Synthesis and Electrochemistry of M(II) N₂O₂ Schiff Base Complexes: X-Ray Structure of {Ni[Bis(3-chloroacetylacetone)ethylenediimine]}

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The synthesis and characterization of [Ni(BCE)] and [Cu(BCE)] (where BCE = bis(3-chloroacetylacetone)ethylenediimine) are described. The coordination geometry of [Ni(BCE)] was determined by X-ray crystallography. It was found to be planar and four coordinate in the solid state. The electrochemical properties of M(Chel), where M = Co(II), Ni(II) and Cu(II), and Chel = BAE (bis(acetylacetone)ethylenediimine), BBE = bis(benzoylacetone)ethylenediimine, BFE (bis(1,1,1-triflouroacetylacetone) ethylenediimine and BCE ligands were investigated in DMF and DMSO as solvents. The oxidation potentials changed from left to right in the periodic table in the trend: Co < Ni < Cu, while the reduction potentials changed according to the trend: Ni > Co > Cu. The oxidation potentials of M(II) to M(III) (M = Ni and Cu) increased according to the Schiff base ligands in the trend: BAE < BBE < BCE < BFE, while the reduction potentials followed a reverse trend: BAE > BBE > BCE > BFE. The oxidation potentials of M(II) to M(III) increased according to the solvent in the trend: DMSO < DMF.

INTRODUCTION

Schiff bases have been widely used as ligands because of the high stability of coordination compounds with different oxidation states. The π-system in a Schiff base often imposes a geometrical constriction and affects the electronic structure as well. Transition metal Schiff base complexes have been studied as catalysts in organic redox and electrochemical reduction reactions [1-4]. Cyclic voltammetry has been a useful instrument to study the mechanisms of the catalysis property of metal Schiff base complexes and their reactivity [2,4-5]. To explore the catalytic activity, the electrochemical properties of Co(III) BAE and Salen Schiff base complexes were studied intensively [6-12]. Also, the electrochemical

properties of tetradentate Ni(II) and Cu(II) Schiff base complexes were investigated [13-19]. The Ni(I) complexes can act as powerful catalysts on chemical or electrochemical reduction of alkyl and aryl halides [15,20]. Also, the Ni(I) and Ni(III) oxidation states play a crucial role in the activity of several hydrogenase reactions [21]. The electronic effects of the different Schiff base complexes with different donor and acceptor functional groups were studied by cyclic voltammetry method. The results show that there is a good relationship between the electron-donating power of Schiff base ligands and redox potentials [19,22-24].

In the present work, we report the synthesis and characterization of [Ni(BCE)], and [Cu(BCE)]. The electrochemical properties of Co(II), Ni(II) and Cu(II) complexes with tetradentate BAE Schiff base ligands (Fig. 1)

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Kianfar *et al*.
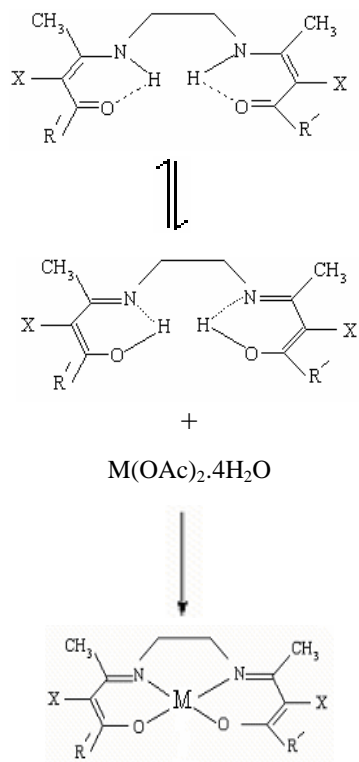
Chel	R'	X	M
BBE	Ph	H	Co, Ni and Cu
BAE	CH₃	H	Ni, Cu
BFE	CF₃	H	Ni, Cu
BCE	CH₃	Cl	Ni, Co

Fig. 1. The structure of Schiff bases and M(Chel) complexes.

in DMF and DMSO as solvents were studied. The crystal structure of [Ni(BCE)] complex is also reported

EXPERIMENTAL

Chemicals and Apparatus

All the chemicals and solvents were used as received, except for the 3-chloroacetylaceton which was distilled to be used. All the Schiff base ligands were prepared using the known methods [12,26-28]. The M(II) BAE, BBE and BFE complexes were prepared following the literature procedure [26]. The elemental analyses were determined on a Heraeus CHN-O-RAPID elemental analyzor. Infrared spectra were

recorded as KBr discs on a Perkin Elmer 781 spectrophotometer in the 4000-400 cm^{-1} range. UV-Vis spectra were recorded on a JASCO V-570 spectrophotometer in the 190-900 nm range.

Cyclic Voltammetric measurements were carried out under argon in DMF and DMSO solutions with 0.1 M tetraethylammonium perchlorate as the supporting electrolyte at room temperature using an autolab modelar electrochemical system (ECO Chemie, Ultrecht, The Netherlands) equipped with a PSTA 20 module and driven by GPES (ECO Chemie). A conventional three electrode cell was used with an Ag/AgCl (saturated KCl)/3 M KCl reference electrode, a Pt wire as counter electrode and a glassy carbon electrode as working electrode.

X-Ray analysis. The X-ray crystallography measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo-K$_\alpha$ radiation. For this complex, a yellow plate crystal with dimensions $0.34 \times 0.207 \times 0.07$ mm was chosen and mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 3763 unique reflections. Data were collected at a temperature of 298(2) K to a maximum 2θ value of 58.46° in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [29] software package. The numerical absorption coefficient, μ, for Mo-K$_\alpha$ radiation was 1.752 mm^{-1}. A numerical absorption correction was applied using X-RED [30] and X-SHAPE [31] softwares. The data were corrected for Lorentz and Polarizing effects. The direct method structure solution [32], different Fourier calculations, and full-matrix least-squares refinement against F^2, were performed using X-STEP32 crystallographic software package [33]. All hydrogen atoms were included in the structure factor calculations at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Atomic factors were used from the International Tables for X-ray Crystallography [34]. Crystal data and the details of data collection and refinement are summerized in Table 1.

Synthesis of the [Ni(BCE)] Complex

Nickel(II) acetate tetrahydrate (1 mmol, 0.2487 g) was added to a refluxed solution of BCE (1 mmol, 0.2933 g) Schiff

Synthesis and Electrochemistry of M(II) N_2O_2 Schiff Base Complexes

Table 1. Crystallographic and Structure Refinements Data for [Ni(BCE)] Complex

Formula	$C_{12}H_{16}Cl_2N_2NiO_2$
Formula weight	349.86
Temperature (K)	298(2)
Wavelength λ (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal size (mm^3)	0.34×0.27×0.07
a (Å)	7.6872(15)
b (Å)	8.8196(18)
c (Å)	11.912(2)
α (°)	69.11(3)
β (°)	73.12(3)
γ (°)	72.87(3)
Volume (Å^3)	705.3(2)
Z	2
Density (calcd.) (g cm^{-1})	1.647
θ ranges for data collection	1.87-29.23
F(000)	360
Absorption coefficient	1.752
Index ranges	$-10 \leq h \leq 10$
	$-11 \leq k \leq 12$
	$-15 \leq l \leq 16$
Data collected	8487
Unique data (R_{int})	3763, (0.0464)
Parameters, restrains	176, 0
Final R_1, wR_2[a] (Obs. data)	0.0477, 0.1262
Final R_1, wR_2[a] (All data)	0.0542, 0.1317
Goodness of fit on F^2 (S)	1.046
Largest diff peak and hole (e Å^3)	0.380, -0.571

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$

base ligand disolved in 40 ml methanol. Green precipitates appeared immediatelly. The mixture was refluxed for 1 h, then allowed to cool at room temperature. The resulting solid was collected, washed with methanol and then recrystalized from acetone-water. Yield (82%). Anal. Calcd. for [Ni(BCE)], ($C_{12}H_{16}Cl_2N_2O_2Ni$): C, 41.18; H, 4.61; N, 8.00. Found: C, 41.25; H, 4.54; N, 8.16%. IR; v (C=N) 1561 cm^{-1}, v (C=C)

1461 cm^{-1}, λ_{max} (ε, M^{-1} cm^{-1}) 365 (4800), 381 (5500), 417 (31000), 576 (130).

Synthesis of the [Cu(BCE)] Complex

Copper(II) acetate tetrahydrate (1 mmol, 0.2535 g) was added to a refluxed solution of BCE (1 mmol, 0.2933 g) Schiff base ligand disolved in 40 ml methanol. Green precipitates appeared immediatelly. The mixture was refluxed for 1 h, and then allowed to cool to room temperature. The resulting solid was collected and washed with methanol. Yield (82%). Anal. Calcd. for [Ni(BCE)], ($C_{12}H_{16}Cl_2N_2O_2Cu$): C, 40.62; H, 4.51; N, 7.89. Found: C, 40.87; H, 4.57; N, 8.06%. IR; v (C=N) 1564 cm^{-1}, v (C=C) 1425 cm^{-1}, λ_{max} (ε, M^{-1} cm^{-1}) 322 (19300), 344 (8400), 546 (220).

RESULTS AND DISCUSION

Infrared and Electronic Spectra

A keto amine structure (Fig. 1) for Schiff base ligands was proposed which showed that the hydrogen atom was bonded to both oxygen and nitrogen (NH/OH) [35-38]. A medium v (NH/OH) was observed in the range of 3070-3200 cm^{-1} and disappeared in the spectra of the complexes. The band corresponding to the azomethine group (C=N) occurred within 1550-1630 cm^{-1}, while the C=C absorption was seen at about 1450-1550 cm^{-1} [35].

The electronic spectra showed that absorption bands of all the Ni(II) complexes occurred below 600 nm. Lack of any electronic transition at longer wavelengths indicated a large crystal-field splitting which was consistent with the square planar geometry of Ni(II) complexes. The apearance of the band about 550 nm in the absorption spectra was consistent with the square planar geometry of Cu(II) complexes [7,39,40].

Description of the structure of [Ni(BCE)]. The complex [Ni(BCE)] crystallized in the triclinic space group $P\bar{1}$. The coordination geometry of the title compound is shown in Fig. 2 and the bond distances and angles are presented in Table 2. As expected, the two six-membered chelates were planar and the angle between the mean planes of the two rings were 4.7(1)°. The angles O(1)-Ni(1)-N(2) = 176.88(9)° and O(2)-Ni(1)-N(1) = 177.01(9)° indicate that the coordination geometry of the nickel atom is planar. The Ni-O distances of
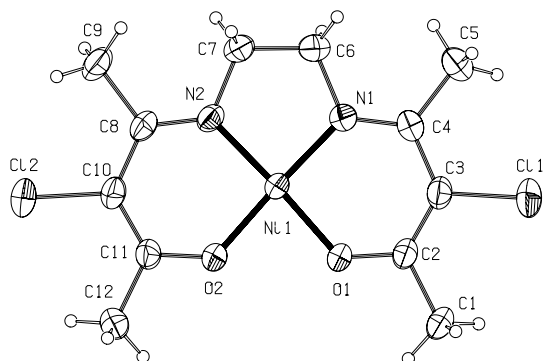
Kianfar *et al*.

Fig. 2. The labeled diagram of [Ni(BCE)] complex. Thermal ellipsoids are at 30% probality level.
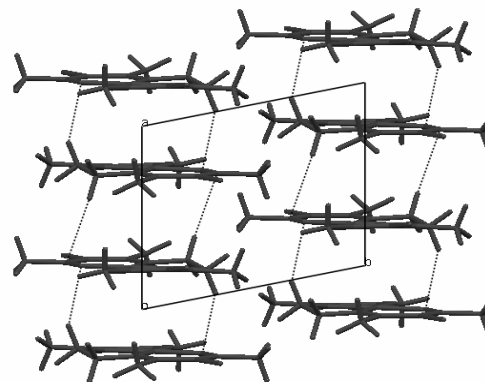

Fig. 3. Crystal packing diagram for [Ni(BCE)] complex in *c*-direction.

Table 2. Selected Bond Distances (Å) and Bond Angles (°) for [Ni(BCE)] Complex

Bond distances		Bond angles	
Ni1-O1	1.845(2)	O1-Ni1-O2	82.91(9)
Ni1-O2	1.842(2)	O1-Ni1-N1	94.37(10)
Ni1-N1	1.853(2)	O1-Ni1-N2	176.88(9
Ni1-N2	1.850(2)	N1-Ni1-N2	88.70(11)
O1-C2	1.290(3)	N1-Ni1-O2	177.01(9)
N1-C4	1.322(4)	N2-Ni1-O2	94.01(10)
N1-C6	1.470(4)	N1-C6-C7	110.6(3)
N2-C7	1.465(4)	N2-C7-C6	111.4(2)
C2-C3	1.362(4)	N1-C6-C7-N2	20.1(4)
C3-C4	1.422(4)		
C6-C7	1.494(5)		

1.845(2) Å and 1.842(2) Å for Ni(1)-O(1) and Ni(1)-O(2) respectively are very close to the corresponding values in the related structures [41]. However, the Ni-N distances of 1.853(2) Å and 1.850(2) Å for Ni(1)-N(1) and Ni(1)-N(2), respectively are significantly shorter than that of a related complex (1.910(4) Å [41,42]. The measured N-C, C-C and C-O bond distances in the six-membered rings of this complex (Table 1) are very close to the values 1.306(5), 1.361(6), 1.413(7) and 1.297(4) Å reported for a related nickel(II)

complex, showing that the enaminoketonate ion is partially delocalized [41,42]. The five-membered rings defined by the nickel atom and diaminoethane moiety are definitely nonplanar, the ethylene bridges have a gauche conformation as usually observed, with torsion angle of 20.1(1)° for N(1)-C(6)-C(7)-N(2). As can be seen from the packing diagram of [Ni(BCE)] complex (Fig. 3), there are some C-H…O [H6a…O2^i = 2.53(2), C6...O2^i = 3.365(5) Å and C6-H6a...O2^i = 144.0(5)°, symmetry code(i) -x, 2-y, 1-z] short contacts

911

which are effective in the stabilization of the lattice.

The Electrochemical Properties of the Studied Complexes

The electrochemical investigation of the N_2O_2 Schiff base complexes studied here can be divided into two parts, based on their potential range (Tables 3 and 4). The oxidation process is in the range of 0.9 to 1.8 V. With a quick glance at the data in Tables 3 and 4, one can gather that a one-electron quasi-reversible or irreversible oxidation will occur. The reversibilities increased in DMSO solvent. The reduction process happened in the range of -1.00 to -2.20 V. The

electrochemical data for this range were also in agreement with the one-electron process. The process was quasi-reversible for Co(II) and Ni(II), while the Cu(II) complexes showed an irreversible reduction process. Multiple scans resulted in nearly superposable cyclic voltammograms showing that the four coordinated geometries were stable in both oxidation states at least on the cyclic voltammetry time scale.

The Oxidation of M(II) to M(III)

The cyclic voltammetric curves for the electrochemical oxidation of the studied M(II) complexes (Tables 3 and 4)

Table 3. Redox Potentials of $[M^{II}(Chel)]$ in DMF Solution

NO	M^{II}	Chel	$E_{pa}(II \rightarrow III)$	$E_{pc}(III \rightarrow II)$	$E_{pa}(I \rightarrow II)$	$E_{pc}(II \rightarrow I)$	$E_{1/2}(II \leftrightarrow I)$
1	Co	BBE	0.218	0.097	-1.550	-1.700	-1.625
2	Ni	BAE	0.909	_	-1.849	-2.021	-1.935
3	Ni	BBE	0.915	_	-1.763	-1.907	-1.835
4	Ni	BCE	1.032	_	-1.629	-1.780	-1.705
5	Ni	BFE	1.266	0.862	-1.334	-1.446	-1.390
6	Cu	BAE	0.973	-	-	-1.596	-
7	Cu	BCE	1.021	-	-	-1.358	-
8	Cu	BBE	0.999	-	-	-1.467	-
9	Cu	BFE	1.511	-	-0.961	-1.133	-1.047

Table 4. Redox Potentials of $[M^{II}(Chel)]$ in DMSO Solution

NO	M^{II}	Chel	$E_{pa}(II \rightarrow III)$	$E_{pc}(III \rightarrow II)$	$E_{pa}(I \rightarrow II)$	$E_{pc}(II \rightarrow I)$	$E_{1/2}(II \leftrightarrow I)$
1	Co	BBE	0.077	-0.070	-1.487	-1.617	-1.552
2	Ni	BAE	0.846	0.676	-1.785	-2.016	-1.901
3	Ni	BBE	0.914	0.685	-1.715	-1.878	-1.797
4	Ni	BCE	0.912	0.784	-1.606	-1.840	-1.723
5	Ni	BFE	1.050	0.741	-1.273	-1.446	-1.360
6	Cu	BAE	0.897	-	-1.337	-1.606	-1.472
7	Cu	BCE	1.052	-	-1.101	-1.345	-1.223
8	Cu	BBE	0.979	-	-	-1.426	-
9	Cu	BFE	1.499	-	-0.952	-1.111	-1.032

Kianfar *et al*.

exhibit a redox couple at potentials in the range of 0.21 to 1.51 V in DMF and 0.07 to 1.63 V in DMSO, which can be atributed to the oxidation of the metal center [43,44]. The Co(BBE) complex exhibits a quasi-reversible oxidation of Co(II) to Co(III) (Fig. 4). The cyclic voltammograms of the Ni(II) complexes with BAE, BBE, BFE and BCE Schiff base ligands were recorded in DMF and DMSO. In the DMF solvent, the voltammograms of Ni(BFE) complex consist of a quasi-reversible redox couple while BAE, BBE and BCE complexes consist of a single anodic redox, and no cathodic wave occurs in the reverse scan. In the DMSO solvent, the N(II) complexes consist of a quasi-reversible redox couple. The voltammograms of Cu(II) complexes consist of a single anodic redox at the potential range of 1.03 to 1.63 V, and no cathodic wave occurs in the reverse scan in DMF and DMSO solvents.

The Effect of Metal Ions on Oxidation Potentials

The voltammograms were recorded for M(II) (M = Co, Ni and Cu for BBE; Ni and Cu for other Schiff bases) complexes. The oxidation potentials of BBE complexes (E_{pa}) of M(II) → M(III) increased from left to right across a period in the trend of Co(II) << Ni(II) < Cu(II) by increasing the effective nuclear charge (Tables 3-4). Other Schiff bases show the same trend for Ni(II) and Cu(II) complexes.

From Tables 3 and 4, it could be inferred that the Co(II)BBE was oxidized in the range 0.07-0.21 V, while the Ni(II) and Cu(II) complexes were oxidized at about 0.84 V and higher potentials. The electrochemical studies of cobalt(II) Salen type Schiff bases showed that the major species in the solution were Co(Schiff baes)(Solvent)$_2$ in DMF and DMSO [6,8]. The following redox reaction is proposed for Co(II) BBE complex in dimethylformamide [12,23-25].

$$Co^{II}(BBE)(Solvent)_2 \rightleftharpoons Co^{III}(BBE)(Solvent)_2^+ + e^- \tag{5}$$
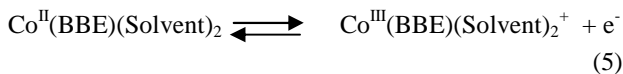
The Ni(II) and Cu(II) complexes with BAE ligands were oxidized in DMF and DMSO by a one-electron metal centered process to six-coordinate M(III) species formulated as $[M^{III}L(Solvent)_2]^+$ (where L = the Schiff bases studied in this work) acoording to the redox reaction of:
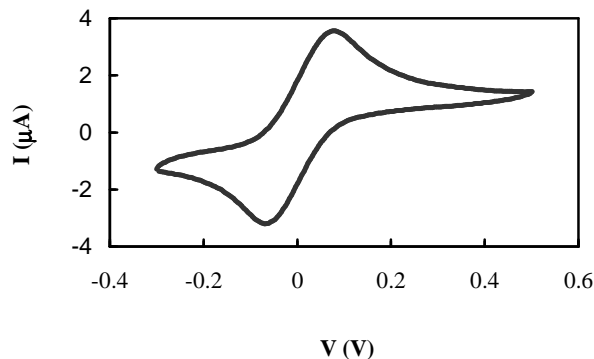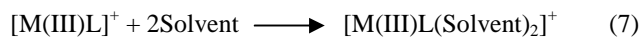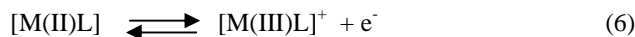

Fig. 4. Cyclic voltammograms of [Co(BBE))], in DMSO at room temperature. Scan rate: 100 mV s^{-1}.

$$[M(II)L] \rightleftharpoons [M(III)L]^+ + e^- \tag{6}$$

$$[M(III)L]^+ + 2Solvent \longrightarrow [M(III)L(Solvent)_2]^+ \tag{7}$$

The oxidation of several N_2O_2 Schiff base Ni(II) complexes was shown to occur with a concomitant axial coordination of the solvent molecule which is rather decisive in the overall charge transfer process, as it controls the final oxidized products and $E_{1/2}$ values [16].

The Effect of Schiff Base Ligands on Oxidation of M(II) to M(III)

Aiming at evaluating the effect of equatorial substitutions on different oxidation states of metal Schiff bases, the tetradentate BAE and its derivatives were examined. The redox potentials of Schiff base complexes markedly depend on the Schiff base ligand and increase in the trend: BAE < BBE < BCE < BFE. As Tables 3 and 4 reveal, E_{pa} becomes more positive in the sequence of increasing electron-withdrawing effects of the substituents on the ligand. Similar results have been reported previously for copper(II) and nickel(II) Schiff base complexes and have been interpreted by assuming that the strong electron-withdrawing groups destabilize the higher oxidation state [23,24,40]. However, another possibility would be that, due to the decrease in the donor ability of the ligand groups, the stabilities of both M(II)L and [M(III)L]$^+$ decrease through the above-mentioned sequence but for the latter to a higher extent.

Reduction of M(II) to M(I)

The cyclic voltammograms for electrochemical reduction of the studied complexes (Tables 3 and 4 and Fig. 5) show a redox couple at the potentials in the range of -1.1 to -2.1 V which can be atributed to the reduction of metal center. The quasi-reversible redox couple of Co$^{II/I}$(BAE) and other cobalt(II) Schiff base complexes are not significantly influenced by the potentials of axial ligands which indicates that only four coordinate species are involved in the electrode reactions. For example, the E$_{1/2}$ value for Co(BBE) complex in this study is closer to those measured from [Co(BBE)(amine)$_2$]$^+$ [12] and [Co(BBE)(PBu$_3$)]$^+$ [25]. The quasi-reversible redox couple of Ni(II) complexes appear in more negative potentials relative to Co(II) complexes (Ref. [25] and Tables 3 and 4).

In the DMF solution, the voltammograms of Cu(II) complexes (except BFE) consist of a single cathodic redox, with no anodic wave occurring in the reverse scan. It is suggested that the Cu(I) species are unstable and undergo rapid decomposition to Cu(II)L. Here, such a reduction process should correspond to an irreversible electron transfer. In the case of BFE and other Schiff bases (except BCE) in DMSO solution, the voltamograms are quasi-reversible. The CF$_3$ electron withdrawing and the DMSO with higher acceptor number stabilized the Cu(I)L species.

The Effect of Schiff Bases on Reduction Potentials

Reduction potentials toward a given M(II) according to the Schiff base ligands changed in the trend: BAE > BBE > BCE > BFE. In contrast to the oxidation potentials, the BFE complexes with electron-withdrawing group were reduced at lower potentials. Similar results have been reported for analogous copper(II), Ni(II) and Co(II) systems and have been interpreted by assuming that the strong electron-withdrawing (with the best π-acceptor quality) effects stabilize the lower oxidation state while the electron-donating group (with the least π-acceptor quality) have a reverse effect. Therefore, the dependence of the M(II/I) couple on the nature of the equatorial ligand is due to the lower oxidation states that are better electron donors to the π* orbitals of Schiff base [15,19,23-24]. From the M(II/I) couples, the π-acceptor property of the studied BAE Schiff base derivatives is as
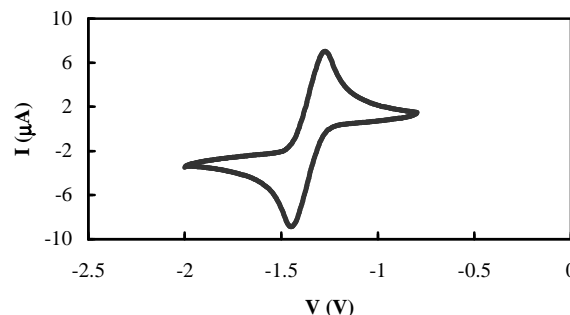

Fig. 5. Cyclic voltammograms of [Ni(BFE)], in DMSO at room temperature. Scan rate: 100 mV s^{-1}.

follows: BFE > BCE > BBE > BAE.

The Effect of Metals on Reduction Potentials

The voltammograms show that the trend of reduction potentials toward a given Schiff base (Tables 3 and 4), according to the M(II) is as follows: Ni(II) > Co(II) > Cu(II). The same trends were found for cobalt(II) and nickel(II) Salen complexes [13]. The reduction process of Ni(II) complexes occurs at more negative direction relative to other metal ions because d^8 is the best electron configuration for the square planar complexes, while the deviation from this electron configuration causes some instabilities in planar complexes with tetradentate Schiff base ligands [17,45]. The higher reduction potentials may arise from the deviations in the structure of nickel complexes by the reduction of Ni(II) to Ni(I) (d^8 to d^9 electron configuration).

The Solvent Effect

The electrochemical measurements were carried out on dimethylformamide and dimethylsolfoxide as solvents. The oxidation potentials decreased with increasing some reversibilities in DMSO solvent. The dimethylsofoxide with higher donor number (D. N. = 29.8 for DMSO and 26.6 for DMF) [46] was coordinated to the complexes and stabilized the M(III) cation. On the other hand, the reversibility of copper complexes increases in DMSO solvent. It seems that the stability of Cu(I) spices is increased by increasing the acceptor property of the solvent (A. N. = 19.3 for DMSO and 16.0 for DMF) [46].

914

CONCLUSIONS

The combination of spectral, structural and electrochemical measurements reveal the main features of the coordination and redox chemistry of the studied complexes. The coordination geometry around the Ni(II) in Ni(BCE) was planar. Electrochemical studies revealed that the oxidation and reduction processes of M(II) were irreversible or quasi-reversible and strongly influenced by the nature of the Schiff base ligands and metal ions. Some irreversible processes turned out to be quasi-reversible in the DMSO as solvent.

SUPPLEMENTARY MATERIAL

CCDC 724896 contains the supplementary crystallographic data for this paper. These data can be obtained at www.ccdc.cam.ac.uk/deposit {or from the Cambridge Crystallographic Data Center 12, Union Road Cambridge CB2 1EZ, UK; Fax: (internet) +44-1223/336-033; E. mail: deposit@ccdc.cam.ac.uk).

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