Spectral and Magnetic Studies of Amino-Acid Schiff Base Complexes of Nickel(II)

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A variety of o-hydroxyacetophenone-glycine imines coordinated to nickel(II) have been synthesized. These complexes have been further characterized by conductivity measurements, magnetic data, electronic, infrared and nuclear magnetic resonance spectral data. The results suggest that the complexes are four coordinate with a square planar configuration. The ligands bind through the imino nitrogen and carboxylate groups.
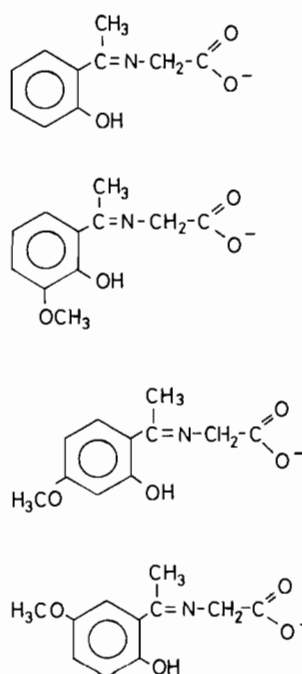
Introduction

Imines (Schiff bases) have frequently been suggested as intermediates in the reaction between pyridoxal (vitamin B_6 aldehyde) and various amino acids [1]. Furthermore, metal ions demonstrate a catalytic effect upon transamination reactions involving vitamin B_6 [2–3]. These concurrent observations seem to indicate that metal complexes of Schiff bases are formed as intermediates in transamination reactions involving vitamin B_6 [4].

Amino-acid complexes of transition metals have served as models for understanding biocatalytic processes [5–7]. For instance, a variety of salicylideneglycine Schiff bases have been synthesized and coordinated to metal ions [8–11]. In order to further extend our knowledge of imine–metal complex chemistry a variety of o-hydroxyacetophenoneglycine imines coordinated to nickel(II) have been synthesized. These complexes have been further characterized by conductivity measurements, magnetic data, electronic, infrared and nuclear magnetic resonance spectral data.

Experimental

All chemicals used were of reagent grade. Substituted acetophenones were prepared by a procedure reported elsewhere [12]. A hot aqueous solution of glycine (0.1 mole) was added with stirring to a hot alcoholic solution of substituted 2-hydroxyacetophenone (0.1 mole). The mixture was refluxed on a water bath for nearly two hours and the excess solvent was removed by slow evaporation. Pale yellow needlelike crystals were filtered and dried.

The following ligands were prepared:
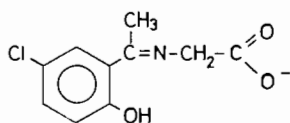
Each complex was prepared by mixing a hot alcoholic solution of the ligand (0.02 mole) with an aqueous alcohol solution of the nickel(II) chloride (0.01 mole). The mixture was refluxed for 15–20 min, then allowed to cool to room temperature. The deep dark-colored precipitate was filtered and dried in vacuum over P_2O_5. The following complexes were prepared:

I. Bis(2-hydroxyacetophenone-glycinato)nickel-(II)

II. Bis(2-hydroxy-3-methoxyacetophenone-glycinato)nickel(II)

III. Bis(2-hydroxy-4-methoxyacetophenone-glycinato)nickel(II)

IV. Bis(2-hydroxy-5-methoxyacetophenone-glycinato)nickel(II)

V. Bis(2-hydroxy-5-chloroacetophenone-glycinato)nickel(II).

Nickel in the complexes was determined gravimetrically as nickel dimethylglyoximate. The method of Kjeldahl was used to determine the nitrogen content.

Molecular weights were determined in nitrobenzene using cryoscopic techniques [13].

Conductivities were measured in dimethylformamide(DMF) using an Elico-CM-82 conductivity bridge with a cell constant of 0.829 cm^{-1}.

All conductivity measurements were performed at room temperature using 10^{-3} M solutions of the complex.

Effective magnetic moments (μ_{eff}) were measured using a Guoy balance at room temperature. All measured susceptibilities were corrected for the diamagnetic contribution of each atom [14]. Hg(Co-(SCN)$_4$) was used as a reference compound.

UV-visible spectra were obtained on a Perkin-Elmer 492-5000 spectrometer.

The infrared spectra (IR) from 4000 to 400 cm^{-1} were obtained using a Carl-Zeiss UR-10 infrared spectrometer while IR spectra in the range, 600–200 cm^{-1}, were obtained using a Perkin-Elmer 5100-4367 spectrometer.

Nuclear magnetic resonance (NMR) spectra were recorded using a S-60-C PMR instrument. All NMR samples were dissolved in deuterated dimethylsulfoxide (d_6-DMSO) and tetramethylsilane (TMS) was used as the internal standard.

Results and Discussion

Analytical and Physical Data

The complexes are brownish-yellow in color, amorphous and soluble in alcohol, nitrobenzene, DMF and DMSO. The elemental analyses for Ni and N (see Table I) agree well with 1:2 (nickel: acetophenone-glycine imine) stoichiometry. The molecular weights indicate that the complexes are monomeric in nature. The molar conductivities are in the range 22–31 ohm^{-1} cm^2 mole^{-1} indicating nonelectrolytic behavior. Magnetic data show that all complexes are diamagnetic and possess square-planar geometry (see Table II).

Electronic Spectra

An intense charge transfer band is observed for the complexes in the region 290–300 nm (34,500–33,300 cm^{-1}) (see Table II) and is characteristic of four coordinate complexes [15]. Two bands around 400 nm (25,000 cm^{-1}) and 525 nm (19,000 cm^{-1}) are also observed. These last two bands indicate a *trans*-planar configuration and are attributed to

TABLE I. Analytical and Physical Data for Imine Complexes of Nickel.

Ligand	Complex No.	Empirical Formula of the Complex	%Ni	%N	Molecular Weight	Molar Cond. ohm^{-1} cm^2 mole^{-1}
A	I	$(C_{10}H_{10}O_3N)_2Ni$	13.16 (13.12)*	6.30 (6.34)*	431 (442)*	22.5
B	II	$(C_{11}H_{13}O_3N)_2Ni$	12.19 (12.34)	5.89 (5.96)	461 (470)	26.1
C	III	$(C_{11}H_{13}O_3N)_2Ni$	12.22 (12.34)	5.91 (5.96)	464 (470)	25.3
D	IV	$(C_{11}H_{13}O_3N)_2Ni$	12.45 (12.34)	6.01 (5.96)	457 (470)	24.5
E	V	$(C_{10}H_{10}O_3NCl)_2Ni$	11.20 (11.35)	5.37 (5.48)	489 (511)	31.1

*Figures in the parentheses are the theoretical values.

TABLE II. Magnetic and Electronic Data for Complexes.

Complex No.	μ_{eff} (B.M.)	Electronic Transitions (nm)		
		Charge Transfer Band	$^1A_g \rightarrow {}^1B_g$	$^1A_g \rightarrow {}^1B_{3g}$
I	2.23	290	390	520
II	2.30	292	400	525
III	2.47	290	400	520
IV	2.35	295	420	530
V	2.48	290	415	510

TABLE III. NMR Shifts[a] of Ligands and their Nickel Complexes.

| Assignments	A	I	B	II	C	III	D	IV	E	V
imino proton	8.9	8.2	8.9	8.2	8.75	8.06	8.92	8.21	9.0	8.23
phenyl protons	7.0 to 8.0	6.85	7.0 to 8.0	6.9	7.0 to 8.0	6.75	7.2 to 8.1	6.9	7.0 to 7.9	7.0
methylene protons	3.21	3.20	3.18	3.20	3.30	3.25	3.15	3.10	3.20	3.20
methyl protons	2.22	2.20 and 2.3	2.25	2.22 and 2.41	2.20	2.3 and 2.45	2.26	2.30	2.23	2.20

[a]In ppm (δ) relative to TMS.

$^1A_g \rightarrow {}^1B_g$ and $^1A_g \rightarrow {}^1B_{3g}$ transitions respectively [16].

On the basis of the above information and other published results, a *trans* square-planar geometry is assigned to the nickel(II) complexes [1, 16, 17].

Infrared Spectra

Important infrared frequencies and their assignments are tabulated and available upon request from the author to whom all correspondence should be addressed.

Schiff bases derived from glycine and substituted *o*-hydroxyacetophenone exist predominantly in keto-enamine form:

R = H, OCH$_3$, Cl
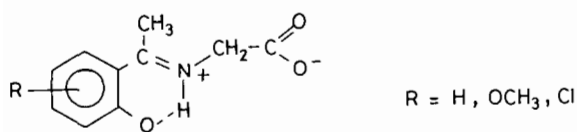
In the spectra of Schiff bases a medium intensity band around 3400 cm^{-1} is ascribed to ν(N–H). A band at 1675 cm^{-1} is assigned to an asymmetric carboxyl stretch. The band at 1610 cm^{-1} results from the overlap of the imine C=N stretch and C=C ring stretching vibrations. A band around 1500 cm^{-1} is attributed to symmetric C=C or C=N stretching modes. A band corresponding to ν_{sym}(COO$^-$) appears at 1380 cm^{-1}.

In complexes (I–V), the band due to ν(N–H) is shifted to 3340 cm^{-1} suggesting coordination of the nickel to the imino nitrogen. The asymmetric carboxyl stretch is shifted to a lower frequency exhibiting a broad band in the range 1640–1620 cm^{-1}. This band now overlaps with the imine C=N stretch and C=C ring stretching vibrations. The ν_{sym} (COO$^-$) shifts from a well-defined sharp band at 1380 cm^{-1} to a broad split peak at approximately 1410 cm^{-1} indicating possible Ni–O bond formation. The separation between the asymmetric and symmetric frequencies is 200 cm^{-1} suggesting that the Ni–O band is covalent in nature [19].

The band at 1280 cm^{-1} assigned to a phenolic (C–O) stretch does not change on complexation indicating that the *o*-hydroxy group of the aceto-phenone moiety is not involved in the bonding. The carboxyl wagging vibration appearing at 690 cm^{-1} in the ligands is shifted to 750 cm^{-1} in the complexes. A strong band at 535 cm^{-1} in complexes I–V is assigned to ν(Ni–N) [20]. A band in the region 460–440 cm^{-1} is attributed to ν(Ni–O). A frequency at 350 cm^{-1} is assigned to the chelate ring deformation associated with the metal-ligand binding.

Finally, all the IR data suggest that nickel is bonded to the salicylideneglycine ligands through the imino-nitrogen and the carboxylate of the glycine moiety.

NMR Spectra

The NMR data are presented in Table III. The NMR spectra for the ligands and their nickel complexes show four types of signal attributable to methyl, methylene, phenyl and imino nitrogen protons.

The signal at 2.2 ppm is assigned to the methyl protons in the ligands and is split on complex formation (complexes I–III). This leads to the assignment of a *trans* geometry for the complexes. The methylene protons are observed at 3.2 ppm. Phenyl protons observed in the range 7–8 ppm for the ligands are shifted upfield to the range 6.5–7.5 ppm in the complexes. A singlet observed around 8.9 ppm and assigned to the imino nitrogen in the ligands has shifted to around 8.2 ppm in the complexes. This shift can be attributed to the nickel coordinating to the imino nitrogen.

Conclusions

The analytical and molecular weight data suggest that the complexes have a 1:2 stoichiometry. The conductivity data indicate the species are non electrolytes. Magnetic moments indicate that the complexes are diamagnetic. IR results suggest that the ligands exist in the ketoenamine form, coordinating through the amide nitrogen and the carboxylic oxygen. These results together with NMR and electronic data suggest that the complexes are four coordinate and have *trans* square planar geometry. The following structure is proposed for these complexes:
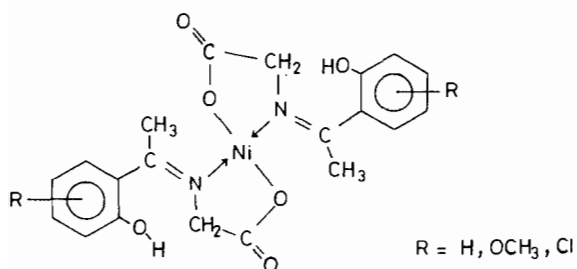
R = H, OCH$_3$, Cl

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