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SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL BEHAVIOUR OF SOME MANGANESE AND COPPER COMPLEXES WITH TETRADENTATE SCHIFF BASE LIGANDS

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ABSTRACT

A series of symmetrical tetradentate Schiff bases derived from substituted salicylaldehyde and ethylenediamine were prepared and characterized by elemental analysis, IR, UV-Visible and ¹H NMR spectroscopy. The interaction of these bases with MnCl₂.4H₂O and CuCl₂.2H₂O have been studied, leading to the preparation of manganese(II) and copper(II) complexes. Microanalysis, molar conductance, IR, UV-Visible spectroscopy, magnetic measurements and ESR spectra have been used to elucidate the stucture of the resultant complexes. The experimental base data show that all the Schiff ligands N.N'-bis(2hydroxybenzyl)ethylenediimine (H_2L^1) , N,N'-bis(2-hydroxyacetophenyl)ethylenediimine (H_2L^2) and N,N'-bis(2-hydroxypropiophenyl)ethylenediimine (H2L3) yield 1:1 compounds except for the ligand H_2L^2 which gave a 2.1 compound with manganese(II). The spectral studies support the binding of the ligands with two N and two O donor sites to the metal(II) ion, giving an arrangement of N2O2 donor groups. Magnetic and ESR data indicate that the manganese(II) adopts a high spin configuration in the complexes studied and the covalent character of the metal-ligand bonding in the copper(II) complexes increases with the increasing electron donating effect of the ligand substituents R. The electrochemical behaviour of the manganese(II) and the copper(II) complexes was determined by cyclic voltammetry which shows that the chelate structure and electron donating effects of the ligand substituents are among the factors influencing the redox potentials of the complexes

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INTRODUCTION

Schiff bases are potentially capable of forming stable complexes with many metal ions. The chemistry of metal complexes with Schiff bases resulting from the condensation of salicylaldehyde with ethylenediamine has been extensively studied¹⁻³. However, little information is available in the literature concerning the substitution of the hydrogen on the carbon atom of the azomethine group. On the other hand, great interest has been developed in the coordination chemistry of manganese(II) and copper(II) with Schiff base ligands in attempts to model the physical and chemical behaviour of biological manganese and copper systems^{1, 4-7}. Our efforts in this area have focused on the preparation, characterisation of new manganese(II) and copper(II) complexes with some tetradentate Schiff bases derived from substituted salicylaldehyde and ethylenediamine (Fig.1) and the determination of the effects of substituents attached to the ligand on the central ion, the chelate structure of the metal-ligand bonding and the redox potentials of the complexes.

EXPERIMENTAL

Analytical and Physical Measurements

The elemental microanalyses were carried out at the Central Service of Analysis, CNRS Vernaison (France). Water of hydration was determined by conventional methods as described by Vogel⁸. Melting points were measured using a Büchi 512 digital melting point apparatus. Conductivity measurements were carried out using 10⁻³ M solutions in DMF on a Tacussel CD 810 apparatus employing a calibrated dip-type cell at 25° C. The IR spectra were recorded on a FTS-7 Biorad fourier transform infrared spectrometer using KBr disks. The electronic absorption spectra in DMF solution were recorded on a Perkin Elmer Lamda 9 spectrometer using suprasil cells. Magnetic susceptibilities were obtained with a B-SU 10 Bruker magnetic balance using Hg[Co(SCN)4] as paramagnetic reference, and diamagnetic corrections were made using Pascal's constants. ESR spectra of the manganese(II) and copper(II) complexes were recorded at room temperature in the powder state and in CHCl₃ and DMSO solution, respectively, with a E.9 X-band Varian spectrometer, using DPPH as a field marker. Electrochemical measurements were recorded with a Princeton Applied Research model 273 potentiostat-galvanostat. Cyclic voltammograms were obtained using a Sefram TGM. 164 recorder. The working, counter and reference electrodes used were, respectively, a platinum



Fig. 1. Structure of the Ligands, R = H: H_2L^1 ; $R = CH_3$: H_2L^2 ; $R = C_2H_5$: H_2L^3

wire, a platinum foil and a SCE (saturated calomel electrode). The SCE was separated from the test solution by a bridge filled with the solvent and supporting electrolyte which was tetrabutylammonium perchlorate (TBAP). The inert gas used was nitrogen. Coulometric measurements were made using a double circular platinum net as working electrode. The auxiliary and reference electrodes, the blank electrolyte solution and the inert gas were the same as in voltammetric measurements.

Materials

DMSO used for electrochemical measurements was dried by distillation over CaH_2 or by storing over 4-A molecular sieves. All other chemical reagents and solvents used in the preparations were Fluka p.a. products and used without further purification.

Preparation of Ligands

The Schiff bases were prepared by a traditional method⁹. A solution of either 0.02 mole of salicylaldehyde, 0.02 mole of 2-OH acetophenone or 0.02 mole of 2-OH propiophenone was dissolved in ethanol and 0.01 mole of ethylenediamine was added and heated for 2 h to obtain a yellow solid. The precipitated was filtred off, recrystallized from ethanol and dried over phosphoruspentoxide in a desiccator.

Preparation of Complexes

The complexes were prepared in a 1:1 metal-ligand stoichiometry¹⁰⁻¹². 10 mL of an aqueous solution of $MnCl_2.4H_2O$ or $CuCl_2.2H_2O$ (1 mmole) were added dropwise to the ligand

(1mmole) dissolved in 10 mL of a EtOH-H₂O solution (25% by volume) The mixture was heated at 40° C with constant stirring until it was concentrated to *ca.* 5 mL. The resulting precipitate was filtered and washed several times with ethanol/water and dried over P_2O_5 in a desiccator. The complexes were purified by recristalization from diethyl ether.

RESULTS AND DISCUSSION

The analyses of the complexes, summarized in Table I, are consistent with the stoichiometry proposed with the exception of the Mn(II) complexe with 2-OH acetophenone ethylenediimine is found to have a 1:2 metal to ligand ratio. All of the prepared complexes are highly stable at room temperature. They are insoluble in water but soluble in common organic solvents such as ethanol, methanol, chloroform, dimethylsulfoxide and dimethylformamide. The conductivity data of the complexes in 10^{-3} M DMF solutions indicate that they are non-electrolytes.

Infrared Spectra

The ligands coordination sites which are involved in bonding with the metal ions have been determined by careful comparison of the infrared absorption spectra of the complexes with those of the parent ligands (Table II). In the IR spectra of [MnL¹(H₂O)₂].0.5H₂O, [MnL³(H₂O₂)₂].H₂O, and [CuL²].H₂O a broad shoulder absorption in the range 3600-3450 cm^{-1} is observed indicating the presence of hydration water in the complexes². A weak shoulder at around 3150 cm⁻¹ in the spectra of $[MnL^{1}(H_{2}O)_{2}].0.5H_{2}O$ and $[MnL^{3}(H_{2}O_{2})_{2}].H_{2}O$ is attributable to the coordinated water¹³. The weak band at 3070 cm⁻¹ is assigned to the hydroxyl vibration of the phenolic group¹⁴, suggesting that the nondeprotonated ligand is coordinated in a bidentate manner to the metal by the two nitrogen atoms of the azomethine group. The v(OH) band corresponding to the two hydroxy groups present in the Schiff bases disapears in all of the manganese(II) and copper(II) complexes with the exception of the ligand in $[Mn(H_2L^2)L^2]$. This means that the Schiff bases have been deprotonated and act as dianionic ligands. Also the band corresponding to the imine group, C=N, is shifted by 20-40 cm⁻¹ to lower frequency in the complexes^{15, 16}. The v(C-N) mode is also shifted by 20-60 cm⁻¹ to lower frequency in the complexes¹⁷. The bands originating from the C-O stretching vibrations exhibit a large shift to higher freqency in the Mn(II) and Cu(II) complexes¹⁴. The new non-ligand bands appearing between 590-430 cm⁻¹ may be assigned to v(M-O) and v(M-N) vibrations^{18,19}. These observations are in accord with the

COMPLEXES WITH TETRADENTATE SCHIFF BASE LIGANDS

Compound	F.wt	Colour	Yield	1 M.p.			Found (Calc.)(%)		
			(%)	(°C)	С	н	N	м	H_2O^3	$\Lambda^{\mathfrak{h}} \text{ in }$
										DMF
$H_2L^1=C_{16}H_{16}N_2O_2$	268.3	light yellow	65	120	71.0	6.2	10.5	-	-	-
					(71.6)	(5.9)	(10.4)	-	-	-
$H_{2}L^{2} = C_{18}H_{20}N_{2}O_{2}$	296.3	vellow	63	127	73.1	69	9.6	-	-	-
					(72.9)	(6.7)	(9.4)	-	-	-
$H_2L^3 = C_{20}H_{24}N_2O_2$	324.4	vellow orange	60	135	74.5	7,5	91	-	-	-
					(74-0)	(7.4)	(8.6)	-	-	-
$[Mn(L^1)(H_2O)_2].0.5H_2O$	366-2	dark brown	65	290	53.0	5.0	7.7	152	2.3	31
$C_{16}H_{19}N_2O_4 < Mn$					(52.4)	(52)	(7.6)	(15.0)	(2.3)	
$[MnL^2(H_2L^2)]$	645.5	dark green	60	190	67.4	6.3	9.2	8.7	-	30
C36H38N4O4Mn					(66.9)	(5.9)	(8,7)	(85)		
{MnL ³ (H ₂ O) ₂] H ₂ O	430.9	dark brown	65	28 0	56.0	6.5	6.6	13.1	4.6	29
C ₂₀ H ₂₇ N ₂ O ₅ Mn					(55.7)	(6.5)	(6.5)	(12.7)	(4.1)	
[CuL ¹]	329.5	dark green	85	315	57.9	4.2	8.5	18.6	-	8
$C_{16}H_{14}N_2O_2Cu$					(58.2)	(4.2)	(8.4)	(192)		
[CuL ²].H ₂ O	375.5	light brown	85	286	57.5	5.2	7.4	17.3	4.8	10
C18H20N2O3Cu					(57.5)	(5.3)	(74)	(16 9)	(47)	
[CuL ³]	385.5	dark green	80	192	65.8	6.2	6.7	16-1	-	7
C20H22N2O2Cu					(66 2)	(5.7)	(72)	(16-4)		

Table I. Characteristic and Analytical Data of the Ligands. Manganese(II) and Copper(II) Complexes

*lattice water, bin ohm 1 cm2 mol-1

coordination of the metal to the Schiff base through the two azomethine nitrogens and the two phenolic oxygens.

Magnetic Measurements and Electronic Spectra

Both of the room temperature magnetic moments corrected for diamagnetism, the electronic spectral data and the assignements are given in Table III. Manganese(II) complexes are high-spin although the room temperature magnetic moments are lower than the spin-only. value for the S = 5/2 state. The low moments in these complexes

Compound	ν(OH) '	v(OH) '	v(OH) ^b	v(C=N)	v(C-N)	v(C–O)	v(MO)	v(M-N)
H_2L^1	-	-	3050 w	1636 s	1283 s	1042 m	-	-
H_2L^2	-	-	3054 w	1613 s	1292 s	1049 m	-	-
H_2L^3	-	-	3065 w	1611 s	1294 s	1065 m	-	-
$[MnL^{1}(H_{2}O)_{2}] = 0.5H_{2}O$	3453 m	3200 m	-	1599 s	1250 sh	1082 m	588 w	467 w
$[MnL^2(H_2L^2)]$		- -	-	1597 s	1236 sh	1098 m	525 w	448 w
$[MnL^{3}(H_{2}O)_{2}]H_{2}O$	3600 m	3100 m	-	1580 s	1246 m	1128 m	485 w	460 w
[CuL ¹]	-	-	-	1597 s	1233 s	1086 s	467 w	440 w
[CuL ²].H ₂ O	3570 m	-	-	1588 s	1238 s	1092 s	467 w	440 w
[CuL ³]	-	-	-	1584 s	1253 m	1098 s	453 w	432 w

Table II. Relevant IR Data (cm⁻¹) of the Ligands and Complexes

a - aqua; b - phenolic; m = medium; sh - shoulder; s = strong; w - weak

Table III. Magnetic and Electronic Spectral Data of the Manganese(II) and Copper(II) Complexes

μ_{eff}	Electronic transitions ^b $(\epsilon)^{c}$
5.75	15748 (175) 25000 (5148)
5.25	17390 (150) 25640 (2322)
5.73	20000 (130) 25640 (1200)
t.92	15500 (396) 18000 (461)
1.89	15600 (340) 18500 (432)
1.85	16120 (3 65) 18500 (445)
	μeff 5.75 5.25 5.73 1.92 1.89 1.85

a: magnetic moment in Bohr magnetons

b: wave number in cm⁻¹

c: absorption molar coefficient in mol⁻¹. L. cm⁻¹

may reveal an antiferromagnetic interaction in the complexes in the solid state and/or a slight contamination by Mn(III) impurity. The room temperature magnetic moments of the copper(II) chelates are in the range 1.85-1.92 B. M. (Table III). These are essentially due to spin-only values and are characteristic of square-planar symmetry around copper(II)^{17,20}. The values are consistent with an orbitally non-degenerate ground state for copper(II) and indicate that the complexes are mononuclear in nature^{7,20}.

The electronic spectra of manganese(II) complexes recorded in DMF gave three absorption bands: two high intensity absorptions in the near UV region²¹, the first at 38,000 cm⁻¹ which is due to the intraligand $\pi \rightarrow \pi^*$ transition associated with the benzene ring, the second intraligand $\pi \rightarrow \pi^*$ transition around 31,200 cm⁻¹ is associated with the azomethine group. The third intraligand band which is less intense than the $\pi \rightarrow \pi^*$ transitions is assigned to the $n \rightarrow \pi^*$ transition and occurs at around 29,400 cm⁻¹. The same intraligand bands are observed for the copper(II) complexes, with the exception of the $\pi \rightarrow \pi^*$ transition associated with the azomethine group, which is not observed. The high-spin octahedral manganese(II) complexes have a ⁶A_{1g} ground state, the only sextuplet of spin state, hence no allowed d-d transitions are expected. The absorption bands between 15,000 and 25,000 cm⁻¹ may be assigned to metal-ligand charge-transfer transitions²². In the visible region, the electronic spectra of the copper(II) chelates displayed two shoulders. The first shoulder at around 15,600 cm⁻¹ is due to the ¹B_{1g} \rightarrow ¹B_{2g} transition. The second one at 18,000 cm⁻¹ is assigned to ²B_{1g} \rightarrow ²Eg transition. These bands are reported to be characteristic of square-planar or tetragonallydistorted symmetry^{14,17,20}

Electron Spin Resonance Spectra

X-band ESR spectra of the polycrystalline powder and in DMSO solution at 298 K of the manganese complexes are of isotropic hyperfine structure (Fig. 2). The spectra consist of six equally spaced hyperfine interactions (I = 5/2) and are of monomeric type spectra.

A not so well resolved super-hyperfine structure consisting of five lines is observed in the ESR spectrum of $[MnL^{3}(H_{2}O)_{2}].H_{2}O$. This super-hyperfine structure is attributable to the interaction of manganese(II) with two nitrogen nuclei ($I_{N} = 1$). This supports the coordination of the Schiff base through the two azomethine nitrogen atoms²³. The g values and the nuclear coupling constants A₀ and a_N values have been obtained and are given in Table IV.

The room temperature ESR spectra of powder samples of the copper(II) complexes are of the simple anisotropic type for mononuclear species with axial symmetry (Fig. 3).

The g_{d} and g_{d} parameters are summarised in Table V. The trend $g_{d} > g_{c} > g_{c} (2.0023)$ observed in



Fig. 2. ESR Spectrum of [MnL³(H₂O)₂].H₂O in DMSO Solution at Room Temperature

Table IV. ESR Spectral Data of the Manganese(II) Complexes

Complex	g ₀	A ₀ (G)	\mathbf{a}_0
$[MnL^{1}(H_{2}O)_{2}] 0.5H_{2}O$	1 992	104	-
$[MnL^{2}(H_{2}L^{2})]$	2.002	98	-
$[MnL^{3}(H_{2}O)_{2}].H_{2}O$	2.004	95	15



Fig. 3. ESR Spectrum of [CuL³] Powder at Room Temperature

Complexes

F				
Complex	g	g⊥	$\alpha^2 \beta_1^2$	$\alpha^2 \beta^2$
[CuL ¹]	2.206	2.053	0.504	0.556
[CuL ²].H ₂ O	2.158	2.039	0.392	0.410
[CuL ³]	2.150	2.032	0.372	0.332

Table V. ESR Spectral Data and Bonding Parameters of the Copper(II)

these complexes shows that the unpaired electron is in the d_x^{2-2} orbital of copper(II)²⁴. The present ESR results (see Table V) show that g_{μ} is less than 2.3 in all cases suggesting that the copper complexes are covalent in nature; they also show that $g_{i} = 2.206-2.150$ which is in conformity with the presence of mixed copper-nitrogen and copper-oxygene bonds in these chelates²⁰. The ESR spectra of the copper complexes in CH₃Cl solution are isotropic with an hyperfine structure and consist of four equally spaced hyperfine groups resulting from the interaction of an unpaired electron with the nuclear spin I = 3/2. The isotropic hyperfine coupling constant A₀ is obtained from the solution spectra and is equal to 98 Gauss. The hyperfine lines are split into five super-hyperfine lines which are partially resolved in the case $[CuL^2]$, H₂O and [CuL³]. The super-hyperfine structure is attributable to the interaction of the unpaired electron of the copper ion with two nitrogen nuclei $(I_N = 1)$. The a_0 constant is about 15 G in the case of [CuL²].H₂O and [CuL³]. The expressions for g_{μ} and g_{μ} gave values of $\alpha^2 \beta_1^2$ and $\alpha^2 \beta^2$, where α and β_1 represent in-plane σ and π bonding, respectively, and β represents out-of-plane π bonding. The magnitudes of $\alpha^2 \beta_1^2$ and $\alpha^2 \beta^2$ presented in Table V are a measure of the combined σ and π covalent bonding effects and lie between 1.0 and 0.25 representing the values of 100 % ionic and covalent character, respectively. They are indicative of a considerable in-plane and a very small out-of-plane covalent character of the metal-ligand bonds in the copper(II) complexes. By examining the trend of the $\alpha^2 \beta_1^2$ and $\alpha^2 \beta^2$ values obtained one may conclude the following. It may be seen that the covalent character in the copper(II) complexes with the alkyl substituted ligands should increase in the order of substituents $H < CH_3 < C_2H_5$. This order satisfactorilly correlates with the increasing order of the donor inductive effect.

In view of the above results, the following schemes may be proposed for the complexes. For the manganese(II) complexes (Figs. 4a, b) the environment of the metal ion is a pseudo-octahedron in which the ligands are bonded in a tetradentate manner in the case of $H_2L^{1.3}$, the other sites being occupied by water molecules or by another ligand molecule in the case of H_2L^2 . In the copper(II)



Fig. 4. Structural Scheme for the Complexes (a) Mn-H₂L^{1, 3} and (b) Mn-H₂L²

complexes (Fig. 5) the ligands are bonded to the metal ion through phenolic oxygens and imine nitrogens providing a square-planar geometry.

Cyclic Voltammetry

The electrochemical behaviour of the present manganese(II) and copper(II) complexes are illustrated by cyclic voltammograms which were obtained in DMSO solution from ± 0.7 to -1.6 V (vs. SCE) Coulometric measurements revealed that in each of the processes one electron is transfered Schiff base ligands H₂L¹⁻³ undergo a one-electron cathodic process which may be attributed to the reduction of the imine group (Table VI). The cyclic voltammogram of MnCl₂ shows an irreversible Mn(II)-Mn(I) couple with $E_c = -1.150$ volt. On the other hand, the cyclic voltammogram of CuCl₂ shows two irreversible reduction processes (Table VI) and a single anodic peak at ± 0.640 Volts without any associated cathodic response. The electrochemical data on the reduction of the two sets of complexes at a sweep rate of 0.1 Vs⁻¹ are given in Table VI. Each complex exhibits one reduction process in the cyclic



Fig. 5. Structural Scheme of the Cu-H₂L¹⁻³ Complexes

Table VI. Electrochemical Data for the Reduction of the Ligands, $MnCl_2$, $CuCl_2$ and Mn(II), Cu(II) Complexes^a in 0.1M TBAP in DMSO

Compound	$E_{pc}(V)$	$E_{pa}(V)$	$\Delta E(V)$
H_2L^1	-1.400	-1.000	-0 400
H_2L^2	-1.380	-0.830	-0 550
H_2L^3	-1.300	-0.610	-0.690
MnCl ₂	-1.150	-0.750	-0,400
CuCl ₂	-0.320	0.140	-0.460
	-0.960	-0.380	0 560
$[MnL^{1}(H_{2}O)_{2}].0.5H_{2}O$	-1.010	-0.580	0.430
	-1.420	-1.050	0.370
$[MnL^2(H_2L^2)]$	-1.180	-0.570	0 550
	-1.400	-0.920	0.480
$[MnL^{3}(H_{2}O)_{2}]H_{2}O$	~1.200	-0.540	0.660
	-1.380	-0.850	0.530
[CuL ¹]	-1:020	-0.630	0.390
	-1.430	-1.080	0.350
$[CuL^2]$ H ₂ O	-0.800	-0.420	0.380
	-1.420	-0.880	0.540
[CuL ³]	-0.710	-0.400	0.310
	-1 350	-0.700	0 650

^aSolute concentration = 10^{-3} M; scan rate = 100 mV/s; E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively, $\Delta E = E_{pa} - E_{pc}$.



Fig. 6. Cyclic Voltammogram of [MnL²(H₂L²)] in DMSO (0.1 M TBAP); Scan Rate = 100 mV

voltammograms, in addition a reduction wave is observed within the limits of the potential range studied for the complexes. By comparing the cyclic voltammograms of the manganese and copper complexes to those of MnCl₂.4H₂O and CuCl₂.6H₂O respectively, taken as references with those of the ligands, a cathodic process (see Figs. 6 and 7) could be assigned to the reduction of Mn(II) to Mn(I). The additional reduction obtained in the case of all the complexes should correspond to a ligand-centered reduction^{6.25}. The metal-centered reduction for all the complexes is in agreement with an irreversible electron transfer. Further, the reduction waves given by the voltammograms with the cathodic scan are of low or medium intensity. But in the anodic domain the peak related to the cathodic waves are of medium or high intensity. This reveals that on cathodic reduction the electrode process may be complicated by a chemical reaction^{26, 27}. It was noted in this study that the reduction potentials for the Mn(II/I) couple of the complexes are slightly sensitive to the electronic effect of the R group on the coordinated ligand. These potentials shift cathodically on going from Mn-H2L¹ to $Mn-H_2L^3$. As the substituent R in the ligand is varied from H to C_2H_5 , the electron density on the manganese ion increases and this increases slightly the difficulty of reducing the metal center²⁸. We have observed in our present study on Cu(II) with the same ligands that Cu(I), which favors a tetrahedral geometry²⁹, is more stabilized as the R groups in the complexed



Fig. 7. Cyclic Voltammogram of [CuL³] in DMSO (0.1 M TBAP); Scan Rate = 100 mV

Table VII. Electrochemical Data for the Oxidation of the Mn(II) Complexes^a in 0.1 M TBAP in DMSO

Compound	E _{pa} (V)	$E_{pc}(V)$	ΔE (V)
$[MnL^{1}(H_{2}O)_{2}].0.5H_{2}O$	-0.180	-0.530	0.350
$[MnL^2(H_2L^2)]$	-0,160	-0 500	0.340
$[MnL^{3}(H_{2}O)_{2}]H_{2}O$	-0.120	-0 450	0.330

^aSolute concentration = 10^{-3} M; scan rate ~ 100 mV/s; E_{pe} and E_{pa} are the cathodic and anodic peak potentials, respectively; $\Delta E = E_{pa} - E_{pc}$

ligands are changed from H to C_2H_5 because the distortion of the unit CuN_2O_2 in the complexes increases in the same order. The reduction potentials in the case of the manganese complexes are not sensitive to steric effects of the substituent R in the ligand because there is not a significant structural change between the oxidized (3d⁵) and reduced (3d⁶) species³⁰.

Potential values of the oxidation process of Mn(III/II) are summarized in the Table VII. They suggest an irreversible process for each complex³¹⁻³⁴. The opposite of the reduction process, the

oxidation of the metal center in the complexes is facilitated on going from hydrogen to ethyl. The electrochemical results for the oxidation of the copper(II) complexes showed one irreversible couple at around +0.500 volt vs SCE and is assigned to the Cu(III/II) charge transfert. This result indicates that the oxidation of the copper(II) complexes is not very sensitive to the electronic effect of the ligands. This suggest that there is not a significant structural change between the oxidized $(3d^8)$ and reduced $(3d^9)$ species.

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