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Characterization Studies of Some Bi- and Tetradentate Bifunctional *Schiff* Base Complexes with Co(II), Ni(II), and Cu(II)

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Co(II), Ni(II) and Cu(II) complexes of some bifunctional arylidene-*o*-phenylenediamine *Schiff* bases have been prepared. Formation, stoichiometry and stability of the complexes have been tested in solution using electronic spectral measurements. Characterization of the complexes has been accomplished primarily by elemental analysis, molar conductance as well as electronic and IR spectral measurements. It is concluded that the *o,o*-hydroxy derivative (L_1) acts as a bivalent ONNO tetradentate ligand while the molecules of the other derivatives (L_2-L_5) are coordinated to the metal ions as bidentate NN ligands. The Cu(II) $-L_1$ complex is suggested to possess a tetrahedral geometry whereas the other complexes are suggested to exhibit a distarted octahedral geometry. The different bands observed in the electronic spectra of the complexes in *DMF* solutions have been assigned to the π-π^*, $L \rightarrow M$ CT and d-d electronic transitions.

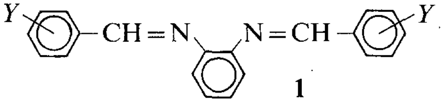
(Keywords: Complex formation constant; Conductance)

Untersuchungen zur Charakterisierung einiger zwei- und vierzähniger bifunktioneller Schiffbasen-Komplexe mit Co(II), Ni(II) *und* Cu(II)

Es wurden die Co(II)-, Ni(II)- und Cu(II)-Komplexe einiger bifunktioneller Aryliden-*o*-phenylendiamin-*Schiff*basen hergestellt. Unter Verwendung elektronenspektroskopischer Methoden wurde die Bildung, Stöchiometrie und Stabilität der Komplexe in Lösung untersucht. Die Charakterisierung erfolgte mittels Elementaranalysen, Leitfähigkeitsmessungen und Elektronen- bzw. IR-Spektroskopie. Es wird darauf geschlossen, daß das *o,o*-Hydroxyderivat L_1 als bivalenter vierzähniger ONNO Ligand wirkt, während die anderen Derivate (L_2 $-L_5$) als zweizähnige NN Liganden an die Metallionen koordiniert sind. Für den Cu(II)$-L_1$ Komplex wird eine tetraedrische Geometrie vorgeschlagen, währenddessen die anderen Komplexe eine verzerrte octaedrische Geometrie aufweisen. Die in den Elektronenspektren der Komplexe in *DMF*-Lösung auftretenden Banden werden den $\pi-\pi^*$, $L \rightarrow M$ CT und d-d Elektronenübergängen zugeordnet.

Introduction

Continuing our studies on metal complexes of mono-, bi- and tridentate monobasic *Schiff* bases[1–5], we report here a study concerning the complexes of some bi- and tetradentate dibasic *Schiff* bases with the transition metal ions Co(II), Ni(II) and Cu(II). The study involves synthesis and characterization as well as the investigation of the effects of molecular structure of the *Schiff* base on the stability of the complex. The dibasic *Schiff* bases used are:



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$Y = o-\mathrm{OH}$, L_1; $=p-\mathrm{H}$, L_2; $=p-\mathrm{N(CH_3)_2}$, L_3; $=p-\mathrm{OH}$, L_4; $=p-\mathrm{NO_2}$, L_5.

Experimental

Reagent grade metal salts and organic solvents were generally used.

The dibasic *Schiff* bases were prepared by refluxing *o*-phenylenediamine and aromatic aldehydes (in 1 : 2 ratio) in absolute ethanol. The solid *Schiff* base was filtered off and recrystallized from ethanol. The structures of the different dibasic *Schiff* bases were confirmed by elemental analyses.

Preparation of Metal Complexes

The general synthetic procedure used indolved dissolution of 1.0 mmol of the *Schiff* base and 0.5 mmol of the metal salt [$Co(NO_3)_2 \cdot 6\,H_2O$, $NiCl_2 \cdot 6\,H_2O$ and $Cu(CH_3COO)_2 \cdot 2\,H_2O$] in the least amount of absolute ethanol. Then both the *Schiff* base and the metal salt solutions were mixed and the resulting solution was refluxed for ~ 3 h. Subsequently, the solution was concentrated to a small volume and the solid complex produced was filtered off, washed with ethanol and stored in a desiccator over dry silica gel. Several trials were made to isolate the solid Co(II) and Ni(II) complexes of L_2, however, all experiments failed.

Due to the sparingly soluble character of L_5 in ethanol its complexes were synthesized in dioxane.

Preparation of Solutions

$10^{-3}\,M$ stock solutions of the *Schiff* bases (L_1–L_5) as well as of metal salts were prepared by dissolving the accurately weighed amount of each in absolute ethanol. In case of L_5 dioxane was used as a solvent. The metal ion solutions were standardized using the conventional procedures.

Characterization Studies

IR spectra of the ligands and their complexes were recorded on a Perkin-Elmer 599 B Spectrophotometer as KBr discs. UV and visible spectra were recorded on both Unicam SP 8000 and SP 8-100 Spectrophotometers using 1-cm matched silica cells. Molar conductance measurements were performed with a PYE conductance bridge. All measurements were carried out at room temperature (~ 25 °C).

Results and Discussion

The complexes isolated are given in Table 1. The elemental analysis data reported in this table reveal that the dianions of L_1 are coordinated to the metal ion while neutral molecules of the other ligands (L_2–L_5) are coordinated to the metal ion. The general formulae of L_1 complexes are $[L_1M\ (H_2O)_2]$ where M = Co(II), Ni(II) and $[L_1Cu]$, while those of the other ligands are $[LM(H_2O)_2X_2]$ where $L = L_2$–L_5, M = Co(II), Ni(II) and Cu(II), $X = NO_3^-$, Cl^- or CH_3COO^-.

Molar conductivity determination of $10^{-3}\,M$ solutions of the complexes in ethanol or *DMF* are consistent with a non-electrolytic behaviour of these complexes (cf. Table 1). On the other hand, the measured molar conductance values for ethanolic solutions of Co(II) and Ni(II) complexes of L_5 suggest a 1 : 1 electrolyte character of these

Table 1. *Analytical data, decomposition temperature and molar conductance values* ($ohm^{-1}\,cm^2\,mol^{-1}$) *of the complexes*

	Decomp. Temp. °C	Molar conductance	Found (calculated) %C	%N
Complexes of L_1				
$[(C_{20}H_{14}N_2O_2)Co(H_2O)_2]$	> 300	1.5[a]	58.85 (58.69)	6.42 (6.84)
$[(C_{20}H_{14}N_2O_2)Ni(H_2O)_2]$	290	1.0[a]	58.50 (58.72)	6.70 (6.85)
$[(C_{20}H_{14}N_2O_2)Cu]$	295	0.5[a]	63.85 (63.57)	7.22 (7.40)
Complexes of L_2				
$[(C_{20}H_{16}N_2)Cu(H_2O)_2(CH_3COO)_2]$	> 300	2.19[b]	57.10 (57.42)	5.40 (5.58)
Complexes of L_3				
$[(C_{24}H_{26}N_4)Co(H_2O)_2(NO_3)_2]$	235	6.2[b]	48.60 (48.90)	14.10 (14.26)
$[(C_{24}H_{26}N_4)Ni(H_2O)_2Cl_2]$	178	5.4[b]	53.50 (53.76)	10.10 (10.45)
$[(C_{24}H_{26}N_4)Cu(H_2O)_2(CH_3COO_2]$	175	7.9[b]	56.95 (57.14)	9.35 (9.35)
Complexes of L_4				
$[(C_{20}H_{16}N_2O_2)Co(H_2O)_2(NO_3)_2]$	195	6–6[a]	45.10 (44.86)	10.20 (10.46)
$[(C_{20}H_{16}N_2O_2)Ni(H_2O)_2Cl_2]$	> 300	7.4[b]	49.60 (49.82)	5.70 (5.81)
$[(C_{20}H_{16}N_2O_2)Cu(H_2O)_2(CH_3COO)_2]$	168	4.8[a]	54.10 (53.98)	5.10 (5.24)
Complexes of L_5				
$[(C_{20}H_{14}N_4O_2)Co(H_2O)_2(NO_3)_2]$	130	33.7[a]	40.10 (40.47)	13.90 (13.16)
$[(C_{20}H_{14}N_4O_2)Ni(H_2O)_2Cl_2]$	180	55.6[a]	44.65 (44.46)	10.10 (10.37)
$[(C_{20}H_{14}N_4O_2)Cu(H_2O)_2(CH_3COO)_2]$	> 300	23.1[b]	48.50 (48.68)	9.30 (9.46)

[a] Measured in ethanol.

[b] Measured in *DMF*.

Table 2. *Some infrared frequencies of the Schiff bases L_1–L_5 and their* Co(II), Ni(II) *and* Cu(II) *complexes*

Compound	Frequency (cm^{-1})		
	ν_{O-H}	$\nu_{C=N}$	$\nu_{phenyl\ C-O}$
L_1	2 800 b*	1 620	1 280
Co(II) – L_1	3 350	1 598	1 325
Ni(II) – L_1	3 500	1 613	1 345
Cu(II) – L_1	–	1 595	1 285
L_2	–	1 622	–
Cu(II) – L_2	3 360	1 558	–
L_3	–	1 618	–
Co(II) – L_3	3 600	1 620	–
Ni(II) – L_3	3 350	1 622	–
Cu(II) – L_3	3 600	1 622	–
L_4	3 300	1 608	1 265
Co(II) – L_4	3 400	1 618	1 270
Ni(II) – L_4	3 360	1 618	1 275
Cu(II) – L_4	3 460	1 620	1 260
L_5	–	1 605	–
Co(II) – L_5	3 460	1 598	–
Ni(II) – L_5	3 395	1 530	–
Cu(II) – L_5	3 500	1 603	–

* H-bonded OH.

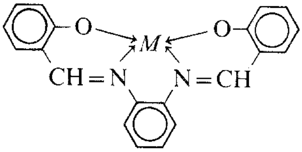
complexes. This behaviour can presumably be ascribed to the displacement of the monodentate NO_3^- or Cl^- ligands by ethanol molecules upon dissolution.

Assignment of the important IR bands, which aids in understanding of the bonding of the complexes, is presented in Table 2. The ν_{OH} band of L_1 appears as a broad one around 2 800 cm^{-1}. This is in consistency with the expected involvement of this group with the azomethine nitrogen through intramolecular hydrogen bonding. This band is totally disappeared in the IR spectra of the resultant L_1 complexes. Therefore, one can conclude that both the OH groups of L_1 have taken part in complex formation. The ν_{phenyl} CO of free L_1 is observed at 1 280 cm^{-1} [6]. Upon complexation this band it is shifted to higher energy confirming the coordination of L_1 OH groups. However, the observed shift in this band to higher energy upon complexation can presumably be attributed to the expected high mesomeric interaction within the chelated rings (cf. structure **2**).

The strong band observed in the range 1 605–1 622 cm^{-1} in the IR spectra of the ligands is assigned to $\nu_{C=N}$. Upon complexation, this band is shifted to lower or higher energies confirming the coordination of the azomethine nitrogen in all the complexes.

Except in case of the Cu(II)$-L_1$ complex, the IR spectra of the complexes show a broad band in the region 3 340–3 600 cm^{-1}. This suggests that water molecules are coordinated to the central metal ion. This is supported by the results of elemental analysis of the synthesized complexes (Table 1). However, the bands observed at 3 300 and 1 265 cm^{-1} in the IR spectra of free L_4 can be assigned to ν_{O-H} and ν_{phenyl} CO respectively.

Spectrophotometric investigations in the visible region of the different complexes were performed to inspect the formation, composition and formation constants of the most stable complexes possibly formed in solution. Comparing the visible spectra of the free ligand solutions with those of the corresponding complex solutions reveals that L_1 is characterized by a high tendency towards complex formation relative to the other ligands (L_2–L_5). This is concluded from the observation that the spectrum of $3.0 \cdot 10^{-5}$ *M* ethanolic solution of free L_1 differs markedly from those of its complex ethanolic solutions. The difference lies mainly in the behaviour of the longer wavelength band of free L_1 (348 nm) acquiring high red shift on complexation (33–65 nm). This behaviour can be explained as follows. The longer wavelength band observed in the spectrum of L_1 can be assigned to an intramolecular CT interaction occuring within the solute molecule[7,8]. Thus the red shift observed in this band on complexation can be ascribed to the expected easier CT interaction in the complexed ligand ($L \rightarrow M$ CT) relative to in the free one (cf. structure **2**). On the other hand, no changes are observed in the spectra of L_2–L_5 solutions upon addition of metal ion even on using high concentrations of these ligands ($\geqslant 5.0 \cdot 10^{-4}$ *M*). The observed high tendency of L_1 to form complexes relative to the other ligands can be attributed to the fact that L_1 acts as tetradentate ONON ligand where three stable chelated rings are formed (structure **2**). On the other hand, the other ligands, L_2–L_5, act as bidentate NN ligands where only one chelated ring is formed (cf. structure **3**).



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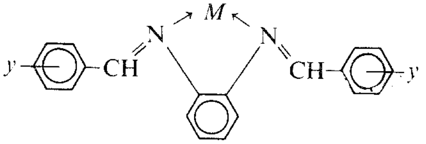

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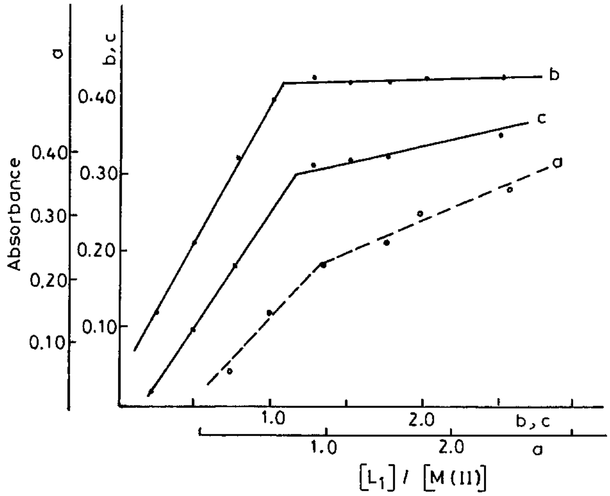

Fig. 1. Molar ratio method for metal complexes of L_1 with *a* Co(II), λ = 440 nm; *b* Ni(II), λ = 420 nm; *c* Cu(II), λ = 420 nm

The spectrophotometric methods, molar ratio[9], and *Job*'s continuous variation method[10] have been applied to detect the stoichiometry of the complexes formed in ethanol solution. In these two methods, an ethanolic solution having the same concentration of ligand as that of the complex solution was used as blank. Both methods revealed 1 : 1 stoichiometry of all the complexes studied. Representative results are given in Figs. 1 and 2. The stability of the 1 : 1 L_1 complexes formed in solution was inspected by determining their apparent formation constant values utilizing the results of continuous variation method[11]. The values obtained are $5.4 \cdot 10^5$, $8.0 \cdot 10^5$, and $2.27 \cdot 10^6$ for Co(II), Ni(II), and Cu(II) complexes, respectively, which are in agreement with the general order of stability of complexes of these metal ions[12,13].

Electronic Spectra of the Complexes

The UV-visible spectra of *DMF* solutions of the different complexes were recorded (Fig. 3). *DMF* was used as a solvent because some of the complexes were insoluble in ethanol and the common solvents. Furthermore, the spectra of metal complexes in *DMF* solutions exhibited no apparent differences from those recorded on mixing ethanolic solutions of both the metal ions and the ligands. This indicates that *DMF* does not act as ligand in these complexes. λ_{max} and ε_{max} values of the different absorption bands observed are listed in Table 3. According to the

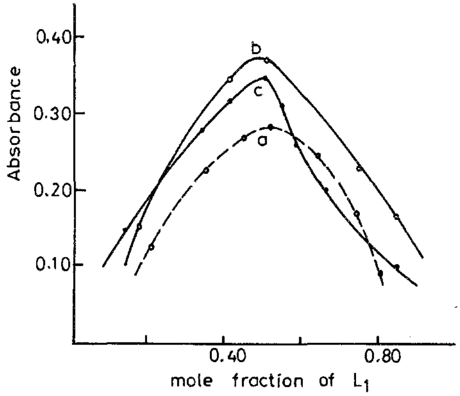

Fig. 2. *Job*'s continuous variation plots of the metal complexes of L_1 with *a* Co(II), $\lambda = 440$ nm; *b* Ni(II), $\lambda = 420$ nm; *c* Cu(II), $\lambda = 420$ nm

Table 3. *UV-visible absorption bands of various ligands and their metal complexes in DMF solutions*

Complex	λ_{max}/nm ($\varepsilon_{max} \cdot 10^{-3}$)	Assignment
Co(II) − L_1	310 (16.60)	$\pi \rightarrow \pi^*$
	360 (9.40)	$L \rightarrow M$CT
	472 (5.80)	$L \rightarrow M$CT
Ni(II) − L_1	284 (26.17)	$\pi \rightarrow \pi^*$
	368 (38.00)	$L \rightarrow M$CT
	472 (12.60)	$L \rightarrow M$CT
	572 sh (1.20)	$^3A_{2}g\,(F) \rightarrow {}^3T_{1}g(F)$
Cu(II) − L_1	300 (29.90)	$\pi \rightarrow \pi^*$
	418 (25.80)	$L \rightarrow M$CT
	576 (0.20)	$^2T_{2}g \rightarrow {}^2Eg$
Cu(II) − L_2	308 (7.33)	$\pi \rightarrow \pi^*$
	376 (1.25)	$L \rightarrow M$CT
Ni(II) − L_3	305 (56.25)	$\pi \rightarrow \pi^*$
	420 (47.50)	$L \rightarrow M$CT
	570 sh (1.00)	$^3A_{2}g(F) \rightarrow {}^3T_{1}g(F)$
Cu(II) − L_3	330 (41.17)	$\pi \rightarrow \pi^*$
	424 (6.40)	$L \rightarrow M$CT
Co(II) − L_4	284 (17.44)	$\pi \rightarrow \pi^*$
	420 (2.20)	$L \rightarrow M$CT
Ni(II) − L_4	352 (9.66)	$L \rightarrow M$CT
	570 sh (0.32)	$^3A_{2}g(F) \rightarrow {}^3T_{1}g(F)$
Cu(II) − L_4	292 (21.90)	$\pi \rightarrow \pi^*$
	418 (6.50)	$L \rightarrow M$CT
Co(II) − L_5	356 (24.70)	$L \rightarrow M$CT
Ni(II) − L_5	320 (25.60)	$L \rightarrow M$CT
Cu(II) − L_5	356 (11.76)	$L \rightarrow M$CT

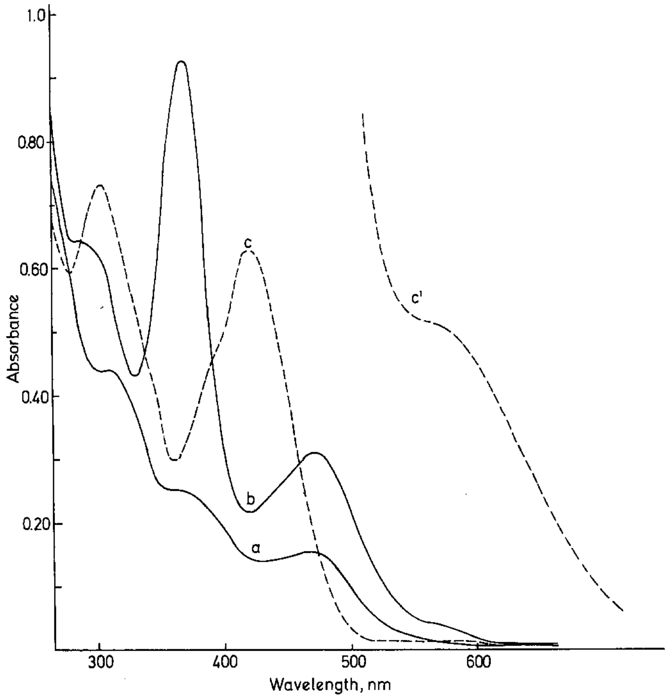

Fig. 3. UV-visible absorption spectra of *DMF* solutions of L_1 complexes with *a* Co(II) ($2.65 \cdot 10^{-5} M$); *b* Ni(II) ($2.44 \cdot 10^{-5} M$); *c* Cu(II) ($2.44 \cdot 10^{-5} M$); *c'* Cu(II) ($2.44 \cdot 10^{-3} M$)

work of *Jaffe'* and coworkers[14], the band observed in the range 284–330 nm can be assigned to a transition between π-orbitals largely localized on the azomethine double bond i.e. π-π^* transition. The one or two bands appearing in the range 320–472 nm can be assigned to $L \rightarrow$ MCT transition. This assignment is based on the observation that such bands are characterized by high molar extinction coefficients (1 250–38 000 g $\mathrm{mol^{-1}\,cm^2}$) as well as the fact that this type of electronic transition is expected to be easier in the complexed ligands due to the positive charge of the coordinated metal ion as shown in structures **2** and **3**.

Furthermore, in all the recorded spectra of the complexes studied, the longer wavelength side of the $L \rightarrow M$CT band is associated with a broad shoulder (cf. Fig. 3) which can be attributed to a d-d electronic transition within the coordinated metal ion.

The low energy broad shoulder associated with the $L \rightarrow M$CT band in the spectrum of the Cu(II)$-L_1$ complex ($\lambda_{max} = 572$ nm, $\varepsilon_{max} = 200$ g $\mathrm{mol^{-1}\,cm^2}$) is indicative of a tetrahedral structure of this complex. This suggestion is substantiated by the previous observation described by *Lever*[15] concerning the electronic spectra of tetrahedral Cu(II) complexes where it was reported that such spectra display a single broad band of $\sim 10^2$ molar obsoptivity in the range of 500–1 000 nm. Accordingly, the low energy shoulder of the Cu(II) $-L_1$ complex can be assigned to a $^2E_2g \rightarrow {}^2T_2g$ electronic transition.

With respect to the other complexes, the low energy broad shoulder appearing in these spectra indicates a hexacoordinated configuration with low symmetry components in the ligand field, i.e. distorted octahedral geometry[15–17]. Thus the shoulder ascertained in the spectra of Ni(II) $-L_1$, $-L_3$ and $-L_4$ complexes at 572, 570 and 570 nm respectively can be assigned to a d-d electronic transition of the type $^3A_2g(F) \rightarrow {}^3T_1g(F)$[16].

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