needles (123 mg, 82%). The complex was moderately stable in air. Similar treatment of maleic anhydride (70 mg, 0.7 mmol) with [bis(*tert*-butyl isocyanide)carbon disulfide]palladium (112 mg, 0.34 mmol) in *n*-hexane (10 ml) at ambient temperature afforded the complex (60 mg, 48%).

[Bis(*tert*-butyl isocyanide)dimethyl maleate]palladium(0). Dimethyl maleate (135 mg, 0.94 mmol) was added to a suspension of bis(*tert*-butyl isocyanide)palladium (255 mg, 0.94 mmol) in ether (20 ml) below −20° and the mixture was stirred for 3 hr at −20–0°. The orange suspension turned into a colorless solution. After stirring 1 hr at ambient temperature, the colorless solution was concentrated *in vacuo* to give a colorless oil which solidified upon addition of *n*-hexane. Recrystallization from a mixture of ether and *n*-hexane gave colorless needles (326 mg, 83%). The complex was moderately stable in air.

Bis(*tert*-butyl isocyanide)diphenylacetylenepalladium(0). A solution of diphenylacetylene (196 mg, 1.1 mmol) in *n*-hexane (15 ml) was added to a suspension of bis(*tert*-butyl isocyanide)palladium (272 mg, 1 mmol) in a mixture of *n*-hexane (20 ml) and ether (15 ml) below −20°, and the suspension was stirred for several hours below −20°. The orange color of the suspension turned to yellowish white. The white precipitate was filtered off, washed with chilled ether (10 ml), and dried *in vacuo* below 0°. When dissolved in ether at 25° this compound decomposed owing to dissociation followed by irreversible reaction (*vide infra*). Recrystallization from ether in the presence of 1 mol of free diphenylacetylene below 0° gave the complex as white microcrystals (0.360 g, 80%) which decompose at 116°. This compound was not too air sensitive in the solid state but was unstable in solution. A complicated solution chemistry is involved, because dissociation produces a highly coordinatively unsaturated species, Pd(*tert*-BuNC)$_2$, which tends to polymerize into polynuclear compounds.

Reaction of Dimethyl Acetylenedicarboxylate with Pd(PhC$\equiv$CPh)(*tert*-BuNC)$_2$. To a solution of Pd(PhC$\equiv$CPh)(*tert*-BuNC)$_2$ (250 mg, 0.55 mmol) in ether (50 ml) was added dimethyl acetylenedicarboxylate (78 mg, 0.55 mmol) at −78°. Colorless needles appeared upon addition of *n*-hexane at −78°. Thermal instability prevented further purification. The ir spectrum of the crude product (Table IV) indicates coordination of dimethyl acetylenedicarboxylate to the Pd(*tert*-BuNC)$_2$ moiety. At ambient temperature the colorless solution containing the crude complex rapidly turned into a red solution which gave only intractable materials.

Reaction of Bis(*tert*-butyl isocyanide)diphenylacetylenenickel(0) with Molecular Oxygen. Dry oxygen was introduced into a solution of bis(*tert*-butyl isocyanide)diphenylacetylenenickel in ether at −30°. Immediately, a pale green precipitate appeared. The pale green compound was identified by its infrared spectrum as the known oxygen complex, Ni(O$_2$)(*tert*-BuNC)$_2$.[10] Evaporation of the mother liquors to dryness *in vacuo* gave a white solid identified as diphenylacetylene by its infrared spectrum and melting point.

Reaction of Bis(*tert*-butyl isocyanide)azobenzenenickel(0) with Molecular Oxygen. Introduction of dry oxygen into a solution of bis(*tert*-butyl isocyanide)azobenzenenickel in ether at −30° afforded Ni(O$_2$)(*tert*-BuNC)$_2$ and azobenzene.

Similarly, treatment with dry oxygen of a solution of bis(*tert*-butyl isocyanide)diphenylacetylenepalladium in ether produced the oxygen complex Pd(O$_2$)(*tert*-BuNC)$_2$[10] and diphenylacetylene, both of which were identified by their ir spectra.

Acknowledgment. We are indebted to Professor J. A. Ibers and Dr. R. Dickson for improvement of the text of this paper.

Nickel(II) and Nickel(IV) Complexes of 2,6-Diacetylpyridine Dioxime

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Abstract: The preparation and properties of bis(2,6-diacetylpyridine dioxime)nickel(II) perchlorate, sodium bis(2,6-diacetylpyridine dioximato)nickelate(II), and bis(2,6-diacetylpyridine dioximato)nickel(IV) are reported. Indirect evidence indicates that the oxidized complex contains a high oxidation state of nickel rather than cation-stabilized radical ligands. The electronic and proton nmr spectra of the Ni(II) complexes and extended Hückel molecular orbital calculations of the protonated and unprotonated ligand are used to support a model which accounts for the ease of oxidation of the anionic Ni(II) complex and the stability toward oxidation of the protonated species. The model proposed stresses the importance of high-energy ligand orbitals of σ symmetry and the relative unimportance of the ligand π system in the stabilization of high oxidation states of nickel.

Although there has been considerable interest in the stabilization of high oxidation states of first-row transition metals, few Ni(IV) complexes have been reported, and of these, the claim is dubious in several instances. The reported examples may be divided into three general classifications—classical six-coordinate, planar four-coordinate, and "sandwich" compounds. In the first group, vicinal aliphatic dioximes (DH$_2$)[2] and trimeric formaldoxime (FoH$_3$)[3] are reported to form complexes of the type M$_2$NiD$_3$ and M$_2$Ni(Fo)$_2$ (M = Na, K), respectively. Heteropoly compounds such as $Na_{12}NiNb_{12}O_{38}$[4] and $Ba_3NiMo_9O_{32}\cdot 12H_2O$[5] and mixed oxides such as $BaNiO_3$[6] and $MNiIO_6\cdot H_2O$[7] contain Ni(IV) in an O$_6$ environment. Other classical six-coordinate complexes include M_2NiF_6,[8] and a claim is made for [Ni(diars)$_2$Cl$_2$]Cl$_2$.[9] Planar four-coordinate complexes originally reported to contain Ni(IV), but about which there is considerable doubt, include bis complexes with ligands of types I and II.[10] Recently, an X-

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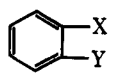
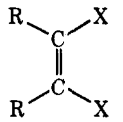


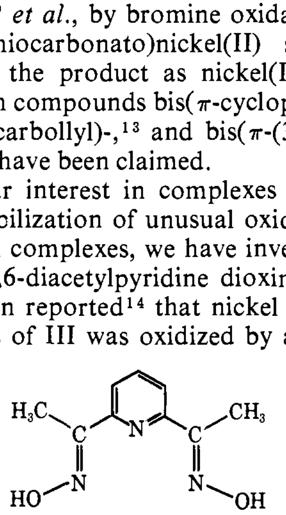
I, X = Y = S, NH
X = S; Y = O, NH



II, X = S; R = CN, CF_3, C_6H_5, $CH_3C_6H_4$
X = NC_6H_5, R = CH_3

ray diffraction investigation[11a] of the product obtained by Brinkhoff,[11b] *et al.*, by bromine oxidation of bis(*N*,-*N*-di-*n*-butyldithiocarbonato)nickel(II) supported the formulation of the product as nickel(IV). More recently, sandwich compounds bis(π-cyclopentadienyl)-,[12] bis(π-(3)-1,7-dicarbollyl)-,[13] and bis(π-(3)-1,2-dicarbollyl)nickel(IV)[12] have been claimed.

Owing to our interest in complexes of free-radical ligands and stabilization of unusual oxidation states of transition metal complexes, we have investigated nickel complexes of 2,6-diacetylpyridine dioxime ($DAPDH_2$), III. It has been reported[14] that nickel in aqueous alkaline solutions of III was oxidized by air. However, failure to isolate and characterize the product left considerable doubt as to its composition. We have studied two Ni(II) derivatives of this ligand, $[Ni(DAPDH_2)_2](ClO_4)_2$ and $Na_2[Ni(DAPD)_2]$, and have subsequently isolated what we think may be described as a Ni(IV) complex, $Ni(DAPD)_2$. Considerable insight into the donor properties of this complicated ligand is provided by SCC extended Hückel-type calculations. We propose a model supported by these results which accounts for the relative ease of preparing Ni(IV) with this ligand and which should serve as the basis for preparation of other stable complexes in this oxidation state.



III

Experimental Section

Preparation of 2,6-Diacetylpyridine Dioxime. The ligand was prepared in a manner similar to that previously reported.[14] To 24.5 g (0.150 mol) of 2,6-diacetylpyridine (Aldrich Chemical Co.), vacuum sublimed and recrystalized from methanol to a melting point of 82°, in 100 ml of warm methanol, were added 13.2 g (0.330 mol) of sodium hydroxide and 23.0 g (0.331 mol) of hydroxylamine hydrochloride in 100 ml of 50% aqueous methanol. The mixture was heated on a steam bath for 2 hr, cooled, filtered, and washed with water. The yield is at least 96%. The crude material is >98% pure, as determined by elemental analysis, and is suitable for immediate use as a ligand without further purification. However, recrystallization from methanol is necessary to prevent decomposition on standing.

Preparation of Bis(2,6-diacetylpyridine dioxime)nickel(II) Perchlorate ($Ni(DAPDH_2)_2(ClO_4)_2$). $DAPDH_2$ (7.72 g, 40.0 mmol) and 7.31 g of $[Ni(H_2O)_6](ClO_4)_2$ (20.0 mmol) were stirred for 10 min in reagent grade acetone and filtered. Ethyl ether was added dropwise, with stirring, to the filtrate, until the cloud point was reached. The beige complex crystallized on cooling. The crude complex was recrystallized from methanol-ether, yielding 12.4 g (96%) of pure $[Ni(DAPDH_2)_2](ClO_4)_2$. *Anal.* Calcd: C, 33.57; H, 3.45; N, 13.04; Ni, 9.11. Found: C, 33.72; H, 3.23; N, 13.10; Ni, 9.04.

Preparation of Sodium Bis(2,6-diacetylpyridine dioximato)-nickelate(II) ($Na_2[Ni(DAPD)_2]$). To 2.50 g of $[Ni(DAPDH_2)_2](ClO_4)_2$ (3.88 mmol) in 20 ml of deoxygenated methanol was added under nitrogen 0.360 g of sodium (15.7 g-atoms) in 25 ml of deoxygenated methanol. After partial evaporation of the solvent in a nitrogen stream, deoxygenated reagent grade acetone was added. After further reduction in volume, 1:1 acetone–ether was added until the cloud point was reached. Brilliant red crystals separated in 90% yield on cooling. The solid was separated by filtration under nitrogen, thoroughly washed with acetone to remove traces of sodium perchlorate, and dried at 60° under reduced pressure. The complex is stable as a solid and in hydroxylic solvents under nitrogen, but is slowly oxidized in solution in the presence of oxygen. It is quite rapidly oxidized in solvents such as dimethylformamide and dimethyl sulfoxide. It is quite soluble in water and alcohols, moderately soluble in highly polar nonhydroxylic solvents, and virtually insoluble in nonpolar solvents. *Anal.* Calcd: Ni, 12.06. Found: Ni, 11.88.

Preparation of Bis(2,6-diacetylpyridine dioximato)nickel(IV) $[Ni(DAPD)_2]$. Method A. $Ni(H_2O)_6Cl_2$ (0.240 g, 1.01 mmol) in 6 ml of water was added to 0.400 g of $DAPDH_2$ (2.06 mmol) in 40 ml of 1:1 acetone–18 *M* aqueous NH_3. To this solution was added 0.57 g of $(NH_4)_2S_2O_8$ (2.50 mmol) in a minimum of water. The stoppered solution deposited 0.36 g (81%) of fine violet needles on standing overnight. *Anal.* Calcd: C, 49.05; H, 4.12; N, 19.03; Ni, 13.30; O, 14.50. Found: C, 49.14; H, 4.13; N, 19.20; Ni, 12.91; O, 14.62; mp 219° dec.

Method B. $Ni(DAPDH_2)_2(ClO_4)_2$ (0.64 g, 1.00 mmol) in 10 ml of 1:1 methanol–acetonitrile was shaken with 1 ml of pyridine and 1.00 ml of 1.00 *M* bromine in carbon tetrachloride. After standing 1 hr, 0.40 g (91%) of long violet needles separated. These were washed with methanol and air dried. *Anal.* Found: C, 48.64; H, 4.02; N, 19.32; Ni, 12.69; O, 15.33. The analysis was satisfactory, and physical properties were identical with those of the product of method A.

Instrumentation. The nmr spectra were obtained on Jeolco C-60H and Varian HA-100 spectrometers. All temperatures were controlled to ±0.5°, and variable-temperature studies were carried out with the Jeolco equipped with a Model V-6040 temperature controller. The temperatures were measured before and after each spectrum by means of a Cole-Parmer YSI Model 42SL Tele-Thermometer reproducible to ±0.5%.

The solution ultraviolet and visible spectra were recorded with a Cary 14 recording spectrometer using 1-cm matched quartz cells at room temperature. Molar extinction coefficients are accurate to about ±5%. Solid-state diffuse-transmittance spectra were obtained as Kel-F mulls supported on quartz plates.

Molecular orbital calculations were carried out on the ligands by a procedure which has been described previously.[15,16] Briefly, it involves approximating the diagonal element of the effective Hamiltonian matrix by valence-orbital ionization potentials of Basch, Viste, and Gray.[17] The off-diagonal elements are estimated by the Wolfsberg–Helmholz method[18] with $K = 1.75$. Overlap matrices were determined by using the atomic double-ζ function of Clementi.[19] Iterative calculations were performed with a charge criterion of 0.04.

Results and Discussion

Electronic Spectra of $Ni(DAPDH_2)_2^{2+}$ and $Ni(DAPD)_2^{2-}$. We shall first discuss the electronic spectrum of the Ni(II) complexes prepared in this study, for these provide considerable insight into and support for the model which is to be presented to account for ease of oxidation of $Ni(DAPD)_2^{2-}$. The electronic spectra of these ions are shown in Figure 1. They are somewhat atypical of octahedral Ni(II) in that only one or two of the three expected d → d transi-

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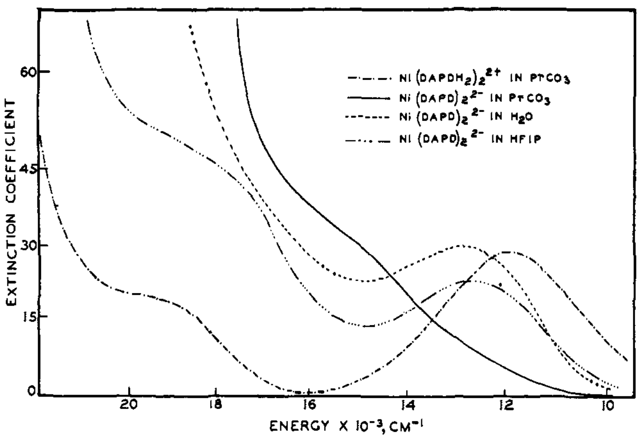

Figure 1. The electronic spectra of $Ni(DAPDH)_2{}^{2+}$ and $Ni(DAPD)_2{}^{2-}$.

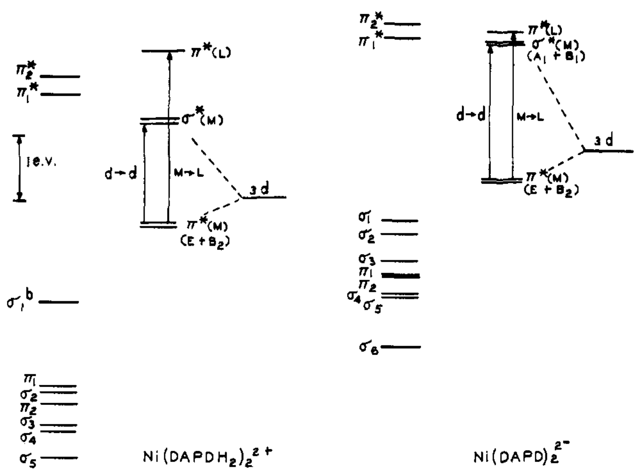

Figure 2. MO description of the difference in the electronic spectra of $Ni(DAPDH)_2{}^{2+}$ and $Ni(DAPD)_2{}^{2-}$.

tions are observed owing to the strong field of the ligands and the relatively low-energy charge-transfer band. The solution spectrum of $Ni(DAPDH_2)_2{}^{2+}$ in a wide variety of solvents—including water, methanol, acetone, propylene carbonate, and 0.1 *M* aqueous perchloric acid—is essentially the same as that of the mull. Although the complex has D_{2d} symmetry, the ligand field is expected to approximate O_h symmetry. The position of ν_1 ($^3T_{2g} \rightarrow {}^3A_{2g}$) is 12,140 ± 20 cm^{-1} (ϵ 30), giving a *Dq* value of 1214 cm^{-1}. This value is midway between those for tris(ethylenediamine)nickel(II) of 1150 cm^{-1} [20] and tris(2,2′-bipyridyl)nickel(II) of 1265 cm^{-1}.[20] $DAPDH_2$ is a strong ligand with a lower average *Dq* value than that for bipyridine, implying that $Dq_{\parallel} > Dq_{\perp}$.

The position of ν_2 ($^3T_{1g}(F) \leftarrow {}^3A_{2g}$) is 19,100 ± 300 cm^{-1}. The large uncertainty, owing to the occurrence of the transition as a shoulder on the charge-transfer band, precludes the calculation of a meaningful value of *B′*. The problem is compounded by the fact that ν_3 ($^3T_{1g}(P) \leftarrow {}^3A_{2g}$), which might be expected to occur at about 30,000 cm^{-1}, is completely obscured by the charge transfer bands.

The spectrum of $Ni(DAPD)_2{}^{2-}$ is different from that of the dipositive cation in that only one d → d transition is observed in all solvents [except hexafluoroisopropyl alcohol (HFIP)], and the position of this band is highly solvent dependent. In propylene carbonate, ν_1 occurs at 15,800 ± 300 cm^{-1} as a shoulder on the charge-transfer band. As the hydrogen-bonding ability or acidity of the solvent increases, ν_1 shifts to progressively lower energy while the charge-transfer band moves to higher energy. Thus, for methanol as solvent, ν_1 = 13,190 ± 20 cm^{-1}; for water, ν_1 = 13,090 ± 20 cm^{-1}; and for HFIP, ν_1 = 12,800 ± 30 cm^{-1}. In the latter case, ν_2 is also observed at 18,350 ± 300 cm^{-1}. These data are consistent with the idea that the negative charge of the complex is highly localized on the oxygens, resulting in both considerable hydrogen bonding to the solvent and some protonation of the complex from solvolysis. This strong interaction with hydroxylic solvents correlates with the greater than tenfold increase in solubility in water of $Na_2Ni(DAPD)_2$ relative to $Ni(DAPDH_2)_2(ClO_4)_2$.

Again assuming an O_h model, one calculates a value of *Dq* for the unprotonated complex of 1580 cm^{-1}, an extremely high value for Ni(II). The value is considerably greater than that[21] for $Ni(NO_2)_6{}^{4-}$, 1359 cm^{-1}, and is even greater than the value 1500 cm^1 calculated from *h* and *k* parameters[22] for the hypothetical complex $Ni(CN)_6{}^{4-}$.

The observed electronic spectra may be accounted for by the simple MO diagram shown in Figure 2. The diagram qualitatively represents the results from our extended Hückel calculation and will be discussed in more detail below. Here we will use it to explain the observed changes in the electronic spectra.

In $Ni(DAPDH_2)_2{}^{2+}$, the metal 3d orbitals are below the lowest $\pi^*(L)$ orbitals or else the ligand would have been reduced. The metal orbitals are above the highest $\sigma^b(L)$ and $\pi^b(L)$ orbitals. Removal of the acidic protons from the ligand increases the energy of both the ligand σ and π orbitals. However, the MO calculations indicate that the energies of the ligand σ orbitals are raised considerably more than those of the ligand π and π^* orbitals in the anion compared to the neutral ligand; *i.e.*, the electronic effect associated with the removal of the proton is more pronounced in the σ than in the π system. Complexation of the anion to the metal ion both raises the energy of the entire d manifold and increases the separation of the metal ion d orbitals. The effect is to bring the metal ion and π^* orbitals together to decrease the energy of the charge-transfer transition and increase 10*Dq*. These effects have been schematically illustrated in Figure 2. The shifts observed in the hydrogen-bonding interactions are in accord with hydrogen bonding to the oxygen moving the relative energies of the essentially d and ligand molecular orbitals toward those of the protonated species. While changes in metal–ligand π bonding and π antibonding interactions might be invoked to interpret the spectral changes observed on deprotonation of the complex, these are considered unimportant because our MO calculations indicate relatively smaller changes in the energies and nature of the π orbitals when the anions are formed.

EHMO Description of $DAPDH_2$ and $DAPD^{2-}$. Examination of the results of the EHMO calculation affords further information useful in describing the

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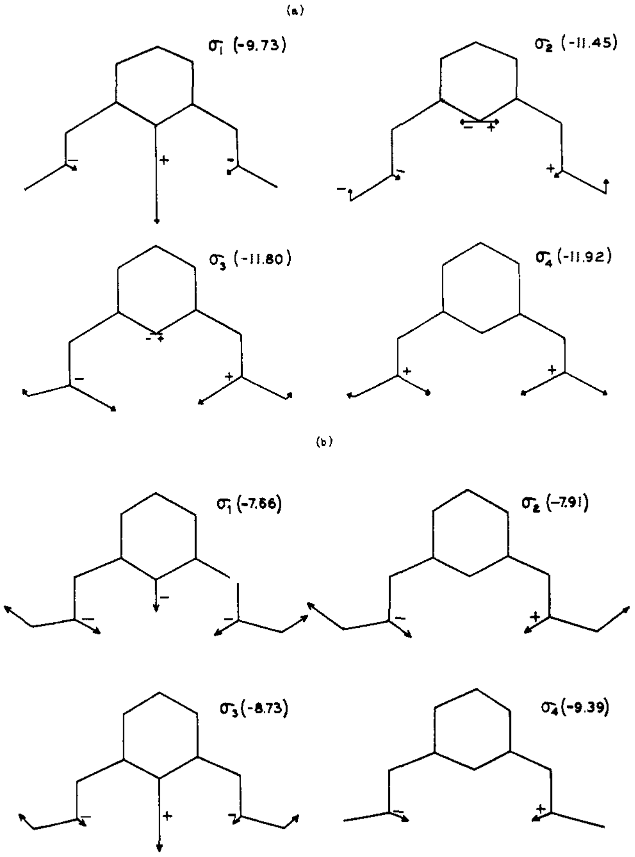

Figure 3. Vector representation of AO contributions to various MO results for (a) $DAPDH_2$ and (b) $DAPD^{2-}$. Signs indicate parity.

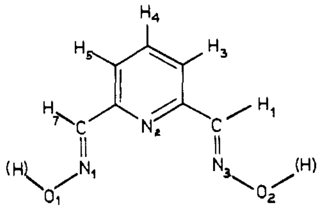

Figure 4. The model ligand used for EHMO calculation of $DAPDH_2$, showing numbering scheme. Bond lengths and angles are based on typical pyridine and oxime ligands in L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 11** (1958); **No. 18** (1965).

properties of these complexes. The extent of the bonding interaction between a metal orbital and a ligand orbital is proportional to the overlap between the two orbitals and inversely proportional to the energy separation between the two. We may estimate the overlap between a metal orbital and a given ligand orbital by considering the spatial characteristics of the orbitals. In Figure 3, the contributions of the nitrogen and oxygen atoms to the higher energy ligand σ MO's are illustrated as vectors, directions are determined by relative contributions of p_x and p_y coefficients and magnitudes by the sum of the squares of the atomic coefficients. Thus, $\sigma_1(DAPDH_2)$ should be very important in the bonding of the complex since it has the proper symmetry to interact with metal ion d orbitals of σ symmetry, has a very large contribution from the pyridine nitrogen labeled 2 in Figure 4, and is the highest energy ligand σ orbital. On the other hand, the contribution from $\sigma_2(DAPDH_2)$ is not important, since it does not have the required symmetry to interact with d orbitals. It is further noted that σ_2 has relatively small contributions from N_1 and N_3. Thus, this vector representation is a very nice way of summarizing the features of the MO calculation of interest to transition metal chemists. The energy separations are illustrated in Figure 2. In $Ni(DPADH_2)_2{}^{2+}$, bonding to the metal by the iminoxy nitrogen occurs largely through interaction of $\sigma_4(DAPDH_2)$ with metal e_g orbitals, since σ_3-$(DAPDH_2)$ has improper symmetry for a σ-bonding interaction with the metal ion. The higher energy of σ_1-$(DAPDH_2)$ causes it to mix more extensively with the metal orbitals, so it probably makes a larger contribution to the bonding than the other σ molecular orbitals. As illustrated by the AO coefficient vectors for $\sigma_1(DAPDH_2)$ in Figure 3, a greater interaction with the metal will occur along the z axis than in the xy plane and $Dq_{\parallel} > Dq_{\perp}$, as inferred from the spectral studies.

The larger value of $10Dq$ of $Ni(DAPD)_2{}^{2-}$ relative to $Ni(DAPDH_2)_2{}^{2+}$ is due primarily to the greatly enhanced bonding to the iminoxy nitrogens when the protons are removed. This enhancement can be attributed not only to the increased energy of the higher energy σ MO's, but also to the substantial increase in imine nitrogen atomic coefficients in the highest energy $\sigma_1(DAPD)$ MO.

Table I summarizes the sum of the squares of the nitrogen and oxygen coefficients in the higher energy σ MO's. The subscripts of the orbitals indicate the order of decreasing energy for the filled σ^b orbitals. Although there is not an exact correspondence, $\sigma_1{}^b$ in $DAPDH_2$ is most like $\sigma_3{}^b$ in $DAPD^{2-}$. These data are illustrated in Figure 3. The MO's $\sigma_1{}^b(DAPDH_2)$ and $\sigma_3(DAPD^{2-})$ have large N_2 coefficients and give rise to the most important "pyridine donor" contribution in $Ni(DAPDH_2)_2{}^{2+}$. On converting $\sigma_1{}^b(DAPDH_2)$ to $\sigma_3(DAPD^{2-})$, the MO energy increases by only 1.00 eV (from −9.73 to −8.73 eV) as a consequence of deprotonation. On the other hand, $\sigma_4{}^b(DAPDH_2)$, the orbital with appropriate symmetry containing the largest imine nitrogen coefficient, increases in energy by 4.26 eV (from −11.92 to −7.66 eV) on deprotonation. This leads to greatly increased metal ion–imine nitrogen interaction in $Ni(DAPD)_2{}^{2-}$ as compared to $Ni(DAPDH_2)_2{}^{2+}$. This increased metal–imine nitrogen interaction could also increase the interaction of the metal with N_2 as well as with the iminoxy moiety.

Table I. Squared Coefficients of Important Orbitals of $DAPDH_2$ and $DAPD^{2-}$

	$\sigma_1{}^a$	σ_2	σ_3	σ_4
		$DAPDH_2$		
$\Sigma N_{1,3}{}^b$	0.090	0.070	0.776	0.696
ΣN_2	0.752	0.129	0.015	0.003
$\Sigma O_{1,2}$	0.008	0.098	0.054	0.046
		$DAPD^{2-}$		
$\Sigma N_{1,3}$	0.414	0.455	0.052	0.247
ΣN_2	0.253	0.001	0.582	0.002
$\Sigma O_{1,2}$	0.484	0.710	0.278	0.526

[a] Subscripts of orbitals refer to relative ordering with respect to energy. [b] Subscripts of atoms defined in Figure 4.

Nmr of $Ni(DAPDH_2)_2(ClO_4)_2$ and $Na_2Ni(DAPD)_2$. Our interest in determining potential uses and limitations of the isotropic shift of paramagnetic complexes has led us to investigate the nmr spectra of these complexes. The isotropic shift has contributions from two factors, contact and pseudocontact terms. The pseudocontact term arises from *g*-tensor anisotropy, and since most Ni(II) complexes are nearly isotropic, this contribution is expected to be negligible. An order of magnitude estimate can be made[23] with eq 1 and the electronic spectrum. For $Ni(DAPDH_2)_2^{2+}$, ν_1 occurs as a broad

$$g_{\parallel,\perp} = 2(1 - 4k\lambda_0/10Dq_{\parallel,\perp}) \qquad (1)$$

symmetrical band ($\nu_{1/2}$ = 3100 cm^{-1}) at 12,140 cm^{-1}. Assuming a maximum undetectable splitting of 2000 cm^{-1}, we estimate $Dq_{\parallel} \sim 1300$ cm^{-1} and $Dq_{\perp} \sim 1100$ cm^{-1}. Choosing $k = 0.9$, an upper limit, and $\lambda_0 = -315$ cm^{-1},[24] and employing eq 1, one obtains values of $g_{\parallel} = 2.155$ and $g_{\perp} = 2.183$. By using geometric factors of a similar complex,[25] the maximum pseudocontact terms are calculated to be very small (−9 to +50 cps). These shifts are insignificant for our purposes and will be neglected in our discussion. Similarly, the pseudocontact terms of $Ni(DAPD)_2^{2-}$ are neglected.

The nmr spectra of $Ni(DAPDH_2)_2(ClO_4)_2$ and $Na_2Ni(DAPD)_2$, corrected for side bands, are illustrated in Figure 5. Assignments of the CH protons are made on the basis of area and width. Upon addition of D_2O, a peak with area equivalent to four protons appears at −115 Hz (relative to acetone), and the broad band at −4500 Hz disappears, confirming assignment of the −4500-Hz peak to O–H. Both complexes gave straight-line plots of $\Delta\nu$ *vs.* $1/T$ over the temperature range studied (−40 to +50° for $Ni(DAPDH_2)_2^{2+}$ and 0 to +80° for $Ni(DAPD)_2^{2-}$). Values of $\Delta\nu$ were calculated relative to diamagnetic $Fe(DAPDH_2)_2^{2+}$, and all 12 experimental points were within ±5 Hz of the least-squares line. Table II gives the essential data of these temperature plots. Electron spin–nuclear spin coupling constants were not calculated because nonzero intercepts were obtained. The values for $\Delta\nu$ are given in Table III.

Table II. Least-Squares Results of $\Delta\nu$ *vs.* $1/T$ Plots for $Ni(DAPDH_2)_2^{2+}$ and $Ni(DAPD)_2^{2-}$ [a]

Proton[b]	$m \times 10^{-5}$, Hz °K	*b*, Hz
	$Ni(DAPDH_2)_2^{2+}$	
CH_3	3.66	−488
H_γ	−2.56	202
H_β	−12.67	533
	$Ni(DAPD)_2^{2-}$	
CH_3	4.12	−180
H_γ	−2.39	260
H_β	−11.46	123

[a] Straight-line plot with $\Delta\nu = m/T + b$. [b] See Figure 4 for definition of subscripts.

The essential conclusion to be drawn from the nmr studies is that upon removal of the protons, the unpaired electrons remain in predominantly metal d orbitals in the complex; *i.e.*, the energies of the ligand MO's relative to the metal are not so drastically affected as to change the metal oxidation state. In both complexes, the delocalization pattern is typical of that expected for O_h Ni(II) with σ delocalization mechanism;[26–28] *e.g.*, in nickel (2,2′bipyridyl)$_3^{2+}$ $\Delta\nu_{3,3'} = -3565$ Hz and $\Delta\nu_{4,4'} = -363$ Hz. Both σ and π delocalization mechanisms contribute in the bipyridyl complex and also are expected in $Ni(DAPDH_2)_2^{2+}$ and $Ni(DAPD)_2^{2-}$. The π mechanism apparently dominates the methyl proton position.

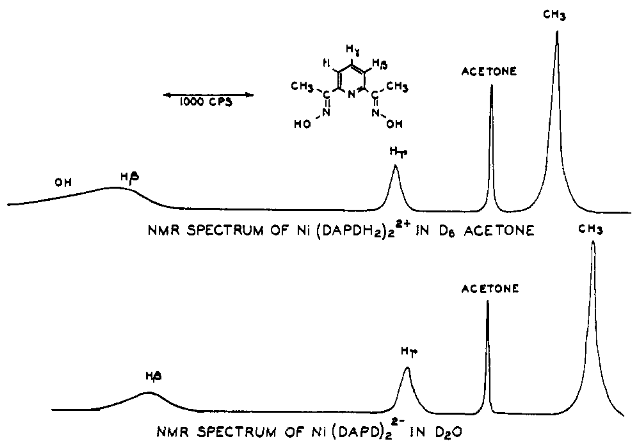

Figure 5. Nmr spectra of nickel(II) complexes.

Table III. Contact Shifts of $Ni(DAPDH_2)_2^{2+}$ and $Ni(DAPD)_2^{2-}$ [a]

	CH_3	H_γ	H_β
$\Delta\nu(Ni(DAPDH_2)_2^{2+})$, Hz	853	−736	−4111
$\Delta\nu(Ni(DAPD)_2^{2-})$, Hz	1329	−615	−4072

[a] Shifts measured at 0° relative to $[Fe(DAPDH_2)_2](ClO_4)_2$ on a 60-MHz instrument.

As can be seen from the data in Table II, all resonances shift upfield on deprotonation of the complex, $Ni(DAPDH_2)_2^{2+}$. This is somewhat surprising because a simplified prediction would lead one to expect an increased contact shift with the increased σ-bonding interaction that accompanies deprotonation.

A qualitative explanation of the observed trend can be proposed from the results of our extended Hückel calculation on the protonated and unprotonated ligands. Ideally, to account for the contact shift, the entire complex should be calculated; however, limitations in the number of orbitals our program can accommodate, uncertainty in the metal parameters, and the qualitative nature of the understanding being sought prompted us to use the simple compound shown in Figure 4 and the corresponding unprotonated anion.

Comparing the wave functions of the protonated and unprotonated species shows an increase in the energies of all the high-energy orbitals in the latter. Formation of the anion is also accompanied by a pronounced decrease in the magnitude of the coefficients for the ring protons and C–H in the high-energy σ orbitals that would be expected to be important in σ bonding with the nickel. This would result in less spin density being delocalized on the ring protons in $Ni(DAPD)_2^{2-}$ than in

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(23) Reference 22, p 295.
(24) Reference 22, p 281.
(25) G. N. LaMar and L. Sacconi, *J. Amer. Chem. Soc.*, **90**, 7216 (1968).
(26) M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, **4**, 840 (1965).
(27) R. E. Cramer, Ph.D. Thesis, University of Illinois, 1969.
(28) M. Wicholas and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 6946 (1968).

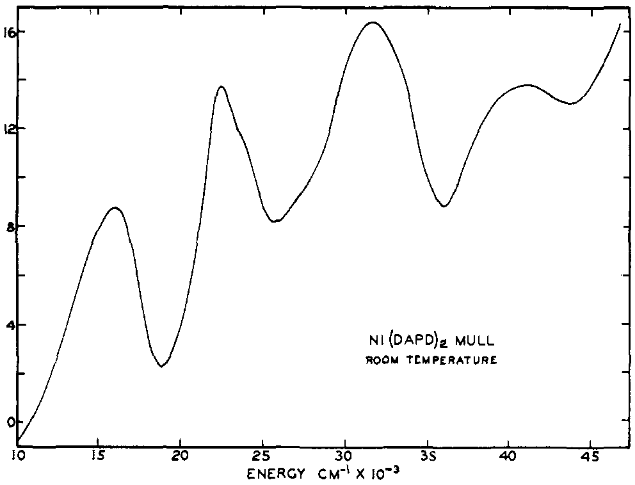

Figure 6. Electronic spectrum of Ni(DAPD)$_2$.

$Ni(DAPDH_2)_2{}^{2+}$ and account for the smaller contact shifts in the former even though the metal–ligand interaction is larger in $Ni(DAPD)_2{}^{2-}$. This is an excellent illustration of one of the pitfalls possible in the qualitative interpretation of contact shifts when no information is available about the nature of the molecular orbitals. The larger negative shift for the methyl protons in the anion than in the neutral ligand is also consistent with less α spin density being placed on the CH_3 group by a σ delocalization mechanism.

Ni(DAPD)$_2$. The diamagnetic complex obtained by oxidation of $Ni(DAPD)_2{}^{2-}$ is isolated as deep violet needles indefinitely stable as a solid and in solution. It is remarkably stable even in nitric acid, in which it readily dissolves. It is a nonelectrolyte, and its solubility at room temperature ranges from about 0.1 to 8 m*M* in most common laboratory solvents except aliphatic hydrocarbons, in which it is insoluble, and very strongly hydrogen-bonding organic solvents, such as HFIP, in which it is fairly soluble. Results from a single-crystal X-ray diffraction investigation have established[29] this formulation of the structure. The electronic spectrum is illustrated in Figure 6. The energy of these transitions is quite dependent on the solvent, as illustrated for ν_1 in Figure 7. The slight increase in transition energy with solvent polarity is attributed either to stabilization of a polar ground state or destabilization of the less polar excited state(s) to which the transition occurs. In either case, one infers that there is considerable charge separation in the ground state. This view is supported by the fact that hydrogen-bonding solvents fall far off the plot of ν_1 *vs.* dielectric constant (Figure 7) formed by non-hydrogen-bonding solvents. The deviation from the expected transition energy, $\Delta\nu_1$, is roughly proportional to the hydrogen-bonding ability of the solvent. Thus, $\Delta\nu_1$ is 160 cm^{-1} for methylene chloride and 1000 cm^{-1} for 2,2,2-trifluoroethanol. This behavior, though considerably less dramatic than that in $Ni(DAPD)_2{}^{2-}$, is also attributed to the strong hydrogen bonding of the solvent to the oxygens of the ligand. The extent of this interaction, somewhat surprising in view of the neutrality of the complex, indicates that the negative charge on the oxygen atoms is quite large even after oxidation of the complex.

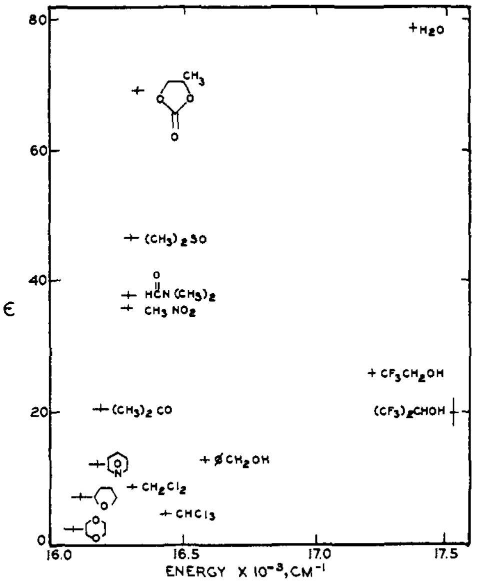

Figure 7. Dependence of electronic spectrum of Ni(DAPD)$_2$ on dielectric constant, ϵ.

While it is tempting to speculate on the oxidation state of the nickel, one must keep in mind how oxidation state is defined. Many of the squabbles in the literature have resulted from this difficulty. The standard definition involves assigning the electron pair in the bond to the most electronegative element. Thus there is no correlation between the charge on the metal and its oxidation state. We simply claim that the bonding molecular orbital has more ligand than metal contribution. In most compounds of this type that have been reported, it is virtually impossible to state categorically that the metal is Ni(IV). There is considerable evidence that the planar four-coordinate complexes originally formulated as containing Ni(IV) are best described as cation-stabilized radical ligands.[30–32]

The supposed Ni(IV) complex, $[Ni(diars)_2Cl_2]^{2+}$, can be reduced to the lower oxidation state, $[Ni(diars)_2Cl_2]^{+}$, which contains a cation-stabilized diarsine radical.[33] Attempts to detect similar behavior in our system by studying the oxidation–reduction one-electron couple $Ni(DAPD)_2 + e^- \rightleftarrows Ni(DAPD)_2{}^-$ by cyclic voltammetry were unsuccessful owing to extreme irreversibility and unknown surface reactions that yielded curves we were unable to interpret. Furthermore, by employing a wide variety of oxidizing agents to oxidize $Ni(DAPD)_2{}^{2-}$, we failed to produce an intermediate oxidation state. Similarly, the species $Ni(DAPD)_2{}^-$ was not observed in the reduction of Ni(DAPD)$_2$. Such an intermediate oxidation state would be expected to exist if Ni(DAPD)$_2$ were simply a metal-stabilized ligand radical. This coupled with the fact that considerable negative charge density is localized on the oxygen of the ligands, as evidenced by the spectral studies described above, suggests formulation of this material as a a Ni(IV) complex.

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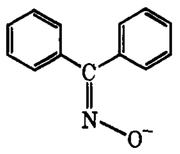

IV

A similar ligand, 2-benzoylpyridine oxime anion (IV), has been shown to stabilize what we believe to be an authentic Ni(III) species.[34] In the present case, the Ni(IV) complex is apparently stabilized relative to Ni(III) by the extremely strong field from the tridentate nature of the ligands. In the final analysis, a molecular orbital description in which the highest occupied orbital has considerable contributions from both the ligand and the metal must be considered the only meaningful description of Ni(DAPD)$_2$ and should be kept in mind during the ensuing discussion.

The unusually large crystal-field splitting produced by DAPD^{2-} is an important factor contributing to the ease of oxidation of the nickel complex. The strong σ bonding of the complex raises the level of the σ^*, predominantly metal, orbitals to a very high energy level from which the electrons are easily removed. In our opinion, the scarcity of nickel complexes of high oxidation state is due in large part to the tendency of nickel to form planar four-coordinate complexes with ligands that have extremely strong ligand fields. As indicated in Figure 8, a strong planar field results in population of the lowest four levels, producing a stable diamagnetic d^8 complex. Since the spherically symmetric component of the electrostatic field generated by four ligands—even four extremely strong ligands—is much less than that generated by six strong ligands, the highest populated energy levels are still of moderately low energy. With extremely strong-field mono- and bidentate ligands, six-coordinate complexes of Ni(II) are not favored relative to the square-planar complex for this reason. By employing a tridentate ligand, we greatly reduce the tendency of the metal to assume a planar geometry, forcing six-coordination. The spherically symmetric component of the electrostatic field raises the unsplit d orbitals to an unusually high energy for Ni(II). The large octahedral component raises the e$_g$ set still higher while stabilizing the t$_{2g}$ set. The small tetragonal component splits the e$_g$ set only slightly. Thus, all levels are populated and the result is a paramagnetic Ni(II) complex which is easily oxidized. According to this model, the two important characteristics that a ligand must possess in order to stabilize a nickel(IV) complex are a strong spherical component of the crystal field and strong σ-bonding properties.

The observed fact that nickel(II) experiences an extremely strong crystal field with the ligand DAPD^{2-} is consistent with the data in Table IV. The negative charge is highly localized on the pyridine nitrogen and iminoxy groups, which are the groups within the ligand nearest the metal. Not only does this concentration of charge raise the energies of ligand orbitals based largely on these donor atoms, but the great negative charge density concentrated in such a small volume near the metal raises the energy of the entire d manifold; *i.e.*, the ligand has a strong spherical component in the crystal field it exerts.

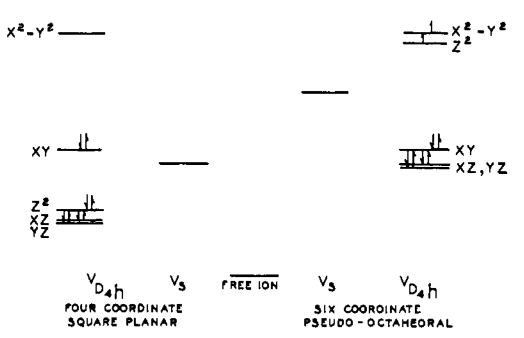
x²-y²
xy
z²
xz
yz
x²-y²
z²
xy
xz,yz
V D4h
Vs
FREE ION
Vs
V D4h
FOUR COORDINATE SQUARE PLANAR
SIX COORDINATE PSEUDO-OCTAHEDRAL

Figure 8. Crystal-field splitting for four- and six-coordinate d^8 metals under successively lower symmetry fields.

The importance of strong σ bonding in stabilizing Ni(IV) cannot be overemphasized. The most important prerequisite is that the ligand possess very high-energy σ^b orbitals with the proper symmetry to overlap strongly with the appropriate metal orbitals. The nature of the π system is important only insofar as inductive effects influence the σ system. Raising the energy of π^b ligand orbitals, allowing more mixing with metal d orbitals, can in no way favor Ni(IV), since there is no net stabilization in the bond so formed. In a subsequent publication, we shall describe unsuccessful attempts to prepare Ni(IV) complexes with ligands which, on removal of the acidic protons, have the opposite effect on the higher σ^b and π^b orbitals; *i.e.*, the π^b orbitals increase greatly in energy while the σ^b orbitals are less effected.

Table IV. Charge Distribution of DAPDH$_2$ and DAPD^{2-} [a]

	DAPDH$_2$	DAPD^{2-}
C$_1$	0.08	−0.09
C$_2$	0.06	0.00
C$_3$	0.02	−0.06
C$_4$	0.00	−0.03
H$_1$	0.04	−0.04
H$_2$	0.16	
H$_3$	0.02	−0.03
H$_4$	0.02	−0.03
N$_1$	−0.08	−0.26
N$_2$	−0.18	−0.22
O	−0.22	−0.38

[a] See Figure 4 for definition of subscripts.

The simple crystal-field model of Figure 8 suggests several other interesting possibilities. It is easy to envision ligands, such as 2,5-diacetylthiophene dioxime, which might be forced by geometry to be "tridentate". The tetragonal crystal-field component of such a complex would be very great, and a diamagnetic tetragonal Ni(II) complex might be formed, or one which exhibits a magnetic crossover, a rarity in Ni(II). In addition, this simple model predicts that certain strong-field ligands with low-lying π^* orbitals should be able to stabilize both six-coordinate Ni(IV) and four-coordinate Ni(I) or Ni(0). Thus, it might be possible to prepare a series similar to the well-known dithiolates but differing in that oxidation or reduction involves removal or addition of electrons to orbitals which are primarily based on the metal.

Acknowledgment. We wish to acknowledge the National Science Foundation for financial support through Grant No. NSF 5498.

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(34) $g_1 = 2.08$, $g_2 = 2.10$, and $g_3 = 2.14$ for a polycrystalline sample of the tris nickel complex at room temperature; $\mu_{\text{eff}} = 1.85 \pm 0.10$ BM.