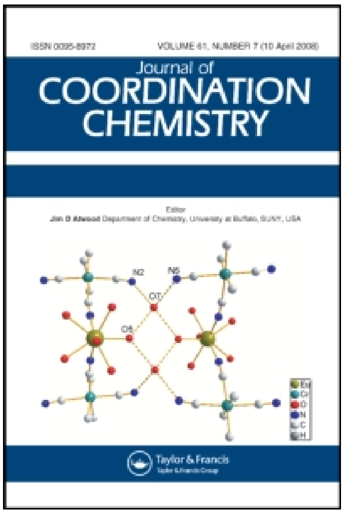

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NICKEL(II) COMPLEXES EMPLOYING BIDENTATE LIGANDS DERIVED FROM 2-(β-KETOALKYL) HETEROAROMATIC COMPOUNDS

R. P. Cassity[a]; L. T. Taylor[a]
[a] Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia

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NICKEL(II) COMPLEXES EMPLOYING BIDENTATE LIGANDS DERIVED FROM 2-(β-KETOALKYL) HETEROAROMATIC COMPOUNDS

R. P. CASSITY and L. T. TAYLOR

Contribution from the Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

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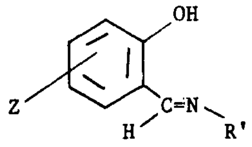
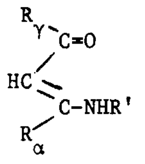
$Ni(L)_2$ complexes, where L equals 2-(trifluoroacetyl) heteroaromatic anion have been prepared and characterized. 2-(Trifluoroacetyl)-picolinato anion (TFAP) gives a $Ni(L)_2$ complex that appears to be a dimeric 5-coordinate square pyramid. The complexes $Ni(4MeTFAP)_2$ and $Ni(5MeTFAP)_2$ are square planar complexes while $Ni(6MeTFAP)_2$ is tetrahedral due to steric interference. In non-donor solvents, the complexes $Ni(TFAP)_2$, $Ni(4MeTFAP)_2$ and $Ni(5MeTFAP)_2$ exhibit properties that indicate a polymer/monomer equilibrium. $Ni(L)_2$ complexes undergo a unique gas-solid dissociation reaction with H_2O and NH_3 to give coordinated NH_2^- and OH^-.

INTRODUCTION

A considerable number of metal complexes have been prepared which exhibit properties that may be explained in terms of a conformational or structural change. These have been[1] categorized into three groups: (1) formation of 5 and 6 coordinate complexes by addition of ligands to square complexes, (2) a monomer-polymer equilibria and (3) a square planar-tetrahedral equilibrium and isomerism. The nickel complex chemistry of salicylaldimines (*I*), β-ketoamines (*II*) and β-ketoenolates (*III*) has been studied in this regard.[2] In many cases the structure of the complex for a given ligand system appears to depend on the substituent groups (i.e. Z, R′, R_α and R_γ).



I



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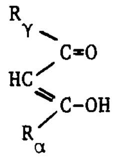
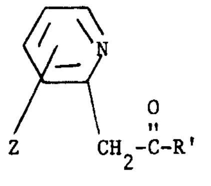


III



IV

The 2-(β-ketoalkyl)pyridines (*IV*) provide a ligand system intermediate to the ones mentioned above; however, they have not been extensively explored. Several abbreviated studies[3–6] employing *IV* wherein R′ = alkyl with various metals have been reported but complexes were either not isolated or not characterized thoroughly. Root and coworkers[7] have prepared the iron(III), cobalt(III), copper(II) and zinc(II) complexes of 2-(trifluoroacetyl)picoline (R′ = CF_3) and the copper(II) complex of 2-(acetyl)-picoline (R′ = CH_3) in an effort to separate geometrical isomers by gas chromatography. All complexes were shown to be monomeric and neutral in solution. As an extension to this study we wish to report the preparation and characterization of a series of nickel(II) complexes which incorporate various derivatives of *IV* (R′ = CF_3) hereafter referred to as HTFAP.

EXPERIMENTAL

General Preparation of Ligands

A modification of the procedure of Levine[3] was used to prepare the various 2-(trifluoroacetyl)-picolines. The appropriately substituted picolyllithium was added over a period of 8 hrs to a solution of ethyl trifluoroacetate (100.5 g, 0.71 mol) dissolved in 250 ml of anhydrous ether maintained at room temperature. The reaction mixture was quenched with ice-HCl, stirred for one hr, made basic with NaOH and extracted three times with 100 ml portions of ether. The extracts were combined and the solvent was removed under aspirator pressure. The crude solid (e.g. HTFAP) was recrystallized from hexane. Yield = 30%, mp = 111–112° (Lit.[3] mp 113–113.4°), mass spectrum (m/e = 189), ^1H and ^{19}F nmr.

Preparation of $Ni(TFAP)_2(py)_2$ To a solution prepared by dissolving HTFAP (3.80 g., 0.02 moles) in 25 ml of methanol was added solid $NaOCH_3$ (1.08 g, 0.02 moles) with stirring. The resulting solution was brought to reflux and a previously filtered methanol solution of $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ (2.48 g, 0.01 mole) was added dropwise. The dark green reaction mixture was allowed to come to room temperature after which 16 ml of pyridine was added dropwise. A gray-blue precipitate formed immediately which was isolated, recrystallized from warm pyridine and dried *in vacuo* at 100°C for 12 hr. Pyridine adducts of methyl substituted TFAP complexes were prepared in an analogous manner.

Preparation of $Ni(TFAP)_2(bipy)$ This compound was prepared in the same manner as the one above except that a stoichiometric amount of 2,2'-bipyridine dissolved in methanol was added in place of pyridine.

Preparation of $Ni(MeTFAP)_2$ The appropriate bis(pyridine) adduct was heated at 150°C and atmospheric pressure for approximately 1 hr until the presence of py could no longer be detected. The resulting green compound was purified by sublimation at 160°C (0.05 Torr).

Preparation of $Ni(6MeTFAP)_2$ To a solution prepared by dissolving H6MeTFAP (4.06 g, 0.02 mol) in 100 ml of MeOH was added solid KOtBu (2.24 g, 0.02 mol). After bringing the solution to reflux, solid $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ (2.48 g, 0.01 mol) was added. The solution was heated for 30 min after which it was filtered hot giving a red brown solid that was dried *in vacuo* for 12 hr.

Preparation of $Ni_2(TFAP)_3(HTFAP)(H_2O)(OH)$ Thoroughly dry $Ni(TFAP)_2$ was placed in a loosely covered vial and allowed to stand for 48 hr in a sealed container to which had been added several drops of water. The solid slowly turned green in color after which it was placed on a piece of filter paper to air dry for 1 hr.

Preparation of $Ni(HTFAP)(TFAP)(NH_3)(NH_2)$ Solid $Ni(TFAP)_2$ was placed in a glass tube and evacuated (10^{-4} Torr). Gaseous NH_3 was admitted to the system at a pressure of 700 Torr. The solid turned to a bluish-green color in about 20 min. After 24 hr the tube was opened and the sample was isolated.

Physical Measurements

Infrared spectra were recorded as Nujol mulls on a Beckman 20-AX spectrophotometer. Microanalyses were obtained on a Perkin-Elmer Model 240 C, H and N Elemental Analyzer. Thermogravimetric analysis (TGA) data were obtained on a Tracor TGA-5 system. Visible spectra were obtained on a Cary 14 spectrophotometer. Magnetic susceptibility measurements on samples in solution were determined by the method of Evans.[8] Molecular weight determinations were performed osmometrically by Galbraith Laboratories Inc., Knoxville, Tenn.

RESULTS AND DISCUSSION

Attempts to prepare $Ni(ZTFAP)_2$ (Z = H, 4-CH_3 and 5-CH_3) directly from solution were futile whereas preparation of the bis(pyridine) or bipyridine adduct (See Table I for analytical data) followed by removal of the base was successful. The pseudo-octahedral blue complexes $Ni(TFAP)_2(py)_2$, $Ni(4MeTFAP)_2$-$(py)_2$ and $Ni(5MeTFAP)_2(py)_2$ lose pyridine when heated to approximately 150°C in vacuo to give mustard color $Ni(TFAP)_2$, olive green $Ni(4MeTFAP)_2$ and olive green $Ni(5MeTFAP)_2$ respectively. $Ni(6MeTFAP)_2$, on the other hand, can be obtained directly from solution. Elemental analyses (Table I), infrared and mass spectral data suggest that these complexes are bis(chelates) derived from 2-(trifluoroacetyl)-picolinato anion. No peaks at masses higher than the parent are observed in the mass spectrum of each material.

Based on the accepted μ_{eff} ranges for nickel(II) in various environments[9] the effective magnetic moments (Table I) suggest that $Ni(TFAP)_2$ and $Ni(6MeTFAP)_2$ may have either tetrahedral or a five-coordinate geometry while a low spin five-coordinate or square planar configuration is predicted for $Ni(4MeTFAP)_2$ and $Ni(5MeTFAP)_2$. Visible spectra in the solid state suggests that $Ni(6MeTFAP)_2$ is tetrahedral (Table I). The 6-CH_3 group no doubt interferes with the formation of the square planar or five-coordinate configuration. Fusion of a ring to the pyridine nucleus was expected to show similar steric hindrance and indeed μ_{eff} for bis[(2-trifluoroacetyl)-

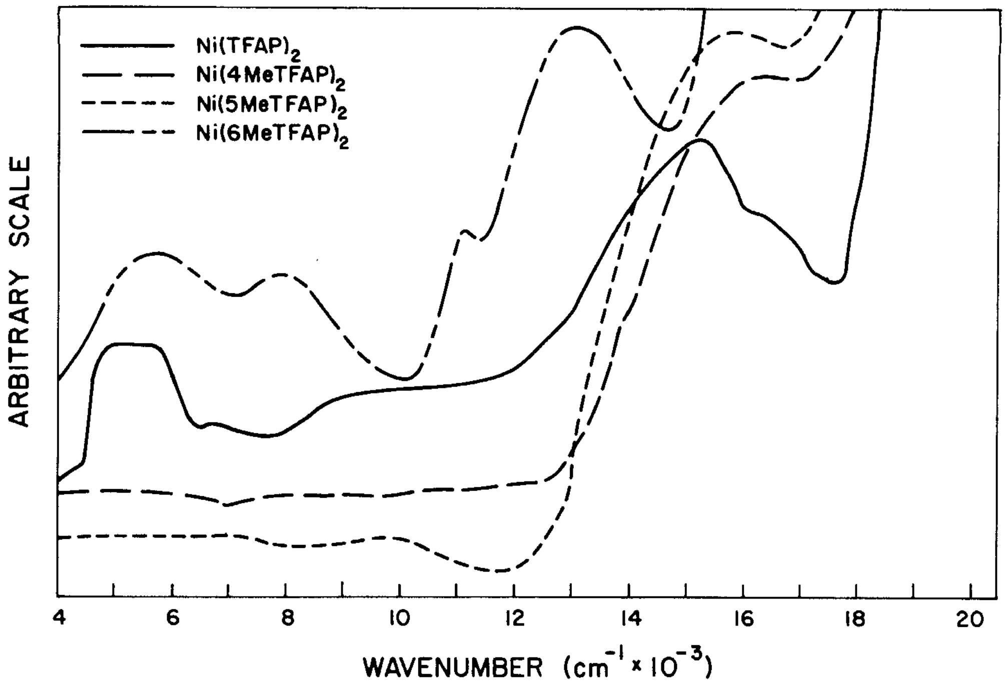


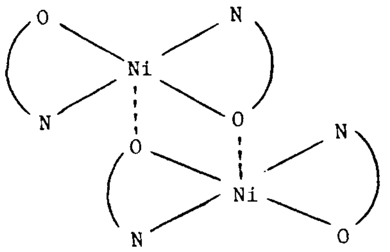
FIGURE 1 Solid state spectra of 2-(β-ketoalkyl)heteroaromatic nickel(II) complexes.

TABLE I
Analytical data for the nickel(II) complexes

Compound		Elemental analyses			μ_{eff} (B.M.)	Band maxima (cm^{-1})
		%C	%H	%N		
Ni(TFAP)$_2$	Calcd:	44.18	2.32	6.44		5400; 7000; 10000;
	Found:	44.22	2.48	6.58	3.48	15250; 20000; 22600
Ni(4MeTFAP)$_2$	Calcd:	46.69	3.05	6.05		
	Found:	46.50	2.87	6.35	1.15	15800
Ni(5MeTFAP)$_2$	Calcd:	46.69	3.05	6.05		
	Found:	46.51	3.19	6.07	0.66	16200
Ni(6MeTFAP)$_2$	Calcd:	46.69	3.05	6.05		5800; 8200; 13100
	Found:	47.10	2.71	6.05	3.40	
Ni(TFAP)$_2$(py)$_2$	Calcd:	52.64	3.41	9.54		
	Found:	52.63	3.46	9.49	3.20	10500; 17500
Ni(TFAP)$_2$(bipy)	Calcd:	52.82	3.07	9.48		
	Found:	52.50	3.21	9.87	3.19	11250; 18250
Ni(4MeTFAP)$_2$(py)$_2$	Calcd:	54.14	3.89	9.02		10310; 13250sh
	Found:	53.84	3.75	9.10	3.18	17240
Ni(5MeTFAP)$_2$(py)$_2$	Calcd:	54.15	3.89	9.02		10360; 13000sh
	Found:	53.69	3.80	8.78	3.11	17240

quinoline] nickel(II) was found to be 3.43 B.M. and its visible spectrum is typical of a tetrahedral complex.[10] Since it is expected that five coordinate nickel(II) complexes having oxygen and nitrogen donors would be high spin, the 4- and 5-methyl derivatives are therefore probably square planar rather than low spin 5-coordinate. Visible spectra in the solid state confirm[11] this assignment (Table I, Figure 1).

The magnetic and spectral features of $Ni(TFAP)_2$ suggest it to be unusual compared to the other complexes. The solid state visible spectrum is complex (Figure 1) and may be interpreted in several ways.[12] A square pyramidal structure (*V*) which is consistent with spectral data can be envisioned for $Ni(TFAP)_2$ wherein the enolic oxygen bridges a pair of nickel(II) ions. In support of this assignment, a square pyramid five-coordinate dimer has been postulated for the nickel(II) complexes of *I* where



V

R′ = CH_3[2]. It should also be noted that the visible spectrum of $[Ni(OAsMePh_2)_4(ClO_4)]ClO_4$ which is known to be square pyramidal is quite similar to the spectrum of $Ni(TFAP)_2$. A dimeric trigonal bipyramidal arrangement for $Ni(TFAP)_2$ cannot be completely eliminated at this point. It is reasonable to expect that the solid state structure for $Ni(TFAP)_2$ may be considerably different from the methylated derivatives since it alone appears to be thermochromic. At its sublimation temperature the material is brown-red and goes through the following color changes on cooling: 80°C (yellow), 25°C (mustard) and −75°C (pale green).

Solutions of $Ni(TFAP)_2$ in donor solvents such as acetone yield visible spectra that indicate an octahedral environment for nickel(II). These results are interpreted as arising from association of two solvent molecules with nickel(II). It is expected that $Ni(4MeTFAP)_2$ and $Ni(5MeTFAP)_2$ will behave similarly in donor solvents since they readily formed pyridine adducts containing two molecules of pyridine per nickel(II). The solution spectrum of $Ni(6MeTFAP)_2$ in acetone, however, indicates that the tetrahedral environment is retained. This observation is consistent with the fact that a bis(pyridine) adduct is not produced with $Ni(6MeTFAP)_2$.

The room temperature visible spectrum of $Ni(TFAP)_2$ is drastically changed when the complex is dissolved in benzene, chloroform, methylene chloride or ethylene dichloride. The visible spectrum in each solvent is concentration dependent and at a fixed concentration, changes in the spectrum are noted as the temperature is raised or lowered. The solution visible spectra $Ni(TFAP)_2$ at 15.5°C, 37°C and 75°C are shown in Figure 2. It is observed that there is a band at approximately 8500 cm^{-1} that decreases in intensity as the temperature increases. Further, the band at approximately 16000 cm^{-1} increases in intensity (i.e., $\epsilon_{15.5^\circ C} = 36$ and $\epsilon_{76^\circ C} = 59$) and is shifted slightly to higher frequencies (i.e., $\bar{\upsilon}_{max\ 15.5^\circ C} = 16190\ cm^{-1}$ and $\bar{\upsilon}_{max\ 76^\circ C} = 16400\ cm^{-1}$ as the temperature is increased. The benzene solution visible spectra for $Ni(4MeTFAP)_2$ and $Ni(5MeTFAP)_2$ are very similar having low temperature bands at approximately 8500 cm^{-1}; 16250 cm^{-1} and 9000 cm^{-1}; 16000 cm^{-1} respectively. These bands are found to vary with temperature in the same manner as $Ni(TFAP)_2$. $Ni(6MeTFAP)_2$ does not show any changes in its solution visible spectrum as a function of temperature or concentration. Molecular weights for $Ni(TFAP)_2$ in benzene were determined at temperatures coincident with the spectral data (Table II). The molecular weight for $Ni(TFAP)_2$ at 37°C is very close to the value calculated for a dimeric species whereas at higher temperatures the molecular weight decreases. An approximate molecular weight for $Ni(TFAP)_2$ in benzene via freezing point depression suggests that association predominates at lower temperatures. This association is verified by obtaining the visible spectrum of the benzene solution at 10°C. The visible spectrum at this temperature is indicative of an octahedral species with band maxima at 8960 cm^{-1} (10.4) and 16050 cm^{-1} (32.7). Solution magnetic moments of $Ni(TFAP)_2$ in benzene also change with temperature (Table II). As the temperature is increased, the magnetic moment per nickel decreases. The temperature effect on magnetism is even more pronounced with $Ni(4MeTFAP)_2$ and $Ni(5MeTFAP)_2$. At 15°C both materials have μ_{eff} characteristic of two unpaired electrons.

The observed data for these solutions can be understood in terms of a polymer/monomer equilibrium similar to that observed for nickel(II) complexes derived from *I*.[13] Since the polymeric

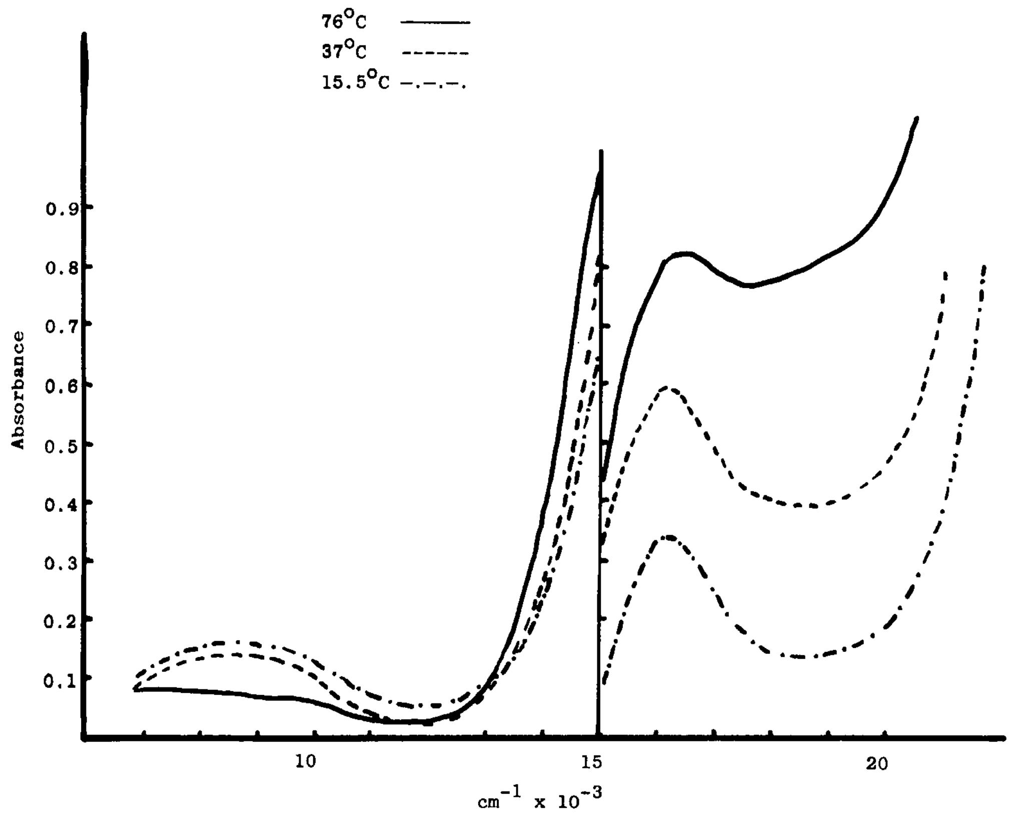


FIGURE 2 Visible spectra of Ni(TFAP)$_2$ in benzene at various temperatures.

species is favored at lower temperatures, the visible band at approximately 8500 cm^{-1} is probably due to the presence of a pseudo-octahedral species (S = 1). As the temperature is increased, the intensity of this band decreases because the polymer species decreases in concentration. The monomer species no doubt is square planar (S = 0) since the magnetic moment decreases as the temperature is increased.

Ni(6MeTFAP)$_2$ exhibits a solution molecular weight indicative of a monomeric species. The visible spectrum of Ni(6MeTFAP)$_2$ in solution is very similar to its solid state spectrum. It appears that

TABLE II
Molecular weight and magnetic susceptibility data for 2-(trifluoroacetyl)-heteroaromatic complexes in benzene

Compound		15°C	37°C	60°C	70°C
Ni(TFAP)$_2$	$\mu_{eff.}$	–	1.90	1.35	1.15
	Mol. Wt.[a]	–	960	–	565
Ni(4MeTFAP)$_2$	$\mu_{eff.}$	3.08	2.48	1.48	–
	Mol. Wt.[a]	–	732	446	–
Ni(5MeTFAP)$_2$	$\mu_{eff.}$	3.06	2.14	1.50	–
	Mol. Wt.[a]	–	760	461	–
Ni(6MeTFAP)$_2$	$\mu_{eff.}$	–	3.20	3.13	–
	Mol. Wt.[a]	–	480	–	–

[a] Molecular weight calculated: Ni(TFAP)$_2$ = 435 a.m.u., Ni(MeTFAP)$_2$ = 463 a.m.u.

the steric requirements of the methyl group in the 6-position of the heterocyclic ring maintain the tetrahedral structure in solution.

Gas Solid Reactions

Solid $Ni(TFAP)_2$ is observed to react with H_2O vapor. The yellow-green color of $Ni(TFAP)_2$ changes to a green color. Elemental analyses of the product (Table III) suggest the empirical formula: $Ni(TFAP)_2(H_2O)$. The elements of H_2O can be easily removed by heating at 100°C *in vacuo* for five minutes. The reactivity of $Ni(TFAP)_2$ appears to be due to its solid state structure since it is the only $Ni(ZTFAP)_2$ which reacts in this manner.

The H_2O appears to dissociate in its reaction with $Ni(TFAP)_2$ as indicated by the infrared spectrum of the water adduct, Figure 3. There is a very sharp absorption at 3610 cm^{-1} which is assignable to an O–H stretching vibrational mode.[14] Also appearing in the spectrum of the gas-solid adduct are two absorptions at 3280 and 3160 cm^{-1} that are indicative of coordinated water. The band at 1625 cm^{-1} broadens on exposure to H_2O and is believed to be a composite of HOH bending,[14] coordinated and noncoordinated C=O stretching modes and the heterocyclic ring absorption. After the solid state water adduct has been dried *in vacuo* for 48 hours at room temperature, the spectrum is identical to the starting material indicating that the reaction of solid $Ni(TFAP)_2$ with H_2O is reversible. An analogous D_2O adduct was prepared in the same manner as the H_2O adduct. The infrared spectrum of the D_2O adduct contains a sharp absorption at 2635 cm^{-1} and two broad absorptions at 2380 and 2300 cm^{-1}. The position of these bands is in good agreement with the expected ratio of 1.37 when comparing OH and OD vibrational modes.

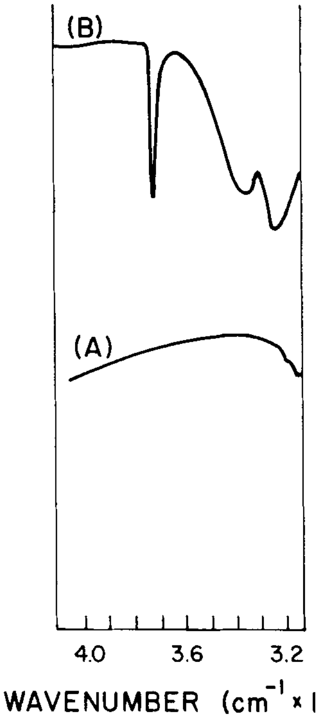


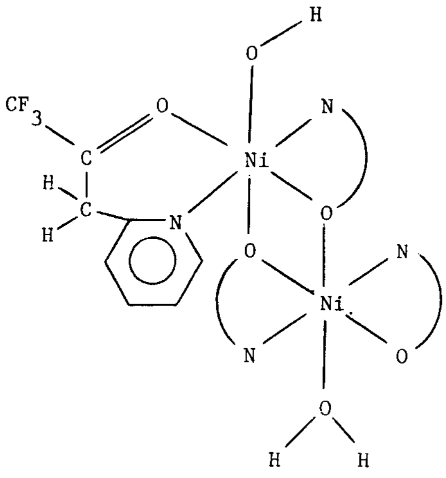
FIGURE 3 Infrared spectra of (A) $Ni(TFAP)_2$ and (B) gas solid product, $Ni(TFAP)_2(H_2O)$.

The magnetic moment (3.32 B.M.) of the gas-solid adduct is in the range for octahedral and 5-coordinate complexes. The solid state visible spectrum exhibits a shoulder at 9500 cm^{-1} and a band maximum at 16000 cm^{-1} prior to the ligand-ligand transition analogous to known octahedral complexes of nickel(II). It should be noted that the visible spectrum was obtained using heat filters since the heat from the light source is sufficient to cause the

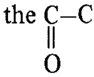
TABLE III
Analytical data for products of gas-solid reactions

Compound		Elemental analyses			$\mu_{eff.}$ (B.M.)	Band maxima (cm^{-1})
		C	H	N		
$Ni_2(TFAP)_3(HTFAP)(H_2O)(OH)$	Calcd:	42.24	3.10	6.16		
	Found:	42.26	2.90	6.40	3.32	9500sh; 1600
$Ni(TFAP)(HTFAP)(NH_3)(NH_2)$	Calcd:	40.97	3.44	11.95		
	Found:	41.00	3.99	11.86	3.11	9900; 16900
$Ni(4MeTFAP)(H4MeTFAP)(NH_3)(NH_2)$	Calcd:	43.49	4.06	11.27		
	Found:	43.67	4.01	10.81	2.96	10200; 17700
$Ni(5MeTFAP)(H5MeTFAP)(NH_3)(NH_2)$	Calcd:	43.49	4.06	11.27		
	Found:	43.54	4.36	10.71	3.17	10000; 17900

sample to change form green to yellow. The single structure that best agrees with the data above is *VI*, where a proton from H_2O has transferred to one of the bidentate ligands. The formation of such a species may be considered to arise from initial attack of a H_2O molecule at one of the open nickel sites in the five coordinate dimer. The attacking molecule could then transfer a proton to the bidentate ligand causing it to now coordinate in the keto form.



VI

Construction of molecular models indicates that the C=C of the enol portion of the ligand is very exposed in the dimeric structure assuming the nickel ion is displaced slightly toward the apical bridging oxygen. One of the nickel ions can now be six-coordinate and should move toward the center of the octahedron. This subtle change in geometry could thus allow the second water molecule to coordinate without dissociation. The ligand receiving the proton is believed to be a non-bridging ligand since it should be more basic. It should be pointed out that TFAP contains the  $\underset{\underset{O}{\|}}{C}-CF_3$ group, and it may be possible for H_2O to attack the carbonyl carbon directly.[15] Evidence to refute this argument lies in the fact that no other $Ni(L)_2$ complexes as well as $Cu(TFAP)_2$ react with H_2O vapour under the same conditions.

Gaseous NH_3 was allowed to react with $Ni(ZTFAP)_2$ in order to test the generality of the gas-solid reaction. Most of the reactions are slow and require several days before uptake of gas is complete. Table IV lists the compounds which could be isolated and characterized. $Ni(6MeTFAP)_2$ was found to react with NH_3, however, when the sample is exposed to the laboratory atmosphere the NH_3 is released yielding the starting material. The infrared spectrum for the ammonia adducts exhibit absorptions characteristic of NH_2^- [16] and NH_3[17]. No doubt the structure of these materials is similar to the latter hydrated material. Thermal gravimetric analysis reveal that the elements of ammonia can be readily removed c.a. 70°C *in vacuo.* Magnetic and visible spectral data are in agreement with an octahedral arrangement of donor atoms. Unlike the H_2O case the 4- and 5-methyl derivatives readily react with ammonia.

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