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Synthesis, spectroscopy, electrochemistry and thermal study of Ni(II) and Cu(II) unsymmetrical N_2O_2 Schiff base complexes

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1. Introduction

The high stability potential of Schiff base complexes with different oxidation states extended the application of these compounds in a wide range. They were studied as catalysts in organic redox and electrochemical reduction reactions [1-4]. Knowledge of electronic and steric effects to control the redox chemistry of these compounds may prove to be critical in the design of new catalysts. The Ni(I) and Ni(III) species can act as a powerful catalysis on chemical or electrochemical reduction and hydrogenase reactions [5–7]. The electronic effects of the functional groups on electrochemical properties of Schiff base complexes were investigated previously [8-11]. Thermogravimetry (TG) and differential thermoanalysis (DTA) are valuable techniques for studying the thermal behaviour of compounds. In view of recent interest in the thermal behaviour of the metal ligand chelates involving Schiff base ligands [12-15], we started to study the thermal behaviour of Schiff base complexes derived from tetradentate ligands involving an N₂O₂ donor atom. This paper describes the synthesis, spectral, electrochemical and thermal studies of new unsymmetrical N₂O₂ tetradentate Schiff base ligands (Fig. 1), and their Ni(II) and Cu(II) complexes. The electrochemical properties of the Ni(II) complexes were studied by cyclic voltammetry in DMF solvent. Kinetics and

ABSTRACT

The new tetradentate unsymmetrical N_2O_2 Schiff base ligands, Ni(II) and Cu(II) complexes were synthesised and chracterized by IR, UV-vis, ¹H NMR and elemental analysis. The electrochemical properties of the Ni(II) complexes were investigated. The thermogravimetry of the Ni(II) and Cu(II) complexes were carried out in the range of 20–700 °C. Decomposition of synthesised complexes is related to the Schiff base characteristics.

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thermodynamic parameters have been calculated using Coats and Redfern [16] method.

2. Experimental

2.1. Chemicals and apparatus

All of the chemicals and solvents used for synthesis and electrochemistry were of commercially available reagent grade and used without purification. The elemental analysis was determined on a CHN–O-Heraeus elemental analyzer. Infrared spectra were recorded as KBr discs on a FT-IR JASCO-680 spectrophotometer in the 4000–400 cm⁻¹. UV–vis spectra were recorded on a JASCO V-570 spectrophotometer in the 190–900 nm. The ¹H NMR spectra were recorded in DMSO-d6 on DPX-400 MHz FT-NMR. TG and DTA were carried out on a PL-1500. The measurements were performed in air atmosphere. The heating rate was kept at $10 \,^{\circ}$ C min⁻¹.

Cyclic voltammograms were performed using an autolab modelar electrochemical system (ECO Chemie, Ultrecht, The Netherlands) equipped with a PSTA 20 module and driven by GPES (ECO Chemie) in conjunction with a three-electrode system and a personal computer for data storage and processing. An Ag/AgCl (saturated KCl)/3 M KCl reference electrode, a Pt wire as counter electrode and a glassy carbon electrode as working electrode (metrom glassy carbon, 0.0314 cm²) were employed for the electrochemical studies. Voltammetric measurements were performed

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Fig. 1. The structure of Schiff bases and their complexes.

at room temperature in DMF solution with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte.

2.2. Synthesis of the threedentate Schiff base ligand

2-Hydroxyacetophenone (1 mmol, 0.2487 g) was added to a solution of 1,2-phenylendiamine (1.5 mmol, 0.2933 g) dissolved in 20 ml methanol. The solution was refluxed for 3 h and methanol was evaporated under reduced pressure. Water was added to such a precipitate to dissolve phenylendiamine. The resulting yellow solid was collected, washed with water and then recrystallized from methanol. HL; yield (80%).

2.3. General procedure for Synthesis of tetradentate ligands

All the tetradentate ligands H_2L^1 , H_2L^2 , H_2L^3 , H_2L^4 , were synthesised in a similar way by stirring a methanolic solution of HL (1 mmol, 0.2263 g) with salicylaldehyde (1 mmol, 0.12 mml), 5-methoxysalicylaldehyde (1 mmol, 0.81 ml), 5bromosalicylaldehyde (1 mmol, 0.1691 g), 5-nitrosalicylaldehyde (1 mmol, 0.1671 g), respectively. Stirring was continued for 3 h at room temperature during which a yellow solid compound separated. It was filtered, washed with methanol, recrystallized from dichloromethane/methanol and dried over CaCl₂.

2.4. General procedure for synthesis of Ni(II) and Cu(II) complexes

The Ni(II) and Cu(II) complexes were synthesised by refluxing a methanolic solution of the tetradentate Schiff base ligands and M(II) acetatetetrahydrate. The reaction was continued for 2 h during which a green or brown precipitate separated. It was filtered, washed with methanol and dried in vacuum.

3. Results and discussion

3.1. Elemental analysis

The elemental analysis (Table 1) is in good agreement with that calculated for the proposed formula.

3.2. Infrared spectra

The IR spectra of the metal complexes of the Schiff base ligands were compared with those of the Schiff bases themselves in order to determine the coordination sites that may be involved in chelation (Table 2).

The IR spectrum of the threedentate ligand exhibit sharp medium intensity bands at 3300 and $3400 \,\mathrm{cm}^{-1}$, which are assigned to the NH₂ functional group. These bands were disappeared in the spectrum of tetradentate ligands. The spectra of the ligands exhibit broad weak intensity band in the 2500–3500 cm⁻¹ range, which is assigned to the intramolecular hydrogen bonding vibration (O-H…N). This band disappeared in the spectra of complexes [14,15,17].

Table 1
Elemental analysis data for the complexes.

Calculated/found (%)	Compounds			
	N	Н	С	
NiL ¹	65.51(65.4)	4.15(4.17)	7.27(6.95)	
NiL ² . H ₂ O	60.73(61.81)	4.63(4.87)	6.43(6.19)	
NiL ³	54.37(55.25)	3.23(3.63)	6.04(6.04)	
NiL ⁴	55.92(56.43)	3.43(3.22)	9.62(9.45)	
CuL ¹	64.39(65.29)	4.08(4.19)	7.15(7.16)	
CuL ²	62.65(61.15)	4.27(4.7)	6.64(6.24)	
CuL ³	53.5(52.12)	3.19(3.36)	5.95(5.55)	
CuL ⁴ ·H ₂ O	57.75(56.36)	3.46(3.73)	9.62(8.98)	

I dDIC 2			
Characteristic IR bands (cm-1) of the ligands and their Ni	II) and Cu(II) complexes.

Compound	$NH_2\left(cm^{-1}\right)$	$C=N(cm^{-1})$	$C = C(cm^{-1})$	C–O (cm ⁻¹)	$NO_2 (cm^{-1})$
HL	3300, 3400	1610	1481	1217	-
H_2L^1	-	1613	1476	1216	-
H_2L^2	-	1614	1491	1219	-
H_2L^3	-	1611	1472	1217	-
H_2L^4	-	1615	1487	1215	1332
NiL ¹	-	1609	1462	1217	-
NiL ²	-	1600	1488	1219	-
NiL ³	-	1603	1516	1216	-
NiL ⁴	-	1617	1542	1216	1340
CuL ¹	-	1603	1423	1216	-
CuL ²	-	1601	1525	1217	-
CuL ³	-	1611	1523	1217	-
CuL ⁴	-	1600	1524	1216	1309

The vibration of azomethine group of the free ligands is observed at $1610-1615 \text{ cm}^{-1}$. For the synthesised complexes this band was shifted to the lower frequencies, indicating that the nitrogen atom of the azomethine group is coordinated to the metal [14,15].

3.3. Electronic spectra

The spectral data of the free ligands and their complexes are listed in Table 3.

The electronic spectra of the Schiff base ligands in solution consists of a relatively intense band in the 300–380 nm region, involving $\pi \rightarrow \pi^*$ transition, and a low intense band in the 360–500 nm region, involving $n \rightarrow \pi^*$ excitation [14,15]. Complexation with Ni(II) and Cu(II) results in two significant changes of the spectra taking place in the UV–vis region (between 300 and 500 nm) of MLCT and $\pi \rightarrow \pi^*$ absorption bands [14–15]. Moreover, an intense d $\rightarrow \pi^*$ charge transfer band appears in the 425–475 nm region in the spectra of the complexes studied here [11,15]. The absorption band at about 600 nm is related to the d-d transition and is consistent with the square planar geometry of Ni(II) and Cu(II) complexes [18–20].

Table 3

UV-vis spectral data (nm) for the ligands and their Ni(II) and Cu(II) complexes.

3.4. ¹H NMR spectra

The chemical shift (δ , ppm) of the different protons of the Schiff base ligands and their Ni(II) complexes has been recorded in Table 4 (the solubility of NiL⁴ was low and we could not record its ¹H NMR).

The ¹H NMR spectra of tetradentate Schiff bases indicate the presence of methyl group (at about 2 ppm), aromatic hydrogens (at about 7 ppm), one azomethine (8–9 ppm) and two types of OH in the range of 11.9–15 ppm. The H_2L^2 shows an additional peak (OCH₃) at 3.50 ppm. Intramolecular hydrogen bonding also accounts for the high frequency of the signals for the orthophenolic hydrogens (OH) in all the tetradentate Schiff bases. Due to the different chemical environments, two signals are recorded in this region. The signal at about 14 ppm is related to the phenolic hydrogen of 2-hydroxyacetophenone. This signal is nearly a constant chemical shift with different Schiff bases. The other signal is related to the phenolic hydrogen of salicylaldehyde and its derivatives. This signal shows a down field shift via increasing the electron withdrawing of functional groups. NO₂ (15 ppm)>Br (12.7)>H (12.5 ppm)>OCH₃ (11.9 ppm).

In all nickel complexes, no signals are recorded for the phenolic hydrogen in the 11–15 ppm region, as in the case of the Schiff bases indicating deprotonation of the orthohydroxyl group. The coordination of all the ligands is also affirmed by almost 0.5 ppm down field change in chemical shift for methyl group and aromatic hydrogens.

3.5. Thermal analysis

TG and DTA were carried out on the Ni(II) and Cu(II) complexes in the temperature range of 20–700 °C. The thermal decomposition of the studied complexes presented characteristic pathways, depending on the nature of the ligands, as can be seen from the TG/DTA curves in Figs. 2 and 3.

Some of the studied complexes showed weight loss up to $80 \,^{\circ}$ C indicating the present of water molecule in the crystalline solid (for elemental analysis the complexes were dried in vacuum at $60 \,^{\circ}$ C). In addition, in these complexes, the TG showed no weight loss up to $150 \,^{\circ}$ C indicating the absence of water molecule coordinated

Compound	$\pi \! \rightarrow \! \pi^{*} \left(\text{phenolic chromophore} \right)$	$\pi \! \rightarrow \! \pi^* \left(C \! = \! N \text{ and benzene ring} \right)$	$\pi \! \rightarrow \! \pi^{*} \left(C \!\!= \!\! N \right)$	$d \mathop{\rightarrow} \pi^*$	$d \rightarrow d$
HL	260	342	-	-	-
H2L ¹	260	342	-	-	-
H_2L^2	257	341	375	-	-
H ₂ L ³	275	341	-	-	-
H_2L^4	257	300	330	-	-
CuL ¹	250	300	350	425	600
CuL ²	250	300	350	425	610
CuL ³	250	310	355	425	605
CuL ⁴	238	320	400	420	650
NiL ¹	270	-	375	490	598
NiL ²	263	-	375	475	605
NiL ³	270	-	375	470	595
NiL ⁴	265	-	375	475	585

Table 4

¹H NMR data (ppm) for the ligands and their Ni(II) complexes.

Compounds	(s, 3H, CH ₃)	(s, 3H, O–CH ₃)	(m, 11H) Aromatic	(s, 1H, HC=N)	(s, 1H, OH _a)	(s, 1H, OH _b)
H_2L^1	2.06	-	6.70-7.10	8.80	12.06	14.10
H_2L^2	2.10	3.50	6.80-7.30	8.80	11.90	14.15
H_2L^3	2.06	-	6.80-7.10	8.85	12.90	14.05
H_2L^4	2.08	-	6.80-7.50	9.00	15.00	14.00
NiL ¹	2.64	-	7.02-8.09	8.87	-	-
NiL ²	2.64	3.49	6.50-7.80	8.60	-	-
NiL ³	2.06	-	6.80-7.80	9.40	-	-





Fig. 3. The TG and DTA of Cu(II) Schiff base complexes.



Fig. 4. Coats–Redfern plot of CuL³ complex, step 2, $A = \log(W_f/(W_f - W))/T^2$.

to complexes [14,15], while NiL² and CuL⁴ complexes indicate this property. The first step in the decomposition sequence of some complexes at 270–325 °C corresponded to the loss of methyl, methoxy, and nitro in the studied complexes, respectively. The NiL³ was decomposed in one step at 460 °C. The inflexion of the TG curve at a temperature range above 390 °C indicates the decomposition of the organic part of the chelate, leaving metallic oxide at the final temperature [14]. The thermal degradation of the studied complexes can be depicted as follows. NIL1

$$C_{21}H_{16}N_2O_2Ni \xrightarrow{T=325}_{-CH_3} CH_{20}H_{12}N_2O_2Ni \xrightarrow{T=430}_{-C_{20}H_{12}N_2O}NiC$$

NIL2

$$C_{22}H_{18}N_{2}O_{3}Ni \cdot H_{2}O \overset{T=120}{\overset{\circ}{\mapsto}} C_{22}H_{18}N_{2}O_{3}Ni \overset{T=390}{\underset{C_{22}H_{18}N_{2}O_{2}}{\overset{T=390}{\overset{\circ}{\leftarrow}}} NiO$$

NIL3

$$C_{21}H_{15}N_2O_2BrNi \xrightarrow{I=460 \circ C} NiO$$

 $C_{21}H_{15}N_2OBr$

NIL4

CUL1

$$C_{21}H_{16}N_{2}O_{2}Cu \cdot H_{2}O_{H_{2}O}^{T=85^{\circ}C}C_{21}H_{16}N_{2}O_{2}Cu \overset{T=275^{\circ}C}{\underset{-CH_{3}}{\longrightarrow}}C_{20}H_{13}N_{2}O_{2}Cu \overset{T=480^{\circ}C}{\underset{C_{20}H_{13}N_{2}O}{\longrightarrow}}CuO$$

CUL2

$$C_{22}H_{18}N_2O_3Cu \cdot H_2O \overset{T=90^{\circ}C}{\longrightarrow} C_{21}H_{18}N_2O_3Cu \overset{T=270^{\circ}C}{\longrightarrow} C_{15}H_{13}N_2O_2Cu \overset{T=490^{\circ}C}{\longrightarrow} CuC_{15}H_{13}N_2O_2$$

CUL3

$$C_{22}H_{15}N_{2}O_{2}BrCu \cdot H_{2}O \underset{H_{2}O}{\overset{7=85}{\longrightarrow}} C_{21}H_{15}N_{2}O_{2}BrCu \underset{-CH_{3}}{\overset{7=285}{\longrightarrow}} C_{20}H_{12}N_{2}O_{2}Cu \underset{C_{20}H_{12}N_{2}O}{\overset{7=490}{\longrightarrow}} CuO$$

CUL4

$$C_{21}H_{15}N_{3}O_{4}Cu \cdot H_{2}O_{H_{2}O}^{T=120\,^{\circ}C}C_{21}H_{15}N_{3}O_{4}Cu \overset{T=305\,^{\circ}C}{\underset{-CH_{3}}{\longrightarrow}}C_{20}H_{12}N_{3}O_{4}Cu \overset{T=395\,^{\circ}C}{\underset{C_{20}H_{12}N_{2}O_{3}}{\longrightarrow}}CuO$$

3.6. Kinetics aspects

All the well-defined stages were selected to study the kinetics of decomposition of the complexes. The kinetics parameters (the activation energy E and the pre-exponential factor A) were calculated using the Coats–Redfern equation [16],

$$\log\left[\frac{g(\alpha)}{T^2}\right] = \log\frac{AR}{\phi E}\left[1 - \frac{2RT}{E_a}\right] - \frac{E_a}{2.303RT}$$
(1)

where $g(\alpha) = [W_f)/(W_f - W)]$. In the present case, a plot of L.H.S. of this equation against 1/T gives straight line (Fig. 4) whose slope and intercept are used to calculate the kinetics parameters by the least square method. The goodness of fit was checked by calculating the

Table 5			
Thermal and kinetics	parameters for Ni	II) and Cu	(II) complexes.

Compounds	ΔT	% calculated (found)	E^{\neq} (kJ mol ⁻¹)	$A \neq (s^{-1})$	S^{\neq} (kJ mol ⁻¹ K ⁻¹)	H^{\neq} (kJ mol ⁻¹)	G^{\neq} (kJ mol ⁻¹)
NiL ¹	250–350 350–470	3/5(5) 70(65)	157.61 108.00	$\begin{array}{c} 2.89 \times 10^{11} \\ 1.82 \times 10^5 \end{array}$	-31 -151	152.80 102.21	170.71 207.30
NiL ²	90–145 320–500	7/1 (6/2) 76(73)	172.32 188.10	$\begin{array}{c} 3.59.10^{10} \\ 1.74 \times 10^{11} \end{array}$	-45.1 -33	169.10 184.40	187.00 199.00
NiL ³	400-550	83(79)	111.93	1.17×10^5	-155	105.92	217.98
NiL ⁴	290–320 355–390 390–540	3/2(3/2) 9.9(10) 64(67)	97.63 143.76 111.90	$\begin{array}{c} 1.19 \times 10^{6} \\ 2.58 \times 10^{9} \\ 1.04 \times 10^{5} \end{array}$	-134. -71.2 -156	92.77 138.40 105.89	170.90 184.19 218.67
CuL ¹	270–300 350–475	3.5(4) 70(69)	228.67 135.05	$\begin{array}{c} 6.17 \times 10^{18} \\ 3.76 \times 10^{9} \end{array}$	110 -67.8	224.08 129.24	163.36 177.19
CuL ²	425–345 410–535	17/5(18) 60(58)	92.24 71.70	$\begin{array}{c} 1.13\times10^6\\ 1.55\times10^2\end{array}$	-134 -211	87.79 65.46	159.48 223.92
CuL ³	255–285 400–590	3(3.1) 71(75)	206.65 73.01	$\begin{array}{c} 2.06\times10^{17}\\ 4.41\times10^3\end{array}$	82 -184	202.35 65.99	157.07 205.41
CuL ⁴	80–125 285–315 320–435	3/9(4) 3/3(3) 74(70)	60.27 12.25 25.28	$\begin{array}{c} 4.38 \times 10^5 \\ 1.09 \times 10^0 \\ 5.62 \times 10^0 \end{array}$	-139 -250 -237	57.13 7.48 19.70	109.45 150.73 178.71

correlation coefficient. The other systems and their steps show the same trend.

The entropy of activation S^{\neq} was calculated using the equation

$$A = \frac{kT_{\rm s}}{h} e^{S^{\pm}/R} \tag{2}$$

where k, h and T_s are the Boltzmann constant, the Planck's constant and the peak temperature respectively. The enthalpy and free energy of activation were calculated using equations

$$E_a = H^{\neq} + RT, \tag{3}$$

$$G^{\neq} = H^{\neq} - TS^{\neq} \tag{4}$$

The various kinetics parameters calculated are given in Table 5. The activation energy (E_a) in the different stages is in the range 12–228 kJ mol⁻¹. The respective values of the pre-exponential factor (A) vary from 1.09 to $6.17 \times 10^{18} \text{ s}^{-1}$. The corresponding values of the entropy of activation (S^{\neq}) are in the range of –283 to +110 J mol⁻¹. The corresponding values of the enthalpy of activation (H^{\neq}) are in the range of 7–224 kJ mol⁻¹. The corresponding values of the free energy of activation (G^{\neq}) are in the range of 112–223 kJ mol⁻¹. There is no definite trend either in the values of activation parameters among the different stages in the present series. But the activation energy for the second stage is smaller than that of the first one due to the unstable intermediate occurring at the later stages. However, the negative values of entropy of activation indicate that the activated complex has a more ordered structure than the reactants [14].

3.7. The electrochemical study of Ni(II) complexes

The electrochemical properties of nickel complexes were investigated in DMF. The Nickel(II) complexes exhibit a one electron quasi-reversible oxidation and reduction process. The electrochemical data are summarized in Table 6. The cyclic voltammograms for NiL³ are shown in Figs. 5 and 6. The anodic process

Table 6	
Redox potential data of Ni(II)	complexes in DMF solution.

compound	$E_{\rm pa}$ (II \rightarrow III)	$E_{\rm pc} (III \rightarrow II)$	$E_{\rm pc}$ (II \rightarrow I)	$E_{\rm pa} (I \rightarrow II)$
NiL ¹	0.900	0.783	-1.370	-1.315
NiL ²	0.900	-	-1.324	-1.261
NiL ³	0.972	0.820	-1.243	-1.190
NiL ⁴	1.064	0.677	-1.396	-1.280



Fig. 5. Cyclic voltammogram of NiL³ in DMF at room temperature (reduction process) Scan rate: 100 mV/s.

is attributed to quasi-reversible one electron oxidation of Ni(II) to Ni(III) process while cathodic process is attributed to quasireversible one electron reduction Ni(II) to Ni(I) process, similar to that of other Ni(II) Schiff base complexes [15]. The E_{pan} value for the Ni(II) complexes increases via increasing the electron-withdrawing property of functional group, while the E_{pca} does not show any trend.



Fig. 6. Cyclic voltammogram of NiL³ in DMF at room temperature (oxidation process) Scan rate: 100 mV/s.

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