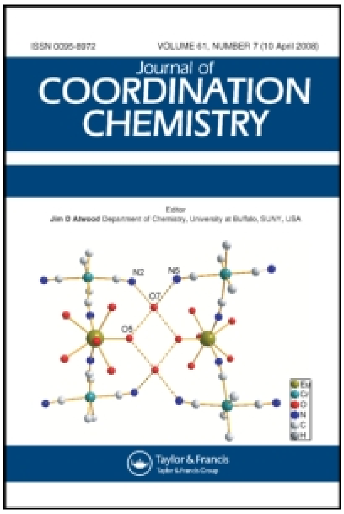

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

The Synthesis, Characterization and Conductance Studies of New Cu(II), Ni(Ii) And Zn(II) Complexes with the Schiff Base Derived from 1,2-Bis-(*o*-Aminophenoxy)Ethane and Salicylaldehyde

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To cite this Article Temel, Hamdi , Çakir, Ümit , Uğraş, H. İbrahim and Şekerci, Memet(2003) 'The Synthesis, Characterization and Conductance Studies of New Cu(II), Ni(Ii) And Zn(II) Complexes with the Schiff Base Derived from 1,2-Bis-(*o*-Aminophenoxy)Ethane and Salicylaldehyde', Journal of Coordination Chemistry, 56: 11, 943 — 951

To link to this Article: DOI: 10.1080/0095897031000135324

URL: http://dx.doi.org/10.1080/0095897031000135324

J. Coord. Chem., Vol. 56, No. 11, 20 July 2003, pp. 943–951

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THE SYNTHESIS, CHARACTERIZATION AND CONDUCTANCE STUDIES OF NEW Cu(II), Ni(II) AND Zn(II) COMPLEXES WITH THE SCHIFF BASE DERIVED FROM 1,2-BIS-(*o*-AMINOPHENOXY)ETHANE AND SALICYLALDEHYDE

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(Received 14 October 2002; Revised 27 January 2003; In final form 16 April 2003)

Cu(II), Ni(II) and Zn(II) complexes with the Schiff base derived from 1,2-bis-(*o*-aminophenoxy)ethane with salicylaldehyde have been prepared. The complexes have been characterized by elemental analysis, magnetic measurements, ^{1}H NMR, ^{13}C NMR, UV, visible and IR spectra as well as conductance measurements. The ligand is coordinated to the central metal as a tetradentate ONNO ligand. The four bonding sites are the central azomethine nitrogen and aldehydic OH groups. The ligand was used for complexation studies. Stability constants were measured by a conductometric method. Furthermore, the stability constants for complexation between $ZnCl_2$ and $Cu(NO_3)_2$ salts and *N*,*N*′-bis(salicylidene)-1,2-bis-(*o*-aminophenoxy)-ethane (H_2L) in 80% dioxane/water and pure methanol were determined from conductance measurements. The magnitudes of these ion association constants are related to the nature of the solvation of the cation and the complexed cation. The mobilities of the complexes are also dependent, in part, upon solvation effects.

Keywords: Schiff base; Cu(II); Ni(II) and Zn(II) complexes; Stability constants

INTRODUCTION

Schiff bases play a central role as chelating ligands in main group and transition metal coordination chemistry [1–4]. Transition metal complexes of tetradentate Schiff-base ligands find applications as models of certain metal enzymes and in catalysis and

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ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897031000135324

materials chemistry [5]. Schiff-base complexes are known to show antifungal activity, which is increased by the presence of a hydroxy group in the ligand [6].

In the present article Cu(II), Ni(II) and Zn(II) complexes with the Schiff base derived from 1,2-bis-(*o*-aminophenoxy)ethane and salicylaldehyde are reported. These have been characterized on the basis of analysis of the solid complexes, elemental analyses, magnetic measurements, ^{1}H NMR, ^{13}C NMR, UV, visible and IR spectra as well as conductance studies. We have used conductivity measurements to determine the stability (formation) constants for the Zn(II) and Cu(II) ion–H_2L ligand interaction [7]. Results for the ligand with Cu(II) and Zn(II) metal salts in 80% dioxane/water and pure methanol at 25°C are reported. This method also yields accurate values for the ion association constants for the cation–ligand complexes with various anions. Our results suggest that a number of cation–H_2L ligand complexes undergo ion association that is highly dependent on the nature of the ion–solvent and ion–ligand interactions.

EXPERIMENTAL

Physical Measurements

Conductivities of 10^{-3} M solutions of the complexes were measured in DMF at 25°C using a Conductivity Hand-held Meter LF 330. The electronic spectra of the complexes in the UV-Vis region were recorded in DMF solution using a Shimadzu Model 160 UV Visible spectrophotometer. The IR spectra of the complexes were recorded with a Midac 1700 instrument in KBr pellets. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker DPX-400 High-performance digital FT-NMR spectrometer. Magnetic moments were determined on a Sherwood Scientific magnetic moment balance (Model No: MK1) at room temperature (23°C) using $Hg[Co(SCN)_2]$ as a calibrant: diamagnetic corrections were calculated from Pascal's constants [8]. The elemental analyses were conducted on a Carlo Erba instrument.

Synthesis of Ligand (*N*,*N'*-bis(Salicylidene)-1,2-bis-(*o*-aminophenoxy)ethane)

A solution of salicylaldehyde (10.00 mmol, 1.06 g) in 25 mL absolute ethanol was added dropwise over 2 h to a stirred solution of 1,2-bis(*o*-aminophenoxy)ethane (5.00 mmol; 1.22 g) dissolved in 25 mL warm absolute ethanol [9]. A solid mass separated out on cooling; the mixture was kept in a refrigerator for better crystallization. It was then filtered, washed with ethanol and ether and subsequently dried over anhydrous $CaCl_2$ in a desiccator. This ligand is insoluble in all common organic solvents, such as acetone, alcohol, benzene, etc. and soluble in polar solvents such as DMF and DMSO. The yellow imines were purified by recrystallization from dimethyl formamide, m.p. 184°C; yield: 1.54 g (68%).

Spectral Characterization of Ligand

Characteristic IR bands (KBr, cm^{-1}): 3062 (arom., C-H), 2960 (aliph., C-H), 2882 (intramolecular H bonded –OH), 1617 (–C=N), 1286 (phen., C–O). Characteristic ^{1}H NMR bands (DMSO-d_6, TMS, δ ppm): 13.12 (OH, s, 2H), 8.80 (HC=N, s, 2H), 7.04–7.90 (arom., CH, m, 16H), 4.40 (O–CH_2, s, 4H). ^{13}C NMR ($CDCl_3$) $\delta = 72.5$, 115.2, 115.3, 118.7, 120.7, 121.0, 121.8, 127.1, 130.5, 132.8, 139.0, 152.2, 157.4, 163.6.

Synthesis of Complexes

A solution of metal acetate (20 mmol) in DMF was mixed with the Schiff-base ligand (20 mmol) in DMF. The contents were refluxed in 150 mL of DMF on an oil bath for 2–3 h. The refluxed solution was then poured into ice-cold water and a colored solid separated out. The product was isolated by filtration, washed with ether, recrystallized from dimethyl sulfoxide and dimethyl formamide and dried over anhydrous $CaCl_2$ in vacuum at room temperature. The yield was 50–60% for all the complexes with respect to the ligand. The complexes decompose at 280°C and are almost insoluble in water but partially soluble in polar solvents (dimethyl sulfoxide and dimethyl formamide).

Spectral Characterization of Complexes

Characteristic IR bands for Ni(II) complex (KBr, cm^{-1}): 3035 (arom., C–H), 2927 (aliph., C–H), 1610 (–C=N), 1244 (phen., C–O), 520 (M–N) and 450 (M–O). Characteristic IR bands for Cu(II) complex (KBr, cm^{-1}): 3034 (arom., C–H), 2939 (aliph., C–H), 1608 (–C=N), 1250 (phen., C–O), 514 (M–N) and 460 (M–O). Characteristic IR bands for Zn(II) (KBr, cm^{-1}): 3042 (arom., C–H), 2916 (aliph., C–H), 1608 (–C=N), 1244 (phen., C–O), 515 (M–N) and 460 (M–O). Characteristic ^{1}H NMR bands of the Zn(II) complex (DMSO-d_6, TMS, δ ppm): 8.90 (HC=N, s, 2H), 7.06–7.89 (arom., CH, m, 16H) and 4.35 (O–CH_2, s, 4H). ^{13}C NMR ($CDCl_3$) $\delta = 73.9$, 116.6, 117.8, 121.6, 121.9, 122.0, 122.7, 128.5, 130.3, 133.6, 142.0, 153.2, 157.6, 164.0.

Complexation Studies and the Determination of Stability Constants (K_e)

Anhydrous $ZnCl_2$ and $Cu(NO_3)_2$ of highest purity were used. Stability constants were measured by a conductometric method. The water used in the conductometric studies was redistilled from alkaline potassium permanganate. Dioxane was dried over sodium metal, and anhydrous methanol was used without further purification (Merck; H_2O content less than 0.01%). The solutions were prepared at constant 1 : 1 ratio of metal salt to ligand (H_2L) in 80% dioxane/water mixture and in methanol. All solutions were prepared in a dry box and transferred to the dry conductivity cell. The conductances were measured at 25.00 ± 0.05°C. The measuring equipment consisted of a glass vessel (Ingold-type) with an external jacket. The system was connected to a thermostatted water-bath (25.00 ± 0.05°C) and a conductivity cell (Cole Parmer 19050–66) with a conductometer (Suntex SC-170 Model). The cell constant was determined as 0.769 cm^{-1} at 25°C, measuring the conductivity of aqueous potassium chloride solutions of various concentrations [10]. Log K_e and $-\Delta G^\circ$ values for reaction of the ligand with the cations were determined by a conductometric procedure outlined previously [7]. Results are reported as the average and standard deviation from four to six independent experimental determinations.

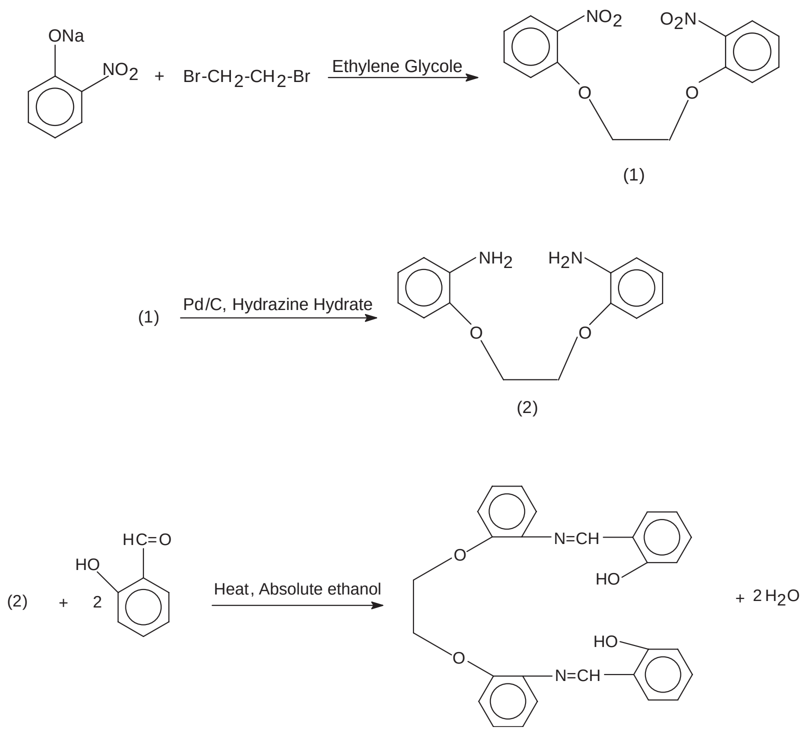

FIGURE 1 Synthesis of the ligand (H_2L): *N*,*N*′-bis(salicylidene)-1,2-bis-(*o*-aminophenoxy)ethane.

RESULTS AND DISCUSSION

The reaction steps for synthesis of H_2L are given in Fig. 1. The first step is synthesis of 1,2-bis-(*o*-nitrophenoxy)ethane (**1**) from reaction of sodium *o*-nitro phenolate and 1,2-dibromoethane. In the second step, 1,2-bis-(*o*-nitrophenoxy)ethane and Pd/C as catalyst in hydrazine hydrate were reacted to obtain 1,2-bis-(*o*-aminophenoxy)ethane (**2**) [11]. In the third step, 1,2-bis-(*o*-aminophenoxy)ethane and salicylaldehyde were reacted to obtain *N*,*N*′-bis(salicylidene)-1,2-bis-(*o*-aminophenoxy)ethane (H_2L). The three substances were characterized by IR, UV-Vis and ^{1}H NMR and ^{13}C NMR. Other analytical data are also given in Tables I and II. The stoichiometries of the ligand and its complexes were confirmed by elemental analyses. The molar conductance measured for 10^{-3} M solutions in DMF of these complexes fall in the range 3.2–3.7 $\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$ indicating their non-electrolytic behavior [12].

Reactions of the transition metal salts with the Schiff base are indicated by the following equations.

$$H_2L + Ni(OAc)_2 \cdot 4H_2O \rightarrow NiL + 2AcOH + 4H_2O$$

$$H_2L + Cu(OAc)_2 \cdot H_2O \rightarrow CuL + 2AcOH + H_2O$$

$$H_2L + Zn(OAc)_2 \cdot 2H_2O \rightarrow ZnL + 2AcOH + 2H_2O$$

TABLE I Some properties of the ligand and its complexes

Compound	*Color*	*F.Wt.* (g/mol)	*M.p.* (°C)	*Yield* (%)	*Elemental analyses calculated* (*found*) (%)			μ_{eff}	Λ^a
					C	*H*	*N*		
Ligand (H_2L)	Yellow	452.00	184.0	68.0	74.34	5.31	6.19		
$C_{28}H_{24}N_2O_4$					(74.39)	(5.35)	(6.29)		
CuL	Brown	513.55	285.0	60.0	65.43	4.28	5.45	1.61	3.6
$C_{28}H_{22}N_2O_4Cu$					(65.50)	(4.27)	(5.55)		
NiL	Red	508.71	290.0	58.0	66.05	(66.20)	4.33	(4.45)	5.50
$C_{28}H_{22}N_2O_4Ni$					(66.20)	(4.45)	(5.40)		
ZnL	Light yellow	515.38	290.0	52.0	65.20	4.29	5.43	Dia.	3.2
$C_{28}H_{22}N_2O_4Zn$					(65.25)	(4.20)	(5.65)		

[a] $\Omega^{-1}\,mol^{-1}\,cm^2$ (measured in 10^{-3} M solution in DMF).

TABLE II Some IR frequencies (in cm^{-1}) of the Schiff base and its complexes

Ligand (H_2L)	*CuL*	*NiL*	*ZnL*	*Assignment*
–	–	–	–	H_2O
2882	–	–	–	Intramolecular H-bonded–OH
1617 (s)	1608 (s)	1610 (s)	1608 (s)	Central C=N stretching
1286	1244	1251	1250	Phenolic C-O stretching
–	510 (w)	520 (w)	514 (w)	ν(M–N)
–	455 (w)	450 (w)	460 (w)	ν(M–O)

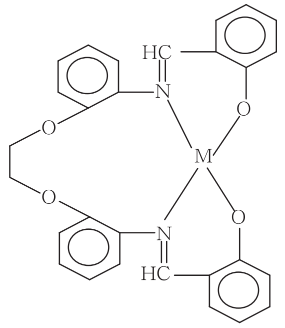

FIGURE 2 Suggested structure of the tetrahedral Zn(II) and Ni(II) and square-planar Cu(II) complexes of the ligand H_2L.

The metal to ligand ratio of the Cu(II), Ni(II) and Zn(II) complexes was found to be 1 : 1 (Fig. 2).

Electronic Spectra

The electronic spectra of all complexes were recorded in 10^{-3} M DMF at room temperature. The absorption spectra of the Schiff base are characterized mainly by two absorption bands in the region 275–400 nm. In the spectra of the Schiff-base ligand, the aromatic bands at 221–297 nm are attributed to a benzene $\pi \rightarrow \pi^*$ transition. The band at 350 nm is assigned to the imino $\pi \rightarrow \pi^*$ transition. The longer wavelength band is assigned to intramolecular charge transfer while the shorter wavelength is due to $\pi \rightarrow \pi^*$ within the C=N bands influenced by CT interactions [13–16].

The electronic spectrum of the Cu(II) complex shows an absorption band at 590 nm ($\varepsilon = 17$) attributed to the ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition, which is compatible with this complex having a square-planar structure [17].

The electronic spectra of the Ni(II) complexes show two absorption bands, at 395 nm ($\varepsilon = 35$) and 610 nm ($\varepsilon = 30$), due to the ${}^3T_1(F) \rightarrow {}^3T_2(F)$ and ${}^3T_1(F) \rightarrow {}^3T_1(P)$ transitions, respectively, observed for tetrahedral Ni(II) complexes [18].

The electronic spectrum of the Zn(II) complex shows an absorption band at 440 nm ($\varepsilon = 5.6$) attributed to the L → M (charge transfer) transition, which is compatible with this complex having a tetrahedral structure [18,19].

IR Spectra

The tentative assignment of the important IR bands of the Schiff base under investigation and its corresponding metal complexes are recorded in Table II. The important features for the Schiff base and its complexes may be summarized as follows:

- The broad band in the IR spectrum of the Schiff base at 2882 cm^{-1} is assigned to the stretch of the intramolecular hydrogen bonded –OH. Similar bands were observed at the same frequency in the IR spectra of salicylidene-anilines [20,21]. This band disappeared in the IR spectra of the complexes. The band at 1286 cm^{-1} in the IR-spectrum of the ligand is ascribed to the phenolic C–O stretching vibration according to the assignment made by Kovacic [22] for salicylidene-anilines. This band is found in the region 1244–1251 cm^{-1} in the IR spectra of the complexes. These changes suggest that the *o*-OH group of this Schiff-base moiety has taken part in complex formation.
- The solid state IR spectra of the complexes compared with those of the ligand indicate that the C=N band at 1617 cm^{-1} is shifted to lower values for complexes of Cu(II), Ni(II) and Zn(II) [3].
- Conclusive evidence of the bonding is also shown by the observation that new bands in the spectra of the metal complexes appear at 450–460 cm^{-1} and 510–520 cm^{-1} assigned to (M–O) and (M–N) stretching vibrations that are not observed in the spectra of the ligand [3,20,23].

Magnetic Properties

The Ni(II) and Cu(II) complexes are paramagnetic and their magnetic moment are 2.61, 1.61 BM, respectively. Since the Ni(II) and Cu(II) complexes are paramagnetic [13,14], their ${}^1H$ NMR spectra could not be obtained. The Zn(II) complex is diamagnetic. Its ${}^1H$ NMR spectra could be obtained.

Conductivity

The complexes are non-electrolytes as shown by their molar conductivity (Λ_M) measurements in dimethyl formamide (DMF), which are in the range [1,3,4,20,21] 3.2–3.7 $\Omega^{-1}\text{cm}^2\,\text{mol}^{-1}$.

The Conductometric Study of H_2L Ligand with Zn(II) and Cu(II) Salts

Structures of H_2L ligand–cation complexes in dioxane/water mixture and pure methanol solvent are estimated from the conductance parameters (κ and Λ) as well as the complex formation constant, K_e, calculated using the equations below [24];

$$\begin{array}{ccccc} M^{m+} & + & L & \rightleftharpoons & ML^{m+} \\ \alpha[M]_0 & & [L]_0 - (1-\alpha)[M]_0 & & (1-\alpha)[M]_0, \end{array} \tag{1}$$

where M^{m+}, L, and α are the cation, ligand compound, and fraction of free cations, respectively. Thus, the complex formation constant (K_{ML}) is defined by

$$\begin{aligned} K_{ML} &= [ML^{m+}]/[M^{m+}][L] \qquad (2) \\ &= (1-\alpha)/\alpha[L] \\ [M]_0 &= [M^{m+}] + [ML^{m+}] \qquad (3) \\ [L]_0 &= [L] + [ML^{m+}] \qquad (4) \\ \alpha &= [M^{m+}]/[M]_0, \qquad (5) \end{aligned}$$

where $[M]_0$, $[L]_0$, are initial concentrations of metal and ligand, and $[M^{m+}]$, [L] and $ML^{m+}]$ are concentration of uncomplexed cation, uncomplexed ligand and complexed cation, respectively. The observed conductivity, κ, is given by

$$\kappa = \kappa_M^{m+} + \kappa_{(ML)}^{m+}, \tag{6}$$

where κ_M^{m+} and $\kappa_{(ML)}^{m+}$ refer to observed conductivities of the electrolyte and the ligand compound-electrolyte complex, respectively. The molar conductivities are

$$\begin{aligned} \Lambda_M^{m+} &= \kappa_M^{m+}/[M^{\mathrm{m}+}] \qquad (7) \\ &= \kappa_{MAm}/\alpha[M]_0 \\ \Lambda_{(ML)}^{m+} &= \kappa_{(ML)}^{m+}/[ML^{\mathrm{m}+}] \qquad (8) \\ &= \kappa_{ML}^{m+}/(1-\alpha)[M]_0, \end{aligned}$$

where Λ_M^{m+} and $\Lambda_{(ML)}^{m+}$ designate molar conductivities of the electrolyte and the ligand compound-electrolyte complex, respectively. As a consequence of Eqs. (7) and (8), Eq. (6) can be transformed into

$$\begin{aligned} \Lambda &= \kappa/[M]_0 \\ &= \alpha\Lambda_M^{m+} + (1-\alpha)\Lambda_{(ML)}^{m+}. \end{aligned} \tag{9}$$

Using Eq. (9), Eq. (2) can be transformed into

$$K_e = (\Lambda_M^{m+} - \Lambda)/(\Lambda - \Lambda_{(ML)}^{m+})[L],$$

where $[L] = [L]_0 - [M]_0(\Lambda_M^{m+} - \Lambda)/(\Lambda_M^{m+} - \Lambda_{(ML)}^{m+})$.

TABLE III Log K_e and $-\Delta G^\circ$ (kcal/mol) values for the interaction of H_2L with $ZnCl_2$ and $Cu(NO_3)_2$ in 80% dioxane/water at 25°C by conductometric study

Ligand	*Value*	*Zn^{2+}*	*Cu^{+2}*
H_2L	log K_e	3.64 ± 0.15	4.03 ± 0.25
	$-\Delta G^\circ$	4958.28 ± 0.03	5488.52 ± 0.06

TABLE IV Log K_e and $-\Delta G^\circ$ (kcal/mol) values for the interaction of H_2L with $ZnCl_2$ and $Cu(NO_3)_2$ in methanol at 25°C by conductometric study

Ligand	*Value*	*Zn^{2+}*	*Cu^{+2}*
H_2L	log K_e	3.84 ± 0.22	3.57 ± 0.11
	$-\Delta G^\circ$	5239.16 ± 0.10	4870.55 ± 0.18

TABLE V Dielectric constant values of 80% dioxane/water and methanol

Water[a]	*Dioxane*[a]	*Methanol*[a]	*80% dioxane/water*[b]
78.54	2.21	33.62	18.23

[a]John A. Dean, *Lange's Handbook of Chemistry* 14th edn. (1992); [b]G. Akerlöf, *J. Am. Chem. Soc.* **54**, 4125 (1932).

Our results suggest that a number of cation–ligand complexes undergo ion association which is highly dependent on the nature of both ion–solvent and ion–ligand interactions. It was observed that for the metal complexes with H_2L ligand in both dioxane/water mixture and methanol, the K_e values were dependent on the chemical characteristics of ligand and solvent, indicating that electrostatic ion–dipole forces, which depend on the macroscopic dielectric constant of the solvents and on the dipole moment of ligands, are strong factors in the complexation processes in such systems.

The stability constants (log K_e) increase as the crystal radii increases in 80% dioxane/water (see Table III) the order Zn(II) < Cu(II) but different behavior has been obtained in methanol (see Table III). The most stable complex is Cu(II)–H_2L in 80% dioxane/water, and Zn(II)–H_2L in methanol. We found that the stabilities of the complex ions are affected not only by the relative sizes of the cationic radii but also by the physical properties of the solvent.

Eight percent dioxane/water mixtures have a lower dipole moment and dielectric constants than methanol (see Table IV). Thus, the consequences of both primary and secondary solvation should be qualitatively different in the two solvents. In Table V, the dielectric constant values for dioxane/water are compared with the values for methanol. On average the Cu(II) complex in dioxane/water must be more stable than those in comparable methanol. Because Cu(II) ions are surrounded by methanol molecules, there is a weaker interaction between a Cu(II) ion and a H_2L ligand in methanol compared with in 80% dioxane/water.

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