J. Chem. Eng. Data **2008,** *53,* 2567–2572

Schiff Base Complexes Derived from 2-Acetylpyridine, Leucine, and Some Metal Chlorides: Their Preparation, Characterization, and Physical Properties

Nasser M. Hosny* and Farid I. El-Dossoki*

Chemistry Department, Faculty of Science, Suez-Canal University, Port-Said, Egypt

Metal complexes of Cu(II), Co(II), Ni(II), Cr(III), and Fe(III) chlorides with the Schiff base ligand (L) derived from the condensation reaction between leucine and 2-acetylpyridine were prepared. The isolated complexes were characterized by elemental analyses, spectral analyses (IR, UV), thermal analyses (TGA), magnetic measurements, and molar conductivities. The IR spectra show that the ligand can act as a neutral tridentate coordinating to Cu(II), Co(II), or Ni(II) through the pyridyl nitrogen, azomethine nitrogen, and carbonyl oxygen. Another mode of chelation has been suggested that the ligand can act as a mononegative tridentate coordinating to Fe(III) or Cr(III) through the pyridyl nitrogen, azomethine nitrogen, and carboxyl oxygen after displacement of hydrogen from the hydroxyl group. The results suggest tetrahedral geometry around Co(II) and Ni(II), octahedral geometry around Fe(III) and Cr(III), and square-planar geometry around Cu(II). Semi-empirical ZINDO/1 calculations have been used to study the harmonic vibrational spectra of Cu(II) and Fe(III) with the purpose to assist the experimental assignment of the complexes. The molar (Λ) and limiting molar ($\Lambda_\circ$) conductances of the prepared complexes were measured experimentally at 298 K. From the values of Λ and $\Lambda_\circ$, the ion-pair association constants (K_A) and the free energy change of association (ΔG_A) were calculated and discussed. Also, the densities (d) and the refractive indices (n) of the prepared complexes were determined in water and 50 % (V/V) dimethylformamide−water solvents at 298 K. Using the values of n and d, the excess refractive indices (n(E) and $\acute{n}$(E)), atomic polarizations (P_A), polarizabilities (α), and molar refractions (R_m) were calculated and discussed.

Introduction

Schiff base complexes of amino acids have gained importance not only from the inorganic point of view but also because of their physiological and pharmacological activities.[1,2] Metal complexes of Schiff base phenolates with favorable cell membrane permeability have been exploited in cancer multidrug resistance[3] and tested as antimalarial agents.[4] Cu(II) salicylidine amino acid Schiff base complexes exhibit antitumor activity.[5]

Many articles have reported antibacterial, antifungal, and anticancer activities for Schiff base complexes.[6−8] The condensation between the NH_2 group of the amino acid and the carbonyl group of the aldehyde or ketone is very difficult because of the Zwitterion effect, and the reaction needs special conditions.

Casella[9] showed that these reactions are facilitated by aldehydes and amino acids of a kind that can form two five-membered rings, chelated to the metal ion because in such a case the Schiff base is more planar.

The role of metal ion is not well-known. Christensen[10] suggested that atoms of the amino acid will not be held in the plane of the aromatic ring unless the chelating joins them to this ring in a planar structure. In our previous work,[11] we showed that pH plays an important role in the process of condensation between glycine and 3-acetylpyridine. The binuclear Schiff base of glycine and 3-acetylpyridine were separated in the case of metal acetates where the pH (5) is suitable for condensation, while in the case of metal chlorides, the lower pH (2 to 4) blocks NH_2 as NH_3^+, glycine, and 3-acetylpyridine coordinate separately to the metal ion to form mixed ligand complexes. The same behavior was observed with the metal complexes of alanine and 2-acetylpyridine.[12] In this work, we were able to separate the Schiff base complexes from the reaction of some metal chlorides with leucine and 2-acetylpyridine (although at the lower pH values 2 to 4). This behavior is explained on the basis of electron-donating ability of the side chain of the amino acid which plays a role in achieving the condensation process between the amino group of leucine and the carbonyl group of 2-acetylpyridine by increasing the electron density on the amino nitrogen, hence increasing the ability of the nucleophilic attack from the amino nitrogen on the carbon atom of the carbonyl group.

The electric conductivity measurements of dilute solutions of electrolytic complexes are considered to be one of the important methods for studying the ion-pair association not only in aqueous solutions but also in nonaqueous or mixed ones.[13,14] Also, it was used to study the nature of the solute−solvent interaction.[15] Refractive index and density measurements were used to shed some light on both the solute−solvent and solvent−solvent interactions.[16,17]

In continuation of our work in searching for the conditions of formation of Schiff bases derived from amino acids, five metal complexes derived from leucine and 2-acetylpyridine have been synthesized and characterized using different physicochemical techniques. Also, we aim to study some physical properties of the prepared complexes such as the density, refractive index, polarization, polarizability, molar refraction, molar and limiting molar conductance, ion-pair association constants, and free energy of association.

---

* Corresponding author. E-mail: feldossoki@yahoo.com; nasserh56@yahoo.com.

10.1021/je800415n CCC: $40.75

Table 1. Analytical Data and Physical Properties of the Complexes

				% calcd (% found)				
compound	color	yield (%)	M.P. (°C)	C	H	M	Cl	$\Lambda(\Omega^{-1}\cdot cm^2\cdot mol^{-1})$DMF
$[CuHLH_2O]Cl_2$	dark brown	45	125 ± 2	40.4(40.9)	5.1(5.3)	16.6(16.0)	18.3(17.8)	80.0
$[CoHLH_2O]Cl_2\cdot 3/2H_2O$	dark green	58	117 ± 2	38.1(38.2)	5.3(5.0)	14.4(15.0)	17.5(18.0)	100
$[NiHL\cdot H_2O]Cl_2\cdot H_2O$	dark green	52	120 ± 2	39.0(38.5)	5.5(5.0)	14.6(14.5)	17.4(17.0)	96.0
$[FeL\cdot 3H_2O]Cl_2$	brown	49	170 ± 2	37.7(38.0)	5.5(6.0)	13.5(13.8)	17.6(18.0)	90.0
$[CrL\cdot 3H_2O]Cl_2$	green	56	185 ± 2	38.0(37.7)	5.6(5.0)	12.7(13.0)	17.5(18.0)	97.0

Experimental

Reagents and Measurements. All the chemicals used in preparation of the metal complexes were of analytical grade and were used without further purification. Dimethylformamide (DMF) was from the Aldrich Chemical Co. Carbon and hydrogen contents (± 0.5) were determined at the microanalytical unit of Cairo University. Molar conductance measurements of the complexes (10^{-3} M) in DMSO were carried out with a conductivity bridge YSI model 32. Infrared spectra were measured using KBr discs on a Mattson 5000 FTIR spectrometer. Calibration with the frequency reading was made with polystyrene film. Electronic spectra were recorded on a UV2 Unicam UV/vis spectrophotometer using 1 cm stoppered silica cells. Thermal analysis measurements (TGA, DTG) were recorded on a Schimadzu model 50 instrument using 20 mg samples. The nitrogen flow rate and heating were 20 $cm^3\cdot min^{-1}$ and 10 $°C\cdot min^{-1}$, respectively. Magnetic measurements were carried out on a Sherwood scientific magnetic balance. The calculations were evaluated by applying the following equations (1, 2, and 3): $\chi_g = Cl(R - R°)/10^3 m$ (1), $\chi_m = \chi_g \cdot Mwt \cdot 10^{-3}$ (2), $\mu_{eff} = 2.84\sqrt{-3} - \chi_m T$(3) (where χ_g = the mass susceptibility per g of sample; C = the calibration constant of the instrument; l = the sample length in cm; R = the balance reading for the sample tube; $R°$ = the balance reading for the empty tube; m = the weight of the sample in g; T = the absolute temperature). Different concentrations (10^{-4} to 10^{-2}) of the prepared complexes in water and 50 % (V/V) (DMF−H_2O) solvents were prepared, and their specific conductances were measured (± 0.1 $\mu S\cdot cm^{-1}$) using a conductivity bridge (Jenway, type 4310) at (298 ± 0.1) K. Saturated solutions of the studied complexes were prepared in water and 50 % (V/V) (DMF−H_2O) solvents, and then their densities (± 0.0001) and refractive indices (± 0.0001) were measured using a weighing bottle (1 mL) and Abbe′ refractometer, respectively. Both the conductivity bridge and Abbe′ refractometer were connected with an Ultrathermostate (Kotterman, type 4130) to maintain the temperature at (298 ± 0.1) K.

Preparation of Metal Complexes Using Template Reaction. The metal complexes were prepared by adding stoichiometric quantities (1.31 g, 0.01 mol) of leucine in 10 cm^3 H_2O to (1.21 g, 0.01 mol) 2-acetylpyridine in 10 cm^3 EtOH. The metal ions (0.01 mol) were dissolved in 5 cm^3 H_2O and then added to the reaction mixture of the ligand dropwise with constant stirring and finally heated under reflux for 3 h on a hot plate at 50 °C. A fine precipitate of the solid complex formed. The copper complex was separated after concentrating the reaction mixture and the addition of a few drops of Et_2O.

The isolated metal complexes were filtered off, washed with Et_2O, H_2O, and EtOH, recrystallized from dichloromethane, and preserved in a vacuum desiccator over anhydrous calcium chloride.

Computational Details. Molecular geometries of the complexes were optimized using molecular mechanics and the semiempirical ZINDO/1 method using the hyperchem series of programs.[18] The molecular mechanics technique was used to investigate rapidly the geometries of the suggested structures. The low-lying conformers obtained from this search were then optimized at ZINDO/1 (Polak-Ribiere) rms 0.01 kcal where these methods are commonly used for the calculations of energy states of transition metal complexes.

Results and Discussion

In this study, two main types of metal complexes have been prepared from the reaction of leucine and 2-acetylpyridine with some hydrated metal chlorides. In the first type, the Schiff base ligand resulting from the condensation of leucine and 2-acetylpyridine (L) can act as a neutral tridentate coordinating to Cu(II), Co(II), or Ni(II) through the pyridyl nitrogen, azomethine nitrogen, and carbonyl oxygen. In the second type, the ligand acts as a mononegative tridentate coordinating to Fe(III) or Cr(III) through the pyridyl nitrogen, azomethine nitrogen, and carboxyl oxygen after displacement of hydrogen from the hydroxyl group. Water−ethanol was used as solvent during the preparation of all metal complexes.

The formation of the chelates may be represented by the following equations

$$L + MCl_2\ (\text{hydrated}) \xrightarrow{\text{EtOH−water, 3 h reflux}} [MHL\ H_2O]Cl_2\cdot nH_2O \quad (1)$$

(where M = Cu(II), Co(II), or Ni(II) and n = 0 to $3/2H_2O$)

$$L + MCl_3\ (\text{hydrated}) \xrightarrow{\text{EtOH−water, 3 h reflux}} [ML\ 3H_2O]Cl_2 + HCl \quad (2)$$

(where M = Fe(III) or Cr(III)).

The analytical data together with some physical properties of the metal complexes are collected in Table 1. All the complexes are colored soluble in water and most organic solvents. The molar conductance values in DMF (80.0 to 100) $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ suggest the electrolytic nature of these complexes.[19] This indicates that the complexes act as 2:1 electrolytes. Consequently, two Cl^- ions are present outside the coordination sphere.

The presence of leucine and 2-acetylpyridine in the metal complexes has been confirmed by the spot test technique[20] and TLC after hydrolysis of the metal complexes. Water of hydration has been determined from thermal analysis measurements.

Infrared Spectra. The most important IR assignments of the metal complexes (Table 2) have been determined by careful comparison of the spectra of leucine and 2-acetylpyridine. IR spectra of all complexes show the disappearance of the bands assigned to the (NH_2) group of leucine and the (C=O) group of 2-acetylpyridine and the appearance of a new band in the range (1642 to 1653) cm^{-1} assigned to the azomethine group C=N*. This behavior indicates that condensation between the amino group of leucine and the carbonyl group of 2-acetylpy-

Table 2. Observed and Calculated Wave numbers (cm^{-1}) of $[CuHLH_2O]Cl_2$, $[CoHLH_2O]Cl_2\cdot3/2H_2O$, $[NiHL\cdot H_2O]Cl_2\cdot H_2O$, $[FeL\cdot3H_2O]Cl_2$, and $[CrL\cdot3H_2O]Cl_2$ by ZINDO/1 [a]

Cu exptl	Cu calcd	Co exptl	Co calcd	Ni exptl	Ni calcd	Cr exptl	Cr calcd	Fe exptl	Fe calcd	assignment
1642	1663	1643	1666	1652	1687	1654	1647	1650	1628	νC=N*
1598	1591	1603	1627	1610	1627	1575	1520	1600	1578	νC=C+νC=N
1623	1631	1624	1648	1634	1644	1621	1600	1625	1613	νCOO
763	741	778	773	780	773	780	747	769	747	δCOO
587	578	594	611	580	590	604	597	577	578	ρCOO
420	445	423	423	405	410	430	455	415	444	ring skeletal
695	692	700	683	715	699	690	692	769	731	νM−O
465	486	480	512	470	468	462	494	480	494	γCOO
365	474	345	317	350	346	360	357	365	324	νM−Npy

[a] ν, stretching; δ, in-plane deformation; γ, out-of-plane deformation; w, wagging; ρ, rocking.

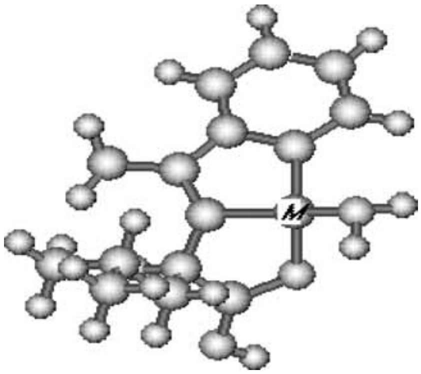

Figure 1. Suggested structure of Cu(II), Co(II), or Ni(II) complexes.

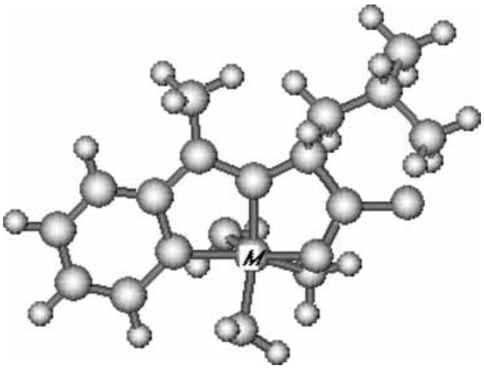

Figure 2. Suggested structure of Fe(III) and Cr(III) complexes.

Scheme 1. General Scheme of Thermal Decomposition of $[CoHLH_2O]Cl_2\cdot3/2H_2O$

$$[Co\ HL\ H_2O]Cl_2.3/2H_2O \xrightarrow{36-127^\circ C} [Co\ HL\ H_2O]Cl_2$$

$$[Co\ HL\ H_2O]Cl_2 \xrightarrow{163-261^\circ C} [Co\ HL\ ]Cl_2$$

$$[Co\ HL\ ]Cl_2 \xrightarrow{261-481^\circ C} [Co\ HL\ ] + Cl_2 + Me$$

$$[Co\ HL^{\backslash}\ ] \xrightarrow{556-750^\circ C} CoPy + (CH_3)_2CHCH_2 + CNCHCOOH$$

(Where L = Schiff base ligand; $L^{\backslash}$ = the remaining of L)

ridine occurred, and the Schiff base has been formed. The Schiff base ligand (L) can act as a neutral tridentate coordinating to Cu(II), Co(II), or Ni(II) through the pyridyl nitrogen, azomethine nitrogen, and carbonyl oxygen (Figure 1). This behavior is suggested on the basis of the following evidence:

(i) The shift of the bands in the regions (1623 to 1634, 763 to 780, 580 to 594, and 405 to 423) cm^{-1} assigned to $\nu(COO^-)$, $\delta(COO^-)$, $\gamma(COO^-)$, and $\rho(COO^-)$, respectively.[21] The presence of these bands is taken as evidence of the participation of the carbonyl group in bonding. (ii) The presence of bands in the regions (3450 and 1642 to 1654) cm^{-1} assigned to ν(OH) and ν(C=N*), respectively. (iii) The shifts of the bands in the regions (1575 to 1603 and 695 to 715) cm^{-1} assigned to ν(C=C) + ν(C=N) and ring skeletal mode, respectively, indicating the participation of the pyridyl ring in chelation.[22] (iv) The presence of new bands in the regions (462 to 480, 500 to 530, and 345 to 365) cm^{-1} assigned to ν(M−O), ν(M−N), and $\nu(M-N)_{(Py)}$, respectively.[22]

The Schiff base ligand (L) coordinates to Fe(III) or Cr(III) as a mononegative tridentate coordinating to the metal ion through the pyridyl nitrogen, azomethine nitrogen, and carboxyl oxygen after displacement of hydrogen from the hydroxyl group (Figure 2). This behavior is suggested on the basis of the following evidence:

(i) The positive shifts of the bands in the regions (1575 to 1610, 690 to 700, 375 to 400, and 345 to 365) cm^{-1} as signed to ν(C=C) + ν(C=N), $Q_{i.p}$, $Q_{o.p.}$, and $\nu(M-N)_{(py)}$, respectively, in addition to the bands observed in the regions (1650 to 1654, 1613 to 1625, 769 to 780, 415 to 430, and 577 to 604) cm^{-1} assigned to ν(C=N*), $\nu(COO^-)$, $\delta(COO^-)$, $\gamma(COO^-)$, amd $\rho(COO^-)$, respectively.[21] Also, the appearance of new bands in the regions (395 to 448 and 465 to 530) cm^{-1} assigned to ν(M−N) and ν(M−O), respectively.[23]

The cause of the difference between the calculated and observed frequencies may result from the hydrogen bonded water molecules which have not been taken into consideration in the optimized molecules. Also, the experimental data were obtained from the solid state, whereas the calculated harmonic frequencies are for the gas phase.

Thermal Analyses. The thermal analyses curves (TG and DTG) of the $[CoHLH_2O]Cl_2\cdot3/2H_2O$ complex were carried out within a temperature range from room temperature up to 800 °C. The estimated mass losses were computed based on the TG results, and the calculated mass losses were computed using the results of microanalyses.

The Co(II) complex gives four stages of decomposition pattern. The first stage within the temperature range (36 to 127) °C represents the loss of one and a half water molecules of hydration (estimated mass loss 6.9 %, theoretical 6.6 %). The second stage at (163 to 261) °C represents the loss of one coordinated water molecule with an estimated mass loss of 5.5 % (theoretical 4.4 %). The third stage of decomposition within the temperature range (261 to 481) °C represents the loss of a Cl_2 molecule and a methyl group (estimated mass loss 22.1 %, theoretical 21.0 %). The next step of decomposition within the temperature range (556 to 650) °C (with an estimated mass loss 15.0 %, theoretical 13.9 %) is accounted for by the loss of $(CH_3)_2CHCH_2$. The last step represents the loss of CNCHCOOH leaving (CoPy) as a residue in the temperature range (650 to 750) °C. The estimated mass loss of this step was 21.7 % which

Table 3. Molar Conductances (for 0.001 M Solution) (Λ, $S\cdot mol^{-1}\cdot cm^2 \pm 0.05$), Limiting Molar Conductances (Λ∘, $S\cdot mol^{-1}\cdot cm^2 \pm 0.03$), and Logarithm of the Association Constants of the Studied Complexes in 50 % (v/v) DMF−H_2O at (298 ± 0.1) K

	in H_2O				in 50 % (v/v) DMF−H_2O			
complex	Λ	Λ∘	log K_A	ΔG_A/kJ·mol^{-1}	Λ	Λ∘	log K_A	ΔG_A/kJ·mol^{-1}
$[CrL3H_2O]Cl_2$	314.71	337.02	1.4714	8.38	95.01	96.81	1.7527	9.99
$[FeL\cdot 3H_2O]Cl_2$	470.61	473.49	1.8061	10.29	133.50	146.12	2.6985	15.38
$[CoHLH_2O]Cl_2\cdot 3/2H_2O$	300.01	303.32	2.5301	14.42	116.70	124.92	2.6715	15.23
$[NiHL\cdot H_2O]Cl_2\cdot H_2O$	216.61	221.38	2.0328	11.59	96.01	97.49	2.1261	12.12
$[CuHL\cdot H_2O]Cl_2$	220.31	225.34	2.0066	11.44	81.21	81.61	2.0776	11.84

Table 4. Densities (d, $g\cdot cm^{-3} \pm 0.0001$), Refractive Indices ($n_1$, n_2, and $n \pm 0.0001$), Excess Refractive Indices (n(E) and ń(E)), Atomic Polarization (P_A), Molar Refractions (R_m, $cm^3\cdot mol^{-1}$), and Polarizabilities (α, $cm^3\cdot mol^{-1}$) of the Studied Complexes in Water and 50 % (v/v) (DMF−H_2O) Solvents at (298 ± 0.1) K

solvent	complex	d	n_1	n_2	n	n(E)	ń(E)	P_A	R_m	α
H_2O										
	$[Cu\ HL\ H_2O]Cl_2$	1.0020	1.4005	1.3350	1.3350	-	0.0020	1.8713	73.48	17.554
	$[CoHLH_2O]Cl_2\cdot 3/2H_2O$	1.0008	1.4007	1.3371	1.3371	-	0.0041	1.8769	78.54	18.764
	$[Ni\ HL\ H_2O]Cl_2\cdot H_2O$	1.0006	1.4008	1.3351	1.3351	-	0.0021	1.8713	74.82	17.873
	$[FeL\ 3H_2O]Cl_2$	1.0010	1.4006	1.3390	1.3390	-	0.0060	1.8826	86.88	20.752
	$[Cr\ L\ 3H_2O]Cl_2$	1.0004	1.4005	1.3340	1.3340	-	0.0010	1.8685	86.89	20.758
DMF−H_2O										
	$[Cu\ HL\ H_2O]Cl_2$	0.9886	-	-	1.3970	0.049	0.0045	2.0492	86.72	20.716
	$[CoHLH_2O]Cl_2\cdot 3/2H_2O$	0.9888	-	-	1.3989	0.049	0.0064	2.0548	92.45	22.683
	$[Ni\ HL\ H_2O]Cl_2\cdot H_2O$	0.9887	-	-	1.3982	0.050	0.0057	2.0527	88.41	21.111
	$[FeL\ 3H_2O]Cl_2$	0.9891	-	-	1.3975	0.046	0.0050	2.0507	101.39	24.220
	$[Cr\ L\cdot 3H_2O]Cl_2$	0.9893	-	-	1.3955	0.048	0.0030	2.0448	102.25	24.425

is close to the theoretically calculated 20.5 %. The stages of decomposition of the complex can be written as shown in Scheme 1.

The thermal analyses results given for Co(II) are representative of those of the other metal complexes under investigation.

Electronic Spectra and Magnetic Moments. The electronic spectrum of $[CoHLH_2O]Cl_2\cdot 3/2H_2O$ in DMF exhibits one intense band at 14 925 cm^{-1} (ε = 150 L·mol^{-1}·cm^{-1}) attributable to the $^4A_2(F) \rightarrow {}^4T_1(P)$ (ν_3) transition, in a tetrahedral ligand field and a shoulder at 16 420 cm^{-1} due to spin-coupling.[24] The band at 21 739 cm^{-1} ($\varepsilon = 0.3\cdot 10^3$ L·mol^{-1}·cm^{-1}) may be assigned to LMCT. Also, the value of the magnetic moment (4.6 B. M.) is additional evidence for the conclusion that the structure around the Co(II) ion is tetrahedral.[25]

The magnetic moment value (3.6 B. M.) for the $[CrL\cdot 3H_2O]Cl_2$ complex is in agreement with the values reported for octahedral geometry around the chromium(III) ion.[25] The electronic spectrum in DMF shows bands at 17 391 cm^{-1} (ε = 80 L·mol^{-1}·cm^{-1}) and 21 739 cm^{-1} (ε = 120 L·mol^{-1}·cm^{-1}) assigned to the $^4A_{2g} \rightarrow {}^4T_{2g}(\nu_1)$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) (ν_3) transitions, respectively, in an octahedral geometry around the Cr(III) ion.[26] The spectrum shows also two shoulder bands at (14 925 and 16129) cm^{-1} assigned to $^4A_{2g} \rightarrow {}^2E_g$ and $^4A_{2g} \rightarrow {}^2T_{2g}$, respectively.[26] The LMCT band is observed at 26 315 cm^{-1} ($\varepsilon = 0.22\cdot 10^3$ L·mol^{-1}·cm^{-1}).

The UV spectrum of $[FeL\cdot 3H_2O]Cl_2$ in DMF shows several bands between (20 000 and 15 000) cm^{-1} that are assigned to d-d transitions. The positions of these bands indicate an octahedral geometry around Fe(III).[26] The value of the magnetic moment (5.6 B. M.) is very close to the spin only value expected for high spin Fe(III).

The electronic spectrum of $[Ni\ HL\ H_2O]Cl_2\cdot H_2O$ in DMF is consistent with tetrahedral geometry showing one d-d transition at 15 267 cm^{-1} (ε = 20 L·mol^{-1}·cm^{-1}) assignable to $^3T_1(F) \rightarrow {}^3T_1(P)$ (ν_3) and a band at 17 391 cm^{-1} (ε = 40 L·mol^{-1}·cm^{-1}) assignable to $^3T_1 \rightarrow {}^1T_1$. The magnetic moment value (3.5 B. M.) lies in the range suggested for tetrahedral Ni(II) complexes.[27]

The magnetic moment (1.9 B. M.) of $[Cu\ HL\ H_2O]Cl_2$ is in the range expected for monomeric copper(II) complexes.[28] The electronic spectrum of the copper(II) complex shows a broad-band at 19 607 cm^{-1} (ε = 300 L·mol^{-1}·cm^{-1}). The band appears to have its origin in d-d transitions, which can be assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions in a square-planar geometry.[29]

The band recorded at ca. 25 000 cm^{-1} ($\varepsilon = 0.7\cdot 10^3$ L·mol^{-1}·cm^{-1}) is a charge-transfer, probably LMCT. The high magnetic moment value of the square-planar complex compared with the observed values for the distorted octahedron may be taken as additional evidence for the presence of a square-planar geometry.

Electric Conductance Measurements. The specific conductance was measured as explained in the experimental section. The molar conductance and limiting molar conductance of a 0.001 M solution was calculated and is presented in Table 3.

The experimental data of the conductance measurements of the studied complexes at 298 K in water and 50 % (V/V) (DMF−H_2O) solvents were treated using the Fuoss and Edelson method,[30] where the association of $[ML]^{+2}$ and A^- can be mono- or bidentate. The first association takes place, while the second association is very small and negligible in comparison with the first one.[30] Then, for the monodentate association, the following equilibrium is present

$$A^- + [ML]^{+2} = ([ML]A)^+$$

According to Fuoss−Edelson, both the limiting molar conductance (Λ∘) and ion-pair association constants (K_A) were calculated using a computer program of Fuoss−Edelson equations.

The free energy changes of association were calculated using eq 3

$$\Delta G_A = -2.303RT \log K_A \qquad (3)$$

The values of the determined molar conductances (Λ) of (0.001 M solution), limiting molar conductances (Λ∘), logarithm of the ion-pair association constants (log K_A), and the free energy change of association (ΔG_A) are presented in Table 3.

From Table 3, it was noticed that the molar and limiting molar conductance and log K_A (association parameter) of the complexes under study in water are higher than that in the DMF−H_2O mixture. This is due to the lower dielectric constant of the DMF−H_2O mixture and so the lower solvation of the complexes in DMF−H_2O. In comparing the molar and limiting molar conductances of the chloride salt complexes under investigation, there is no fixed trend with the ionic radii of the used cations (Cr(III), Fe(III), Co(II), Ni(II), and Cu(II)). This may be due to the different solute−solvent interactions. In comparing limiting molar conductances of the chloride salt complexes under investigation in water at 298 K with that in the literature (limiting ionic conductance of $Cl^- = 78.1\ S\cdot mol^{-1}\cdot cm^2$),[31] we note that the values of the limiting molar conductances of the chloride salt complexes under investigation include that of the two chloride ions present in these complexes in addition to that of the cation in the same conditions. The limiting molar conductances of the chloride salt complexes under investigation in 50 % (v/v) DMF−H_2O at 298 K do not include that in the literature (in water) which can be related to the lower dielectric constant of the DMF−H_2O mixture and so the lower solvation of the complexes in DMF−H_2O.

The negative values of the free energy changes indicate the exothermic nature of the association processes; i.e., the association processes are less energy consuming and more stabilized.

Refractive Index and Density Measurements. The refractive indices and densities of the complexes under investigation were measured as reported in the Experimental section. The values of the excess refractive indices $\{n(E)\}$, were calculated[32] by applying eq 4

$$n(E) = n - (X_1n_1 + X_1n_2) \qquad (4)$$

where n_1, n_2, and n are the refractive indices of the complexes in DMF, H_2O, and 50 % (v/v) DMF−H_2O solvents, respectively. X_1 and X_2 are the mole fractions by weight of DMF and H_2O (0.1893 and 0.8107), respectively, which were calculated using eq 5

$$X_1 = (v_1d_1 / M_1)/[(v_1d_1 / M_1) + (v_2d_2 / M_2)] \qquad (5)$$

where d_1, d_2, M_1, M_2, v_1, and v_2 are the densities, molecular weights, and volume percentages of DMF and H_2O, respectively. The value of X_2 is then equal to $(1 - X_1)$.

The difference between the refractive indices of the complex solution (n) and the refractive indices of the pure solvents (DMF−H_2O =1.3925 and H_2O = 1.3330) were also calculated and represented by $\acute{n}(E)$.

The molar refraction R_m which is a measure of volume occupied by a molecule was also calculated[33] using eq 6

$$R_m = (n^2 - 1)/(n^2 + 2)](M/d) = P_A + P_E = P_T = P_D \qquad (6)$$

where M and d are the molecular weight of the complexes and the density of the complexes saturated solution, respectively. The molar refraction was found to be dependent on the temperature and the refractive index. The right-hand side of eq 6 is equal to the summation of both the atomic polarization (P_A) and electronic polarization (P_E), which is the total molar (P_T) or distortion (P_D) polarization. The atomic polarization (P_A) was calculated[34] from the equation

$$P_A = 1.05n^2 \qquad (7)$$

The mean value of the molecular dipole polarizability (α: dipole moment induced by the electric field) can be calculated from the optical refractive index (n) of a material containing N molecules per unit volume. The refractive index is related to the polarizability of the molecules by the Lorentz−Lorenz formula[35] as follows

$$[(n^2 - 1)/(n^2 + 2)] = (4/3)\pi\acute{n}\alpha \qquad (8)$$

where $\acute{n} = N/V$; N is Avogadro's constant; and V is the molar volume. From eq 8, the polarizabilities of the complexes under investigation were calculated. The values of the densities, refractive indices, excess refractive indices, atomic polarizations, polarizabilities, and molar refractions are recorded in Table 4. From Table 4, it was noticed that the densities of the saturated solutions of the complexes in water are higher than that in DMF−H_2O and indicate a higher solvation process and a higher solute−solvent interaction in water than in the DMF−H_2O. This is due to the lower dielectric properties of the DMF−H_2O mixture and the electrolytic nature of these complexes. The refractive indices, atomic polarizations, molar refractions, and polarizabilities of the complexes in water are lower than that in the DMF−H_2O mixture. This may be due to the higher refractive index of the DMF−H_2O solvent (1.3925) than that of water (1.3330) indicating that the solvent−solvent interactions are higher than the solute−solvent interactions.

The smaller difference in the densities and refractive index values between all complexes under study in the same solvent, i.e., in water or in DMF−H_2O solvent, indicate nearly the same solvation process and electrolytic nature of these complexes in the same solvent.

The positive values of the excess refractive indices $n(E)$ indicate also that the solvent−solvent interactions are higher than the solute−solvent ones.

The values of $\acute{n}(E)$ (the refractive indices of the complex molecule itself) in DMF−H_2O are higher than those in water. This is also due to the lower solvation, i.e., lower solute−solvent interactions, and the lower dielectric properties of the DMF−H_2O solvent, i.e., the higher association of these complexes in DMF−H_2O than in water.

Literature Cited

(1) Tai, A. E.; Lien, E. J.; Lai, M. M. C.; Khawaja, T. A. K. Novel N-hydroxyguanidine Derivatives as Anticancer and Antiviral Agents. *J. Med. Chem.* **1984**, *27*, 238.

(2) Wang, P. H.; Keck, G. J.; Lien, E. J.; Lai, M. M. C. Design, Synthesis, Testing, and Quantitative Structure-Activity Relationship Analysis of Substituted Salicylaldehyde Schiff Bases of 1-Amino-3-Hydroxyguanidine Tosylate as New Antiviral Agents against Coronavirus. *J. Med. Chem.* **1990**, *33*, 608.

(3) Sharma, V.; Worms, D. P. Metal Complexes for Therapy and Diagnosis of Drug Resistance. *Chem. Rev.* **1999**, *99*, 2545.

(4) Goldberg, D. E.; Sharma, V.; Oksman, A.; Gluzman, I. Y. Probing the Chloroquine Resistance Locus of Plasmodium Falciparum with a Novel Class of Multidentate Metal(III) Coordination Complexes. *J. Biol. Chem.* **1997**, *272*, 6567.

(5) Zhoo Wang, M.; Xing Meng, Z.; Liliu, B. Novel Tumor Chemotherapeutic Agents and Tumor Radio-Imaging Agents: Potential Tumor Pharmaceuticals of Ternary Copper(II) Complexes. *Inorg. Chem. Commun.* **2005**, *418*, 368.

(6) Chohan, Zahid, H.; Praveen, M.; Ghaffar, A. Synthesis, Characterization and Biological Role of Anaions (Nitrate, Sulfate, Oxalate and Acetate) in Co(II), Cu(II) and Ni(II). *Synth. React. Inorg. Met.-Org. Chem.* **1998**, *28*, 1673–1687.

(7) Yadav, R.; Gielen, M; Dalil, H. Synthesis, Characteristic Spectral Studies and Invitro Antimicrobial and AntiTumor Activities of Organotin (IV) Complexes of Schiff Bases Derived from Amino- Acid. *Appl. Organomet. Chem.* **1997**, *11*, 727–736.

(8) Pou-Hsiung, W.; James, G. K.; Eric, J. L.; Michael, M. C. L. Design, Synthesis, Testing and Quantitative Structure Activity Relationship Analysis of Substituted Salicyaldehyde Schiff Bases of 1-Amino-3-hydroxyguanidine Tosylate as New Antiviral Agents Against Coronavirus. *J. Med. Chem.* **1990**, *33*, 608–641.

(9) Pasini, A.; Casella, L. Some Aspects of The Reactivity of Amino Acids Coordinated to Metal Ions. *J. Inorg. Nucl. Chem.* **1974**, *36*, 2133.

(10) Christensen, H. N. Metal Chelates of Pyridoxylidine Amino Acids. *J. Org. Biol. Chem.* **1957**, *79*, 4073.

(11) Nawar, N. A.; Shallaby, A. M.; Hosny, N. M.; Mostafa, M. M. Mono- and Binuclear Schiff Base Complexes Derived from Glycine, 3-Acetylpyridine and Transition Metal Ion. *Transition Met. Chem.* **2001**, *26*, 180.

(12) Hosny, N. M. Synthesis, Characterization, Theoretical Calculations and Catalase-like Activity of Mixed Ligand complexes Derived from Alanine and 2-Acetylpyridine. *Transition Met. Chem.* **2007**, *32*, 117–124.

(13) Bhat, J. I.; Shivakumar, H. R. Conductometric Studies on Solvation Behaviour of Tartaric Acid in Various Solvent Mixtures. *J. Mol. Liq.* **2004**, *111* (1), 101–108.

(14) Bakr, M. F.; Mohamed, A. A. Ion-Solvent Interaction of Biunivalent Electrolytes in Dioxane-Water Mixtures from Conductivity Data at Different Temperatures. *J. Chin. Chem. Soc.* **1999**, *46* (6), 899–904.

(15) Tsurko, E. N.; Neueder, R.; Barthel, J.; Apelblat, A. Conductivity of Phosphoric Acid, Sodium, Potassium and Ammonium Phosphates in Dilute Aqueous Solutions from 278.15 to 308.15 K. *J. Solution Chem.* **1999**, *28*, 973–999.

(16) El-Dossoki, F. I. Thermodynamic and Solvation Parameters of Some Ions, Crown Ether Compounds and Their Complexes in Some Solvents. Ph. D. Thesis, Mansura Univ., Fac. of Sci., Egypt, 1998.

(17) Bevilaqua, T.; Da Silva, D. C.; Machado, V. G. Preferential Solvation of Brooker's Merocyanine in Binary Solvent Mixtures Composed of Formamides and Hydroxylic Solvents. *Spectrochim. Acta, Part A* **2004**, *60* (4), 951–958.

(18) *Hyperchem 7*; developed by Hypercube Inc., 2002.

(19) Huheey, J. E. *Inorganic Chemistry, Principles of Structure and Reactivity*; Harper and Row: United Kingdom, 1975.

(20) Feigl, R. *Spot Test in Organic Analyses*; Elsevier: Amsterdam, 1966.

(21) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; John Wiley: New York, 1970.

(22) Sahni, S. K.; Sangal, S. K.; Gupta, S. P.; Rana, V. B. Some 5-Coordinated Nickel(II) Complexes of Dipicolinic Acid Hydrazide. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1098.

(23) Ferraro, J. R. *Low Frequency vibrations of Inorganic and Coordination Compounds*; Plenum press: New York, 1971.

(24) Goodgame, D. M. L.; Goodgame, M.; Cotton, F. A. The Electronic Structures of Tetrahedral Cobalt(II) Complexes. *J. Am. Chem. Soc.* **1961**, *83* (23), 4690–4699.

(25) Nawar, N.; Khattab, M. A.; Hosny, N. M. Some Metal (II) Complexes of o-Aminoacetophenone Benzoyl Hydrazone (AABH): Their Preparation, Characterization and Antimicrobial Activity. *Synth. React. Inorg. Met.-Org. Chem.* **1999**, *29*, 1365–1384.

(26) Lever A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1986.

(27) Cotton F. A.; Wilkinson, G. *Advanced Inorganic Chemistry. A Comprehensive Text*, 4th ed.; John Wiley: New York, 1980.

(28) Nawar, N.; Hosny, N. M. Transition Metal Complexes of 2-Acetylpyridine o-Hydroxybenzoylhydrazone (APo-OHBH): Their Preparation, Characterization and Antimicrobial Activity. *Chem. Pharm. Bull.* **1999**, *47*, 944–949.

(29) Hamada, M. M.; Shallaby, A. M.; El-Shafai, O.; El-Asmy, A. A. Spectroscopic Characterization and Catalytic Activity of Some Cu(II) Thiosemicarbazide Complexes. *Transition Met. Chem.* **2006**, *31*, 522–529.

(30) Fuoss, R. M.; Edelson, D. Bolaform Electrolytes. I. Di-(j3-trimethylammonium Ethyl) Succinate Dibromideand Related Compounds. *J. Am. Chem. Soc.* **1951**, *73*, 269.

(31) Atkins, P. W. *Physical Chemistry*, 3rd ed.; W. H. Freeman and Co.: New York, 1986; pp 663−671.

(32) El-Dossoki, F. I.; Gomaa, E. A. Excess Refractive Index, Polarizability, Polarization and The Molar Volume of Some Mixed Solvents. *J. Indian Chem. Soc.* **2005**, *82*, 219–224.

(33) Mongnaschi, E. R.; Laboranti, L. M. Association of Pure Polar Liquids: dielectric Properties of Docosanoic Acid. *J. Chem. Soc., Faraday Trans.* **1996**, *92* (18), 3367–3369.

(34) Bottcher, C. J. F. *Theory of Electric Polarization*; Elsevier: Amsterdam, 1973; Vol. 1.

(35) Hasted, J. B. *Aqueous Dielectrics*; Chapman and Hall: London, 1973.

Received for review June 10, 2008. Accepted September 5, 2008.

JE800415N