

procedure reported here. This may be attributed to the short length of the bridging groups in the amine backbone which precludes wrapping of the ligand around all five coordination sites. Similar behavior has been noted for pentadentate Schiff bases derived from salicylaldehyde.<sup>4</sup> Instead, square-planar Ni(II) and Cu(II) complexes which contain singly condensed, unsymmetrical Schiff base ligands have been obtained from H<sub>2</sub>(tfacdien) as a result of partial hydrolysis of the pentadentate ligand. This unusual reaction

and others are discussed in the paper which follows.

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

**Registry No.** H<sub>2</sub>(tfacDPT), 50599-75-2; Ni(tfacDPT), 50600-59-4; Cu(tfacDPT), 50600-60-7; Ni(py)(tfacDPT), 50600-61-8; tfac, 367-57-7; DPT, 56-18-8.

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## Square-Planar Nickel(II) and Copper(II) Complexes with Unsymmetrical Anionic Tetradentate Schiff Base Ligands

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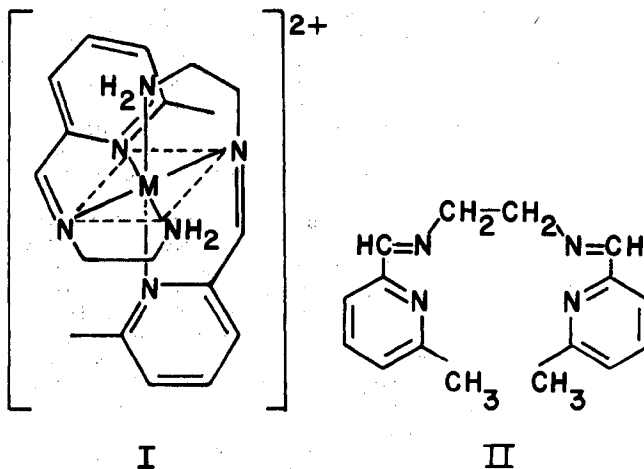
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Eight new square-planar Ni(II) and Cu(II) complexes with unsymmetrical anionic singly condensed Schiff base ligands derived from acac, tfac, and dien have been prepared and characterized as I<sup>-</sup> and PF<sub>6</sub><sup>-</sup> salts. Formation of the complexes has been achieved by reaction of the metal hydroxides with singly condensed ligand salts or with doubly condensed pentadentate Schiff bases. The latter method involves a most unusual partial hydrolysis of the Schiff base ligand. While the mechanism of this reaction is unclear, the role of the metal ion may be to sequester the tetradentate ligand and render it inactive to further hydrolysis.

### Introduction

Over the past 100 years, numerous transition metal complexes with  $\beta$ -ketoamine and salicylalimine ligands have been prepared,<sup>1</sup> but only a very few of the ligands reported have been derived from carbonyl compounds and linear polyamines which have undergone condensation at only one end of the amine. This can be attributed to the difficulties encountered in preparing these types of unsymmetrical ligands by the usual condensation procedures. For example, addition of 1 equiv of acetylacetonone to 1 equiv of ethylenediamine in an appropriate solvent followed by the usual method of isolation<sup>2</sup> produces lower yields of *N,N'*-ethylenebis(acetylacetonimine) instead of the singly condensed product. For this reason, workers interested in preparing the unsymmetrical monosubstituted Schiff base ligand have used *N*-substituted alkyl- or arylethylenediamines whose structures preclude reaction at the secondary or tertiary amine end of the molecule.<sup>3,4</sup> Most ligands which have been reported are tridentate chelating agents which have been prepared by condensation of various substituted salicylaldehydes with the aforementioned diamines. Complexes containing these uninegative ligands are of interest since they can exhibit four, five, or six coordination depending upon the nature of the nitrogen and salicylaldehyde substituents.<sup>3-6</sup> No singly condensed Schiff base ligands prepared from  $\beta$ -diketones appear to have been studied, although one very interesting complex has been reported (I), where M(II) is Cu or Fe and the neutral tridentate ligand results from partial hydrolysis of the tetradentate

Schiff base derived from 6-methylpyridine-2-aldehyde and ethylenediamine (II) in the presence of the metal ions.<sup>7</sup>



While the presence of metal ions is known to catalyze the hydrolytic cleavage of some Schiff bases, a partial hydrolysis of this type must be considered unusual.<sup>8-10</sup>

During our investigations of complexes with pentadentate Schiff base ligands derived from various  $\beta$ -diketones and tridentate polyamines,<sup>11</sup> we have discovered that partial hydrolysis of the pentadentate ligands occurs with ease. We have improved the procedure involved in this unusual reaction so that it now provides a convenient method for the synthesis of unsymmetrical, singly condensed tetradentate ketoamines.

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**Table I.** Analytical Data for Ni(ad)X, Ni(tad)X, Cu(ad)X, and Cu(tad)X Complexes

Compd	Percentage <sup>a</sup>							Mol wt
	C	H	O	N	M	F	Other	
Ni(ad)PF <sub>6</sub>	27.88	4.64	4.12	10.83	15.14	29.39	7.99, P	387.70
	28.00	5.07	3.95 <sup>b</sup>	10.78	15.09	29.09	7.79	400 <sup>c</sup>
Ni(ad)I	29.24	4.87	4.32	11.36	15.88		34.33, I	369.69
	29.14	4.77	4.27	11.22	16.01		34.55	396
Ni(tad)PF <sub>6</sub>	24.47	3.39	3.63	9.51	13.29	38.70	7.01, P	441.67
	24.05	3.21	5.49 <sup>b</sup>	9.34	13.03	37.91	6.97	468
Ni(tad)I	25.51	3.54	3.77	9.91	13.86	13.45	29.95, I	423.66
	25.25	3.46	3.87 <sup>b</sup>	9.79	14.01	13.44	30.18	370
Cu(ad)PF <sub>6</sub>	27.54	4.59	4.07	10.70	16.19	29.03	7.89, P	392.53
	27.55	4.73	4.33 <sup>b</sup>	10.53	16.19	28.89	7.78	416
Cu(ad)I	28.86	4.81	4.27	11.21	16.96		33.88, I	374.52
	28.91	4.81	4.30	11.10	16.90		34.00	368
Cu(tad)PF <sub>6</sub>	24.21	3.36	3.58	9.40	14.23	38.28	6.94, P	446.50
	24.09	3.10	3.30 <sup>b</sup>	9.35	14.49	38.54	7.13	444
Cu(tad)I	25.22	3.50	3.73	9.80	14.83	13.30	29.62, I	428.49
	25.00	3.41	3.65 <sup>b</sup>	9.66	14.87	13.53	29.88	450

<sup>a</sup> First value calculated, second found. <sup>b</sup> By difference. <sup>c</sup> All molecular weight measurements done in methanol.

In this note we report on the synthesis and characterization of the acid salts and square-planar nickel(II) and copper(II) complexes derived from acetylacetonone, acac, or trifluoroacetylacetonone, tfac, and diethylenetriamine, dien.<sup>12</sup>

### Experimental Section

**Ligands.** The best method for preparing acid salts of the ligands is as follows. A 51.1-g sample (0.5 mol) of dien was diluted with 400 ml of acetone and the solution was chilled to 20°. To this was added slowly with stirring a 50-g sample (0.5 mol) of acac in 100 ml of acetone. During the addition of the  $\beta$ -diketone, heat was evolved and the solution turned pale yellow. A 75-g sample (0.5 mol) of NaI or an 81.1-g sample (0.5 mol) of NH<sub>4</sub>PF<sub>6</sub> was added and the pH was adjusted to about 5 with glacial acetic acid. The solution was allowed to stand at room temperature for a week while a white precipitate formed. The precipitate was removed by filtration, washed with acetone, and dried on the filter; yield, ~60%. Analyses for these salts in general gave poor agreement with theoretical values; however, the complexes prepared from them were analytically pure.

**Complexes.** The four-coordinate nickel(II) and copper(II) complexes were prepared in several ways. Those which provided the highest yields are described below. All analyses are reported in Table I.

**2-Amino-2'-(acetylacetoniminato)diethylaminenickel(II) Iodide, Ni(ad)I.** A 0.93-g sample (0.01 mol) of freshly prepared Ni(OH)<sub>2</sub> was ground in a mortar and pestle with a water slurry of 3.13 g (0.01 mol) of H<sub>2</sub>(ad)I until no further color change was observed. Methanol (200 ml) was added and the mixture was refluxed for 3 hr. The solution was concentrated under an air stream and the bright orange crystals which formed were recovered. The product was recrystallized from acetonitrile and then methanol; yield, 20–30%. Blue crystals of Cu(ad)I could be prepared by this procedure when CuO was used in place of Ni(OH)<sub>2</sub>; yield, 20%.

**2-Amino-2'-(acetylacetoniminato)diethylaminenickel(II) Hexafluorophosphate, Ni(ad)PF<sub>6</sub>.** A 0.93-g sample (0.01 mol) of freshly prepared Ni(OH)<sub>2</sub> was dissolved in 200 ml of NH<sub>4</sub>OH and 3.31 g (0.01 mol) of H<sub>2</sub>(ad)PF<sub>6</sub> was added. The solution was refluxed for 3 hr, then concentrated to about 50 ml and filtered to remove unreacted starting materials. The solution was further concentrated under an air stream. The bright orange needles which formed were isolated and then recrystallized from acetonitrile; yield, ~40%. Bluish-purple crystals of Cu(ad)PF<sub>6</sub> could also be prepared by this procedure when CuO was used in place of Ni(OH)<sub>2</sub>; yield, 40%. *Note: these procedures should be performed in a well ventilated hood to minimize exposure to ammonia vapor.*

**2-Amino-2'-(trifluoroacetylacetoniminato)diethylaminenickel(II) Iodide, Ni(tad)I.** This complex was prepared in the same manner as described for Ni(ad)I except that the pentadentate ligand, H<sub>2</sub>(tfacdien), whose synthesis has been reported earlier,<sup>11</sup> was used in place of the ligand salt. After the reflux period the solution was concentrated, filtered, and then added to an aqueous solution of 1.48 g (0.01 mol) of NaI. The orange complex was isolated and recrystallized from

acetonitrile and then methanol; yield, ~50%. Blue crystals of Cu(tad)I were also prepared by this method when CuO was substituted for Ni(OH)<sub>2</sub>; yield, ~45%.

**2-Amino-2'-(trifluoroacetylacetoniminato)diethylaminenickel(II) Hexafluorophosphate, Ni(tad)PF<sub>6</sub>.** This procedure was analogous to that given above for Ni(tad)I except that 1.63 g (0.01 mol) of NH<sub>4</sub>PF<sub>6</sub> was used in place of the NaI. Cu(tad)PF<sub>6</sub>, reddish-purple crystals, was also prepared by this method using CuO instead of Ni(OH)<sub>2</sub>; yield, ~50–65%.

**Physical Measurements.** Infrared spectra were recorded on a Perkin-Elmer Model 457 ir spectrophotometer as KBr disks and Nujol mulls. Visible and uv spectra were measured on 10<sup>-2</sup>–10<sup>-5</sup> M methanolic solutions and as Nujol mulls on filter paper with a Cary 14 recording spectrophotometer. Magnetic susceptibility measurements were obtained by the Faraday method. Calculated values were corrected for the diamagnetism of the ligands using Pascal's constants. Proton nmr spectra were recorded on a Varian A-60 nmr spectrometer. d<sub>4</sub>-Methanol was used as solvent and TMS as the internal standard. Chemical analyses and molecular weight data were provided by Alfred Bernhardt, Mikroanalytisches Laboratorium, Elbach, West Germany.

### Results and Discussion

**Ligand Syntheses.** Salts of the singly condensed tetradentate ligands were first prepared as a result of our attempts to isolate the pentadentate Schiff base derived from 2 equiv of acac and 1 equiv of dien. In the preceding paper we have reported a procedure for synthesis of H<sub>2</sub>(tfacDPT) and H<sub>2</sub>(tfacdien), pentadentate fluorinated Schiff bases. When the same general scheme is used with acac instead of tfac, a yellow oil forms which could not be made to crystallize. Addition of NaI or NH<sub>4</sub>PF<sub>6</sub> to an acetone solution of the yellow oil, followed by acidification to pH ~5 with glacial acetic acid, yields the I<sup>-</sup> or PF<sub>6</sub><sup>-</sup> salts of the protonated singly condensed tetradentate Schiff bases. The weakly acidic solution appears to catalyze the formation of the partially hydrolyzed product. Since our initial isolation of these products, we have discovered that higher yields are obtained by the direct addition of 1 equiv of acac to 1 equiv of dien in acetone followed by treatment with I<sup>-</sup> or PF<sub>6</sub><sup>-</sup> and acid. Unfortunately, repeated recrystallizations of the acid salts from various solvents failed to give analytically pure samples. This may be due to the instability of these materials toward further hydrolysis on recrystallization. Although the ligand salts are somewhat impure, they do exhibit reproducible infrared spectra which are characterized by broad bands of medium intensity in the 2800–2450-cm<sup>-1</sup> region which are assigned to the NH stretching modes of the protonated amine. Three absorption bands between 1600 and 1500 cm<sup>-1</sup> indicate the presence of C=C and/or C=N functional groups. Low solubilities of the salts made pmr studies impossible. Although

(12) Taken in part from the M. S. thesis of W. N. Wallis, Wright State University, August 1972.

the ligand salts could not be well characterized, the metal complexes formed from them could be completely studied by a variety of methods as discussed below.

**Synthesis of Metal Complexes.** The general scheme for synthesis of complexes containing the nonfluorinated singly condensed Schiff base ligand involves reaction of the acid salt  $H_2(ad)X$ , where  $X^- = PF_6^-$  or  $I^-$ , with either Ni(II) or Cu(II) ions in strongly basic solution. Strong base is necessary to neutralize the acid salt and to remove the weakly acidic amine proton to give the iminato complex shown in Figure 1.

The Ni(II) complexes can also be isolated from the crude reaction mixture of acac, dien, and  $Ni(OAc)_2 \cdot 4H_2O$ , but this is not preferred because of low yields and the difficulties of purifying the sample. Similar complexes with unsymmetrical fluorinated Schiff base ligands are formed by the reaction of the pentadentate ligand,  $H_2(tfacdien)$ ,<sup>11</sup> with either Ni(II) or Cu(II) ions as shown in Figure 2. This reaction requires strong base to catalyze the hydrolysis of one of the azomethine linkages in a reaction which is similar to the partial hydrolysis reported by Goodwin and Lions.<sup>7</sup> While the mechanism of this reaction is unclear, the role of the metal ion may be to sequester the tetradentate ligand and render it inactive to further hydrolysis.

**Characterization of Metal Complexes.** Elemental analyses and molecular weight data for the eight new Ni(II) and Cu(II) complexes, listed in Table I, indicate the presence of one anion and one Schiff base per metal ion. Molar conductances in methanolic solutions indicate that the complexes are 1:1 electrolytes with  $\Lambda_M$  of 88–113 (mhos  $cm^2$ )/mol<sup>13</sup> which requires that the Schiff bases coordinate as uninegative ligands.

The infrared spectra of all of the Ni(II) and Cu(II) complexes are very similar. The spectrum of Ni(ad)I, which is typical of the new complexes, exhibits strong bands at 3190, 3100, and 3030  $cm^{-1}$  which are assigned to the stretching vibration of the backbone NH and to the asymmetric and symmetric stretching modes of the terminal  $NH_2$  group. Bands at 1585 and 1505  $cm^{-1}$  are assigned to the  $C=C$  and/or  $C=N$  stretching vibrations. The only differences between the spectra of the  $I^-$  and  $PF_6^-$  derivatives is that the NH and  $NH_2$  stretching modes for the latter occur at slightly higher energies (3350, 3290, and 3250  $cm^{-1}$ ) due to the absence of hydrogen bonding with the anion and the appearance of bands attributable to the  $PF_6^-$  anion at  $\sim 850$  and  $\sim 565$   $cm^{-1}$ , which show that the anion is not coordinated. Spectra of the Ni(II) and Cu(II) complexes with the fluorinated ligands also show higher energy absorptions in the amine region and new bands in the 1300–1100- $cm^{-1}$  region due to the  $CF_3$  groups.

The pmr spectra of Ni(ad)PF<sub>6</sub> and Ni(tad)PF<sub>6</sub> obtained in deuterated methanol are listed in Table II. Singlets at 1.72, 1.91, and 4.60 ppm in Ni(ad)PF<sub>6</sub> with relative intensities of 3:3:1 are assigned to the protons of the methyl group adjacent to the imine and to the protons of the methyl group adjacent to the  $C=O$  and to the vinylic =CH proton, respectively. The lower field position of the second methyl resonance is attributed to the higher electronegativity of oxygen which deshields these protons. Singlets at 1.76 and 5.37 ppm in Ni(tad)PF<sub>6</sub> with relative intensities of 3:1 are assigned to protons of the  $CH_3$  adjacent to the  $C=N$  and to the vinylic =CH proton. The fact that the  $CH_3$  signal which is absent from the spectrum of Ni(tad)PF<sub>6</sub> is that found at 1.91 ppm provides unequivocal evidence that condensation has occurred at the carbonyl carbon adjacent to the  $CH_3$  group rather than

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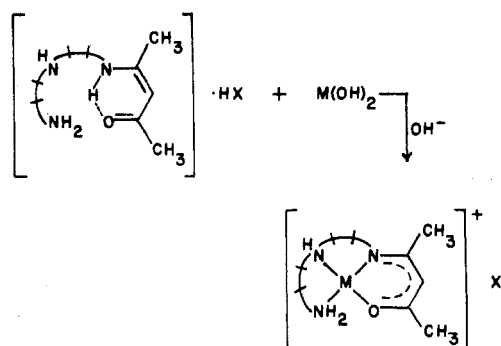


Figure 1. General reaction scheme for formation of square-planar metal complexes from ketoamine ligand salts.

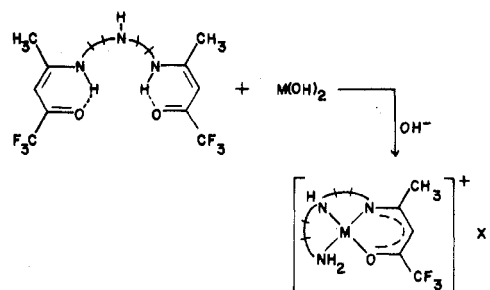


Figure 2. General reaction scheme for formation of square-planar metal complexes via partial hydrolysis of  $H_2(tfacdien)$ .

Table II. 60-MHz Pmr Spectra of Ni(ad)PF<sub>6</sub> and Ni(tad)PF<sub>6</sub> in *d*<sub>4</sub>-Methanol

Compd	Chemical shift ( $\delta$ ), ppm, <sup>a</sup> assignments		
	$CH_3$	$CH_2$ <sup>b</sup>	=CH
Ni(ad)PF <sub>6</sub>	1.72, 1.91	2.50–3.05	4.60
Ni(tad)PF <sub>6</sub>	1.76	3.88–4.45	5.37

<sup>a</sup> Relative to TMS as the internal standard. <sup>b</sup> Range of the multiplet.

to the  $CF_3$  group. This conclusion is in agreement with results from dipole moment and nmr studies on other fluorinated Schiff bases.<sup>14–16</sup> The multiplet pattern in each spectrum is assigned to the methylene protons of the amine backbone. No resonances due to backbone NH nor terminal  $NH_2$  protons were observed due to exchange with the deuterated solvent. Deuteration of these protons under these conditions has been confirmed by infrared spectral measurements.

All of the Ni(II) complexes are diamagnetic ( $\mu_{eff} = 0.5$  BM), while the Cu(II) complexes exhibit the values expected for one unpaired electron ( $\mu_{eff} = 1.80$  BM). Electronic spectra confirm the square-planar geometry of the new complexes. The lowest energy absorption band in the visible spectrum of the Ni(II) complexes occurs at 23,000  $cm^{-1}$  ( $\epsilon \approx 200$ ) and is assigned to the  ${}^1B_{1g} \leftarrow {}^1A_{1g}$  transition of singlet ground state nickel(II). Six high intensity transitions between 29,000 and 50,000  $cm^{-1}$  are assigned as charge transfer or parity allowed intraligand transitions. Visible spectra of the Cu(II) complexes exhibit two low energy bands at 18,000 ( $\epsilon \approx 130$ ) and 27,500 ( $\epsilon \approx 400$ )  $cm^{-1}$ . These have been assigned as the  ${}^2A_{1g} \leftarrow {}^2B_{1g}$  and  ${}^2E_g \leftarrow {}^2B_{1g}$  transitions of square-planar Cu(II).

So far we have been unable to isolate other derivatives of these complexes, although metatheses with several different

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sodium salts with strongly coordinating anions were tried. We are continuing our efforts to prepare species with coordinated anions since some of these complexes should have interesting five-coordinate geometries with five different donor groups.

**Acknowledgment.** Acknowledgment is made to the donors

of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

**Registry No.** Ni(ad)PF<sub>6</sub>, 50601-07-5; Ni(ad)I, 50601-06-4; Ni(tad)PF<sub>6</sub>, 50600-69-6; Ni(tad)I, 50600-70-9; Cu(ad)PF<sub>6</sub>, 50600-72-1; Cu(ad)I, 50600-73-2; Cu(tad)PF<sub>6</sub>, 50600-75-4; Cu(tad)I, 50600-76-5.

## Notes

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### Structural Assignments of Some Nickel(II) Complexes Containing Macrocyclic Ligands Derived from Benzilmonohydrazone

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Condensation reactions between amines and nickel(II) complexes containing tetradentate ligands with an N<sub>2</sub>O<sub>2</sub> donor set derived from benzilmonohydrazone<sup>1</sup> have recently been described.<sup>2</sup> With ethylenediamine and 1,2-propanediamine, low-spin square-planar nickel(II) complexes containing macrocyclic ligands were obtained. Although the ligand structures were established unequivocally, the mode of coordination of the ligands to nickel(II) was assumed and the stereochemistry of the new chelate rings within the macrocycles was not established.

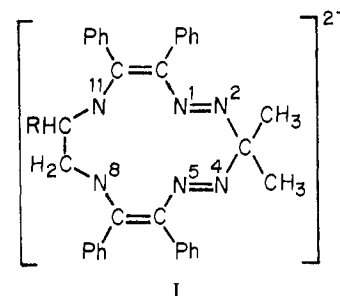
This note reports a study of the proton magnetic resonance spectra of these complexes and circular dichroism spectra of the macrocyclic complex obtained from (-)-1,2-propanediamine. The data obtained has enabled detailed structural assignments to be made for the complexes.

#### Experimental Section

3,3-Dimethyl-6,7,12,13-tetraphenyl-1,2,4,5,8,11-hexaazacyclotrideca-1,4,6,12-tetraenatonickel(II), (NiHcyclo13),<sup>3</sup> and 3,3,9-trimethyl-6,7,12,13-tetraphenyl-1,2,4,5,8,11-hexaazacyclotrideca-1,4,6,12-tetraenatonickel(II), (NiMyclo13),<sup>3</sup> were prepared as previously reported<sup>2</sup> from  $\alpha,\alpha'$ -[isopropylidenebis(azo)]di- $\alpha$ -stilbenolatonic nickel(II), NiMMK,<sup>1,3</sup> and ethylenediamine or 1,2-propanediamine, respectively. R-(-)-1,2-Propanediamine was kindly supplied by Professor F. L. Urbach of Case Western Reserve University for the synthesis of (-)-NiMyclo13. Proton magnetic resonance spectra were obtained using a Varian HA-100 spectrometer. Tetramethylsilane was used as an internal standard. Circular dichroism spectra for (-)-NiMyclo13 were obtained by Professor F. L. Urbach using techniques previously described.<sup>4</sup>

#### Results and Discussion

The proton magnetic resonance spectrum of NiHcyclo13, a nickel(II) complex containing the ligand Ia, R = H, is recorded in Table I. Resonances are observed in three distinct regions of the spectrum, each of which may be correlated with protons of the ligand. The singlet (relative intensity 6) at 1.74 ppm is assigned to the hydrogens of the geminal



methyls attached to the carbon bridging N<sup>2</sup> and N<sup>4</sup>. This is in a similar position to the geminal methyl hydrogens of the parent compound NiMMK<sup>1</sup> from which NiHcyclo13 is derived. The methyl groups are thus in equivalent positions, located above and below the plane of the macrocyclic ligand in the complex. The multiplet centered at about 7.14 ppm is assigned to the hydrogens of the phenyl groups, again in a position similar to those in NiMMK.

The most informative region of the spectrum from a structural viewpoint is that between 3 and 4 ppm. In this region, a complex, but symmetrical, pattern is observed (Figure 1, upper spectrum) with integrated relative intensity 4. This absorption is thus due to the protons of the dimethylene chain. The observed pattern may be simulated<sup>5</sup> (Figure 1, lower spectrum) by assuming an A<sub>2</sub>B<sub>2</sub> system for these protons. Thus, within the dimethylene chain, there are two sets A and B of equivalent hydrogens, with  $n_A = n_B = 2$ . Such a system may be described by two parameters only, the coupling constant between the nonequivalent protons,  $J_{AB}$ , and  $\delta$ , the chemical shift difference.<sup>6</sup> For NiHcyclo13,  $J_{AB} = 6.5$  Hz and  $\delta = 32$  Hz. The value of  $J_{AB}$  suggests vicinal coupling between the nonequivalent protons.<sup>7</sup> The spectrum does not change either on increasing the temperature to 80° in bromoform (decomposition takes place above this temperature) or decreasing the temperature to -40° in deuteriochloroform.

The macrocyclic ligand I has six potential donor nitrogen atoms, although the magnetic properties and visible spectrum of the nickel(II) complex suggest it coordinates by four nitrogens in a square planar manner.<sup>2</sup> Three modes of coordination are possible depending on which donor atoms are involved: (a) N<sup>1</sup>, N<sup>5</sup>, N<sup>8</sup>, and N<sup>11</sup>; (b) N<sup>1</sup>, N<sup>4</sup>, N<sup>8</sup>, and N<sup>11</sup> (or its equivalent N<sup>2</sup>, N<sup>5</sup>, N<sup>8</sup>, and N<sup>11</sup>); (c) N<sup>2</sup>, N<sup>4</sup>, N<sup>8</sup>, and N<sup>11</sup>. Possibilities a and c cause the dimethylene carbons to be equivalent, but this is not the case for possibility b. A

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