solution. Conductivity, magnetic, and infrared and visible spectral measurements indicate that $[Ni(diars)_2](ClO_4)_2$ exists in solution as the four-coordinate, approximately square-planar $[Ni(diars)_2]^{2+}$.

Figure 1 shows the spectra of the two complexes in frozen solution at 77°K. Complete results of the spectral measurements on these compounds are set out in Table I. The low-temperature spectra are better resolved, with narrower bands and somewhat higher molar extinction coefficients. The spectrum of $[Ni(diars)(triars)]^{2+}$ in the visible region exhibits two resolved bands, at 18,620 cm^{-1} (ϵ 1150) and 23,365 cm^{-1} (ϵ 2380), and a shoulder at 26,850 cm^{-1} (ϵ ~385). The spectrum of $[Ni(diars)_2]^{2+}$, on the other hand, shows only one resolved band, at 23,200 cm^{-1} (ϵ 880), and a shoulder at 26,250 cm^{-1} (ϵ ~195). The two spectra are quite similar except for the presence in the five-coordinate spectrum of the band at 18,620 cm^{-1}.

The spectra of $[Ni(diars)(triars)]^{2+}$ and $[Ni(diars)_2]^{2+}$ may be analyzed satisfactorily by assuming the point microsymmetries C_{4v} and D_{4h}, respectively. In the C_{4v} case, there are three spin-allowed transitions, $^1A_1 \rightarrow {}^1B_1$ ($z^2 \rightarrow x^2 - y^2$), $^1A_1 \rightarrow {}^1E$ ($xz, yz \rightarrow x^2 - y^2$), and $^1A_1 \rightarrow {}^1A_2$ ($xy \rightarrow x^2 - y^2$). One of these transitions, $^1A_1 \rightarrow {}^1E$ ($xz, yz \rightarrow x^2 - y^2$), is also orbitally allowed. It is reasonable to assign the most intense band (ν_2) in the visible spectrum of $[Ni(diars)(triars)]^{2+}$ as the $^1A_1 \rightarrow {}^1E$ transition. In support of this assignment, the integrated intensity of the ν_2 band is independent of temperature. Similarly, we assign the band which appears at 23,200 cm^{-1} in the spectrum of $[Ni(diars)_2]^{2+}$ as the $^1A_{1g} \rightarrow {}^1E_g$ ($xz, yz \rightarrow x^2 - y^2$) transition. We note that the latter transition is parity forbidden, which is consistent with the fact that a smaller molar extinction coefficient is observed. However, data in Table I show that the ϵ of the band is solvent dependent, which suggests that a relatively good donor such as C_2H_5CN may bind to the axial coordination site of $[Ni(diars)_2]^{2+}$.

The low-energy band (ν_1) which appears at 18,620 cm^{-1} in the spectrum of the five-coordinate complex, but is absent in the four-coordinate case, is logically assigned as $^1A_1 \rightarrow {}^1B_1$ ($z^2 \rightarrow x^2 - y^2$). The apical ligand in the five-coordinate complex should strongly destabilize the z^2 orbital and thus shift the ($z^2 \rightarrow x^2 - y^2$) electronic transition to a relatively low-energy position. Also, the delocalization of the z^2 orbital to the apical ligand should increase the intensity of the ν_1 band in comparison to the corresponding band in the four-coordinate complex.

The weak shoulder at 26,850 cm^{-1} in $[Ni(diars)(triars)]^{2+}$ is assigned as $^1A_1 \rightarrow {}^1A_2$ ($xy \rightarrow x^2 - y^2$). The rather high intensities exhibited by all the ligand-field bands reflect the fact that the so-called d-orbital levels must have a significant amount of arsenic character. Ligand-field bands with high extinction coefficients are commonly observed in complexes involving ligands with heavy donor atoms (P, As, S, Se).[15,19] This is generally interpreted as evidence for considerable ligand character in the molecular orbitals derived from the metal d orbitals in these complexes.

In the complex $[Ni(diars)_2]^{2+}$ there are two transitions not yet accounted for, $^1A_{1g} \rightarrow {}^1A_{2g}$ ($xy \rightarrow x^2 - y^2$) and $^1A_{1g} \rightarrow {}^1B_{1g}$ ($z^2 \rightarrow x^2 - y^2$). There is, however, only one band left unassigned, the shoulder appearing at 26,250 cm^{-1}. It is probable that this band is $^1A_{1g} \rightarrow$

[19] G. Dyer and L. M. Venanzi, *J. Chem. Soc.*, 2771 (1965), and references therein.

$^1A_{2g}$, because of its proximity to the $^1A_1 \rightarrow {}^1A_2$ band in [Ni(diars)(triars)]$^{2+}$. The $^1A_{1g} \rightarrow {}^1B_{1g}$ band must be at higher energy than the $^1A_1 \rightarrow {}^1B_1$ band in [Ni(diars)(triars)]$^{2+}$; it could be buried in the strong absorption of the $^1A_{1g} \rightarrow {}^1E_g$ band.

The uv absorption spectra out to 40,000 cm^{-1} of the two complexes under discussion here are also given in Table I. Between 30,000 and 40,000 cm^{-1}, intraligand transitions of the diarsine apparently are mixed heavily with the charge-transfer transitions of the complexes.[16] For this reason we shall not attempt a detailed analysis of the uv spectra.

[Ni(diars)$_2$X]$^+$ (X = Cl, Br, I). The electronic spectrum of [Ni(diars)$_2$Br]$^+$ in the visible region is representative of this class of compounds and is pictured in Figure 2. At room temperature, the spectrum exhibits one broad, slightly asymmetric absorption centered at 21,050 cm^{-1}. At 77°K, there is an increase in ϵ and a narrowing of the central band, and one lower intensity absorption is resolved on either side of the main band. Complete results of the spectral study, along with band assignments, are reported in Table II.

In order to verify the five-coordinate composition of these compounds in solution, we have measured the absorption spectra of both Ni(diars)$_2$X$_2$ and [Ni(diars)$_2$X]ClO$_4$ and observed that they are the same for any particular X, and are readily distinguished from that of [Ni(diars)$_2$]$^{2+}$. Thus the complexes must all be five coordinate, because for stoichiometric reasons [Ni(diars)$_2$X]ClO$_4$ could give a six-coordinate [Ni(diars)$_2$X$_2$] species only if a corresponding amount of [Ni(diars)$_2$]$^{2+}$ were produced. Dissociation of [Ni(diars)$_2$X]^z to [Ni(diars)$_2$]$^{2+}$ + X^{z-2} in the concentration range employed for the spectral measurements appears to occur only with X = thiourea, and this dissociation is easily detected by observing a very asymmetric main ligand-field band in the visible region of the spectrum at 77°K. One component of this composite peak falls at approximately the position of the main absorption in [Ni(diars)$_2$]$^{2+}$ ($\nu \sim$ 23,000 cm^{-1}) and the other band occurs at lower energy.

The pattern of three bands in the visible region which was observed in the spectrum of [Ni(diars)(triars)]$^{2+}$ at 77°K appears in this case also. The assignment of the visible spectrum of [Ni(diars)$_2$X]$^+$ is the same as that proposed for [Ni(diars)(triars)]$^{2+}$. For [Ni(diars)$_2$X]$^+$, however, the central band (ν_2) clearly dominates the spectrum. This result is expected in C$_{4v}$, since one ligand-field band is symmetry allowed and the other two are symmetry forbidden. The reason for the relatively high intensity of ν_1 for [Ni(diars)(triars)]$^{2+}$ is most likely that the $a_1(z^2)$ orbital has a significant amount of ligand character in that case. Mixing of ligand orbitals with metal d orbitals is expected to be considerably stronger for arsenic than for halide. In accord with this interpretation is the observed dependence of the extinction coefficient of ν_1 on X in the halide series. The value of ϵ decreases in the order I > Br > Cl, which is also the order of decreasing tendency to form covalent bonds with metal ions.

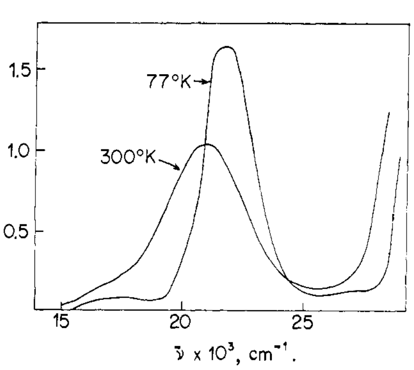

Figure 2. Electronic spectra of [Ni(diars)$_2$Br]Br in 2-methyltetrahydrofuran–methanol at 300 and 77°K.

The usefulness of the low-temperature ligand-field spectrum is best seen for these halide complexes. The room-temperature spectrum shows one broad band with a shoulder on one side or the other of this main band. All three bands can be detected in the spectra at 77°K (see Table II). The oscillator strength of ν_2

Table II. Electronic Spectra of [Ni(diars)$_2$X]X and [Ni(diars)$_2$X]ClO$_4$[a]

$^1A_1 \rightarrow$	300°K	77°K	300°K	77°K
	[Ni(diars)$_2$Cl]Cl		[Ni(diars)$_2$Cl]ClO$_4$	
$^1B_1$		18,030 (sh 65)		
^1E	21,285 (1060)	22,080 (1530)	21,270 (905)	22,065 (1270)
$^1A_2$	25,895 (sh 170)	26,285 (190)		26,345 (290)
	Charge-Transfer and Intraligand Transitions			
	30,345 (sh 3740)	30,425 (4670)	30,245 (sh 2360)	30,455 (3420)
	33,410 (sh 9340)	34,275 (sh 11,220)	33,265 (sh 9050)	34,275 (sh 9340)
	36,245 (sh 21,500)	36,695 (37,800)	36,285 (sh 19,000)	36,940 (30,400)
	40,000 (sh 21,000)	40,715 (20,000)	39,960 (sh 17,700)	40,700 (15,300)
	[Ni(diars)$_2$Br]Br		[Ni(diars)$_2$Br]ClO$_4$	
$^1B_1$	16,395 (sh 110)	17,660 (80)	16,325 (sh 154)	17,560 (165)
^1E	21,055 (1030)	21,820 (1820)	21,055 (1025)	21,860 (1960)
$^1A_2$		26,275 (sh 110)		27,025 (sh 260)
	Charge-Transfer and Intraligand Transitions			
	30,625 (sh 5300)	30,675 (sh 5180)	30,660 (sh 5950)	30,315 (sh 5600)
		33,280 (sh 6950)		33,110 (sh 6470)
	38,240 (24,000)	38,095 (33,800)	37,901 (26,000)	37,996 (33,800)
	[Ni(diars)$_2$I]I		[Ni(diars)$_2$I]ClO$_4$	
$^1B_1$	16,130 (sh 170)	17,330 (165)	16,230 (sh 330)	17,305 (190)
^1E	20,265 (1145)	21,455 (1950)	20,275 (1075)	21,465 (1850)
$^1A_2$		26,665 (sh 225)		27,025 (sh 230)
	Charge-Transfer and Intraligand Transitions			
	30,035 (sh 5250)	30,245 (7500)	30,155 (sh 4900)	30,245 (6450)
		34,365 (sh 7000)		34,070 (sh 5800)
	37,075 (22,750)	37,620 (30,500)	37,200 (20,800)	37,265 (27,300)

[a] $\bar{\nu}$, cm^{-1} (ϵ, l. mol^{-1} cm^{-1}); solvent, 2-methyltetrahydrofuran–methanol or –ethanol; ethyl ether–ethanol; some ϵ's determined in methanol.

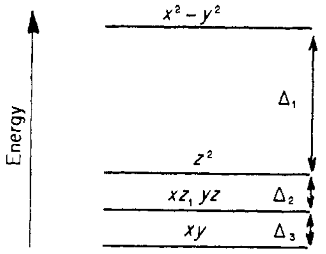

Figure 3. d-orbital energy levels for square-pyramidal complexes: $\Delta_1 = \Delta\epsilon^{\text{core}}[(x^2 - y^2) - (z^2)]$; $\Delta_2 = \Delta\epsilon^{\text{core}}[(z^2) - (xz, yz)]$; $\Delta_3 = \Delta\epsilon^{\text{core}}[(xz, yz) - (xy)]$.

is not changed on decreasing the temperature, which is strong evidence of the symmetry-allowed character of the band.[20] Because the weaker bands appear as shoulders, it is not possible to measure the half-widths or to obtain accurate values of ϵ. It does appear, however, that the lowest energy band decreases in intensity at low temperature.

The band assigned as $^1A_1 \rightarrow {}^1A_2$ ($xy \rightarrow x^2 - y^2$) is relatively weak, and appears in the same position for these complexes as was reported for $[Ni(diars)_2]^{2+}$ and $[Ni(diars)(triars)]^{2+}$. The positions of the other two ligand-field bands do change, the energy ordering being Cl > Br > I for both bands. A rationalization for this ordering will be offered later. There is also a striking shift of these two bands to higher energy at low temperature, in some cases by more than 1000 cm^{-1}. This could reflect a small change in the equilibrium location of the fifth ligand at low temperature.

The uv spectra of these complexes are reported in Table II. As described for $[Ni(diars)(triars)]^{2+}$ and $[Ni(diars)_2]^{2+}$, there is substantial overlapping and mixing of the charge-transfer bands with the intraligand diarsine absorption.

Table III. Electronic Spectra of $[Ni(diars)_2X]^z$ Complexes[a]

$^1A_1 \rightarrow$	300°K	77°K	300°K	77°K
	$[Ni(diars)_2CN]ClO_4$		$[Ni(diars)_2NO_2]ClO_4$[d]	
$^1B_1$	18,595	19,170	16,200	16,490
	(420)	(400)	(sh 135)	(140)
^1E	25,945	26,415	21,865	22,950
$^1A_2$	(1235)	(1730)	(625)	(1040)
	Charge-Transfer and Intraligand Transitions			
		32,205		
		(sh 1880)		
	35,300	36,195		
	(11,500)	(18,400)		
	36,765	37,040		
	(11,700)	(17,700)		
	$[Ni(diars)_2CNS]ClO_4$		$[Ni(diars)_2(tu)](ClO_4)_2$[b]	
$^1B_1$	16,235	17,635		16,425
	(sh 140)	(sh 325)		(0.04)[c]
^1E	20,950	21,600	19,740	20,940
	(865)	(1410)	(1220)	(0.38)[c]
$^1A_2$		26,665		
		(sh 210)		
	Charge-Transfer and Intraligand Transitions			
	30,355	30,580		29,330
	(2320)	(3810)		(1.48)[c]
	37,445	37,970		
	(16,100)	(21,800)		

[a] $\tilde{\nu}$, cm^{-1} (ϵ, l. mol^{-1} cm^{-1}); solvent, 2:1 mixture of 2-methyltetrahydrofuran and methanol or ethanol. [b] Excess thiourea added. [c] *Relative* extinction coefficient. [d] $[Ni(diars)_2](ClO_4)_2 + NaNO_2$ in solution. Solid compound not isolated.

$[Ni(diars)_2X]^z$ (X = CN, NO$_2$, CNS, tu). The spectral data and assignments for these complexes are set out in Table III. It is easy to identify the symmetry-allowed $^1A_1 \rightarrow {}^1E$ ($xz, yz \rightarrow x^2 - y^2$) ligand-field band ($\nu_2$) by the dependence of the extinction coefficient on temperature. The ϵ value for this band shows a considerably greater increase than for any other band in the visible spectrum. The value of f for ν_2 is independent of temperature. The band which appears as a weak shoulder (ν_3 ~26,000 cm^{-1}) in the other compounds is not seen in the NO$_2$ or the thiourea (tu) derivatives because of absorption due to X. This band is also not seen in $[Ni(diars)_2CN]^+$, because the allowed $^1A_1 \rightarrow {}^1E$ ($xz, yz \rightarrow x^2 - y^2$) transition appears at ~26,000 cm^{-1}.

Certain experimental difficulties were encountered with the thiourea complex. In order to suppress dissociation of the complex in the ethanol–2-methyltetrahydrofuran solvent mixture, a large excess of thiourea had to be added, which rendered the glass unstable and subject to cracking at low temperature. With an insufficient amount of thiourea to suppress dissociation, a stable glass was formed, and the value of ν_{max} was obtained by extracting it from the asymmetric peak which contained this band and also that due to $[Ni(diars)_2]^{2+}$. It was confirmed that the composite band was made up of one band due to $[Ni(diars)_2]^{2+}$ and one due to $[Ni(diars)_2tu]^{2+}$, by adding a small amount of thiourea and observing the change in the intensities of the two components of the band at 77°K.

It is not certain whether the thiocyanate complex contains N- or S-bonded thiocyanate at 77°K in this solvent. We have obtained infrared spectral evidence[16] that both the N- and S-bonded isomers of this complex coexist at equilibrium in acetonitrile, dichloromethane, and DMSO at room temperature. The main ligand-field band (ν_2) appears to be symmetric at 77°K, and so does not provide evidence in favor of the coexistence of the two isomers under these conditions. The position of ν_2 should not differ greatly for the two isomers, however.

d-Orbital Energies. The one-electron d-orbital energies (ϵ^{core}) may be calculated from the assignments by correcting for interelectronic repulsions. A diagram defining the spacing of the d-orbital levels in these square-pyramidal complexes is given in Figure 3, and values of the splitting parameters Δ_1, Δ_2, and Δ_3 for the complexes are set out in Table IV. The d-level

Table IV. Ligand-Field Splittings for Square-Pyramidal Complexes

Complex	Lf splittings[a] Δ_1	Δ_2	Δ_3
$[Ni(diars)(triars)]^{2+}$	24.1	4.25	1.99
$[Ni(diars)_2Cl]^+$	23.6	3.54	2.75
$[Ni(diars)_2Br]^+$	23.1	3.73	3.31
$[Ni(diars)_2I]^+$	22.8	3.64	3.74
$[Ni(diars)_2CN]^+$	24.7	6.75	*b*
$[Ni(diars)_2CNS]^+$	23.1	3.47	3.57
$[Ni(diars)_2(tu)]^{2+}$	21.9	4.02	*b*
$[Ni(diars)_2NO_2]^+$	22.0	5.96	*b*

[a] Energies in kcm^{-1} for Racah parameter values $B = 0.5$, $C = 3.5$ kcm^{-1}. [b] Insufficient data.

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(20) C. J. Ballhausen, "Introduction to Ligand-Field Theory," McGraw-Hill, San Francisco, Calif., 1962, pp 185–188.

Table V. Comparison of Ligand-Field Bands in TBP and SPY Complexes[a]

$[Ni(diars)_2Cl]^+$	$[Ni(TAA)Cl]^+$ [b]	$[Ni(diars)_2Br]^+$	$[Ni(TAA)Br]^+$ [b]	$[Ni(diars)_2CN]^+$	$[Ni(TAA)CN]^+$ [b]
18,030	15,600	17,660	15,100	19,170	21,230
(sh 65)	(3900)	(80)	(3720)	(400)	(5450)
22,080	20,790	21,820	19,800	26,415	27,625
(1530)	(sh 120)	(1820)	(sh 170)	(1730)	(360)
26,285		26,275			
(190)		(sh 110)			

[a] All measurements at 77 °K in 2-methyltetrahydrofuran–ethanol or –methanol; $\bar{\nu}$, cm^{-1} (ϵ, l. mol^{-1} cm^{-1}). [b] From ref 16.

ordering $xy < xz, yz < z^2 \ll x^2 - y^2$ is observed in all the cases where three bands are resolved. This includes the $[Ni(diars)(triars)]^{2+}$ complex, in which all the donor atoms are arsenic. One rather unexpected feature of this ordering is that the xy orbital is placed below the degenerate xz, yz level. Our spectral data also suggest that this particular aspect of the d-level ordering is found in the square-planar $[Ni(diars)_2]^{2+}$ complex. We may recall that a simple crystal-field model predicts $xy > xz, yz$ for both square-pyramidal and square-planar complexes, because the xy orbital interacts with all four equatorial ligands. Furthermore, Dyer and Meek have presented spectroscopic evidence that the xz, yz level is lowest of the d levels in the square-pyramidal complexes of cobalt(II) with certain phosphorus and sulfur donor ligands.[21] The result that xy is of lower energy than xz, yz for the square-planar and square-pyramidal complexes involving diarsine as the equatorial ligands may be taken as evidence of the importance of metal ($d\pi$) → diarsine (π) back-bonding. Instead of being destabilized as the simple crystal-field model suggests, the metal xy orbital in fact becomes more stable than xz, yz because it overlaps orbitals of π symmetry on all four equatorial arsenic atoms. It is probable that the order $xz, yz > xy$ will be found in other square-planar and square-pyramidal complexes containing π-acceptor ligands.

Some information concerning the relative σ and π bonding abilities of the axial ligand X may be found in the value of the Δ_2 parameter. Examination of the Δ_2 values in Table IV reveals the order $CN^- \gg -NO_2^- > -As\!< \sim tu > CNS^- \sim Cl^- \sim Br^- \sim I^-$. This order approximately follows the ordinary spectrochemical series, as would be expected because Δ_2 reflects the difference in σ and π antibondedness of the axially oriented orbitals d_{z^2} and d_{xz}, d_{yz}, respectively. Perhaps a more interesting number is Δ_3, which in principle is directly related only to the π-donor strength of X. The observed Δ_3 values provide a π-donor order of $I^- > CNS^- > Br^- > Cl^-$ for low-spin Ni(II) situations. This order is consistent with qualitative ideas concerning π-donor effects.

Comparison with Trigonal-Bipyramidal Spectra. We turn now to a comparison between the electronic spectral characteristics of the two limiting geometries in five coordination, the trigonal bipyramid (TBP) and the square pyramid (SPY). It was anticipated that it might be possible to develop some empirical guidelines for classifying five-coordinate complexes as SPY or TBP on the basis of electronic spectra measured at room temperature and at 77 °K. We consider here only the case of the low-spin d^8 complexes, primarily involving nickel(II) as the central metal. There are a reasonable number of complexes of this type for which structural determinations have been carried out, and it would be worthwhile to carry out detailed spectral measurements and apply the guidelines discussed below to some of these compounds which have not been the subject of careful spectral study.

The six compounds used for comparison here are $[Ni(diars)_2X]^+$ (X = Cl, Br, CN) and $[Ni(TAA)X]^+$ (X = Cl, Br, CN).[22,23] In each analogous SPY–TBP pair, the coordinated ligand atoms are identical, the only difference besides the geometry of the two complexes being the nature of the aliphatic and aromatic groups attached to the arsenic donor atoms. The spectral data for these complexes are set out in Table V.

The one characteristic of the visible spectrum which is diagnostic of the TBP is the intense, asymmetric room temperature band which becomes more symmetrical at 77 °K.[16] As shown in Figures 1 and 2, the SPY structures do not exhibit this behavior. Rather, bands appearing as shoulders in the room temperature spectrum of the SPY complexes are resolved at 77 °K. This is perhaps best seen in the spectrum of $[Ni(diars)(triars)]^{2+}$, in which two bands that appear close together and are of comparable intensity are resolved at 77 °K.

The number and intensity pattern of the ligand-field bands, as well as their temperature dependence, are useful in diagnosing the geometry. The TBP complexes mentioned above exhibit two bands, and the one at lower energy is considerably more intense. The less intense band is sometimes difficult to observe because it is often as little as one-fiftieth as intense as the main band.[16] The main band is often asymmetric at 300 °K, and there is some evidence that the degree of asymmetry depends upon the static distortion of the TBP complex.[23] For some complexes, though none of the group under discussion here, the asymmetric band is replaced by two distinct bands at 300 °K. This is the case for $Ni[(CH_3)_3P]_3X_2$ (X = Br, I).[24] The lower energy component is of lower intensity in the cases observed thus far. This is consistent with the idea that the spectral pattern in such complexes is changing over to the SPY.

The SPY complexes $[Ni(diars)_2X]^+$ exhibit three ligand field bands, the central one being the most intense. In every case examined in this study, the SPY structure does show the less intense, lowest energy band at 77 °K, and often does at room temperature also. The highest energy member (ν_3) of the three ligand field bands is occasionally not observed.

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[21] G. Dyer and D. W. Meek, *J. Amer. Chem. Soc.*, 89, 3983 (1967).

[22] TAA = $[(CH_3)_2As(CH_2)_3]_3As$.

[23] J. W. Dawson, H. B. Gray, J. E. Hix, Jr., J. R. Preer, and L. M. Venanzi, to be submitted for publication.

[24] Y. Dartiguenave, unpublished results.

The known mixed halide–phosphine (or –arsine) TBP complexes of nickel(II) are blue, green, or purple. The corresponding SPY complexes are red, brown, or purple, and if the number and kind of ligands are the same in the two geometries, as in those discussed here, the lowest energy ligand-field band occurs at lower energy in the case of the TBP. When we go to the mixed cyanide–arsine, however, the result is that the lowest energy absorption maximum is found in the SPY spectrum. The lowest energy band in the SPY complex is of relatively low intensity (for $[Ni(diars)_2CN]^+$, ϵ is 420 in 2-methyl-TBP–methanol at 300°K). If we compare the most intense ligand-field bands for the two compounds, we find that for both cyanides and halides, the *intense* absorption at lower energy is found in the TBP.

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Structural Characterization of the Dinuclear Metal Carbonyl Anions $[M_2(CO)_{10}]^{2-}$ (M = Cr, Mo) and $[Cr_2(CO)_{10}H]^-$. The Marked Stereochemical Effect of a Linearly Protonated Metal–Metal Bond

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Abstract: Single-crystal X-ray structural determinations of the metal carbonyl anions $[Cr_2(CO)_{10}H]^-$, $[Cr_2(CO)_{10}]^{2-}$, and $[Mo_2(CO)_{10}]^{2-}$ not only have unambiguously established their architectures but also have made possible for the first time a direct stereochemical comparison of two closely related transition metal complexes *with* and *without* a hydrogen atom as a bridging ligand. The $[Cr_2(CO)_{10}]^{2-}$ and $[Mo_2(CO)_{10}]^{2-}$ anions possess the D_{4d}-$\bar{8}2m$ $Mn_2(CO)_{10}$-type structure. The different metal–metal bond length changes observed between the isoelectronic $[Cr_2(CO)_{10}]^{2-}$–$Mn_2(CO)_{10}$ pair (Δ(M–M) = 0.05 Å) and the isoelectronic $[Mo_2(CO)_{10}]^{2-}$–$Tc_2(CO)_{10}$ pair (Δ(M–M) = 0.09 Å) as well as the significant difference in metal–metal bond length changes between the former pair and the isoelectronic $[Fe_2(CO)_8]^{2-}$–$Co_2(CO)_8$ (nonbridged isomer) pair of D_{3h}-$\bar{6}2m$ geometry are analyzed. The prototype $[Cr_2(CO)_{10}H]^-$ structure, which is an unprecedented example of a *linear* three-center two-electron X–H–X system, may be formally derived from the protonation of the Cr–Cr electron-pair bond in the $[Cr_2(CO)_{10}]^{2-}$ anion. This linear protonation of a metal–metal bond produces a conformational change of the two sets of equatorial carbonyl ligands from the staggered D_{4d} arrangement in the $[Cr_2(CO)_{10}]^{2-}$ anion to an exactly eclipsed arrangement (crystallographically required by symmetry) in the $[Cr_2(CO)_{10}H]^-$ anion which approximately possesses a D_{4h}-4/m2/m2/m geometry. The conformation in the $[Cr_2(CO)_{10}H]^-$ anion is ascribed to the two halves of the hydrogen-bridged anion being sufficiently far apart that the attractive part of van der Waals forces dominates to give an eclipsed orientation of the equatorial carbonyl groups. The marked shortening by 0.44 Å between the two chromium atoms in the $[Cr_2(CO)_{10}H]^-$ anion (3.41 ± 0.01 Å) due to deprotonation to give the resulting $[Cr_2(CO)_{10}]^{2-}$ anion (2.97 ± 0.01 Å) apparently causes a sufficient increase in the repulsive part of van der Waals forces to give the staggered conformation. The three-center electron-pair bonding representation of the Cr–H–Cr framework of the $[Cr_2(CO)_{10}H]^-$ anion is discussed with regard to the possibility of either a symmetric double-minimum potential well or a single-minimum potential well. It is accented that in a linear M–H–M system, which represents a maximum separation of the two metal atoms, as well as in other known "bent" M–H–M systems, where the contact distance between the two metal atoms decreases toward that of a deprotonated electron-pair metal–metal bond, there is extensive metal–metal bonding character due to the large direct overlap of the metal orbitals with each other as well as with the hydrogen 1s orbital. The X-ray analysis of the $[Cr_2(CO)_{10}H]^-$ anion was carried out on the tetraethylammonium salt, while both dianions were structurally characterized as bis(triphenylphosphine)iminium salts, $\{[(C_2H_5)_3P]_2N\}_2[M_2(CO)_{10}]\cdot CH_2Cl_2$ (M = Cr, Mo). The $[(C_2H_5)_4N][Cr_2(CO)_{10}H]$ salt crystallizes with one formula species in a triclinic unit cell of dimensions a = 6.82 ± 0.01 Å, b = 10.13 ± 0.01 Å, c = 8.91 ± 0.01 Å, α = 102.0 ± 0.2°, β = 101.6 ± 0.2°, γ = 86.3 ± 0.2°; the crystal-disordered model utilized in the least-squares refinements assumes an average unit cell of centrosymmetric $P\bar{1}$ symmetry with the one $[Cr_2(CO)_{10}H]^-$ anion located on an average center of symmetry and the one cation randomly oriented in one of two centrosymmetrically related positions. The isomorphous $\{[(C_6H_5)P]_2\}_2[M_2(CO)_{10}]\cdot CH_2Cl_2$ (M = Cr, Mo) salts crystallize in the monoclinic system with symmetry C2/c and with a = 13.125 ± 0.009 Å, b = 25.973 ± 0.016 Å, c = 22.491 ± 0.015 Å, β = 94.11 ± 0.02°, ρ_{obsd} = 1.32 g/cm³ *vs.* ρ_{calcd} = 1.35 g/cm³ (z = 4) for the chromium comopund; and with a = 13.362 ± 0.008 Å, b = 26.243 ± 0.016 Å, c = 22.256 ± 0.015 Å, β = 94.21 ± 0.02°, ρ_{obsd} = 1.36 g/cm³ *vs.* ρ_{calcd} = 1.40 g/cm³ (z = 4) for the molybdenum compound.

In recent years there has been considerable interest concerning the stereochemistry and bond properties of systems involving a transition metal to hydrogen bond. Our previous work on several polynuclear tran-

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