Inorganica Chimica Acta 388 (2012) 148-156

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Iron(III) and nickel(II) complexes of O,N,N,O-chelating benzophenone thiosemicarbazone: Electrochemistry and *in situ* spectroelectrochemistry

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ARTICLE INFO

Article history: Received 21 October 2011 Received in revised form 29 February 2012 Accepted 8 March 2012 Available online 22 March 2012

Keywords: Thiosemicarbazone ONNO complexes Electrochemistry Spectroelectrochemical analysis X-ray analysis

ABSTRACT

New complexes, [Fe(L)Cl] (1 and 2) and [Ni(L)]-C₂H₅OH (3 and 4), were synthesized by template condensation of 2,4-dihydroxy-benzophenone-*S*-methyl-thiosemicarbazone with 5-bromo- and 5-chloro-2hydroxy-benzaldehyde and characterized by elemental analysis, conductivity measurements, IR, NMR and mass spectra. Complex 4 crystallizes in monoclinic space group $P_{2_1/c}$ with unit cell dimensions, a = 13.1091 (3) Å, b = 24.2308 (3) Å, c = 15.5808 (4) Å, $\beta = 102.2632$ (11)°, V = 4836.22 (18) Å³, Z = 8. The asymmetric unit of 4 contains two main molecules and two ethanol molecules. Electrochemical behaviors of 1–4 were studied using cyclic voltammetry and square wave voltammetry. Voltammetric analysis of the complexes shows a quasi-reversible metal-based reduction processes between -0.55 and -0.78 V followed by an irreversible reduction process within -0.91 and -1.27 V versus SCE. An irreversible oxidation is also observed within -1.10 to -1.23 V versus SCE during anodic potential scans. While the thiosemicarbazone moiety stabilizes +3 and +2 oxidation states for the iron complexes, only Ni^{II} is stable in solution with the same ligand in dichloromethane and dimethylsulfoxide. *In-situ* spectroelectrochemical studies were employed to determine the colors and spectra of electrogenerated species of the complexes. © 2012 Elsevier B.V. All rights reserved.

1. Introduction

After platinum complexes of thiosemicarbazide were found to have antitumor activities [1], structures and biological potentials of metal complexes of thiosemicarbazone derivatives have been intensively studied [2,3]. Research on cytotoxic properties of thiosemicarbazone complexes have been centralized to ONS and NNS chelates of copper(II), platinum(II) and palladium(II) obtained especially from 2-acetyl pyridine derivatives [4–9]. In 2007, we reported the cytotoxic activity against K562 chronic myeloid leukemia of some N_2O_2 thiosemicarbazone complexes of iron(III) and nickel(II) [10], and then our research has been focused on the synthesis of N_2O_2 chelate structures [11].

The N₂O₂ coordination mode based on thiosemicarbazones is usually obtained from substituted 2-hydroxy benzaldehydes with Fe(III) [12] and Ni(II) [13], but there are a limited number of such complexes including a benzophenone moiety. Some of the N₂O₂[14] and N₄O₂[15] complexes of 2-hydroxy-benzophenone thiosemicarbazone has been reported, previously. Herein, we present four N₂O₂ complexes of iron(III) and nickel(II) obtained from 2,4dihydroxy-benzophenone-S-methylthiosemicarbazone as shown in Fig. 1. The complexes (**1–4**) were characterized by means of elemental analysis, conductivity measurements, IR, NMR and mass spectra. The crystal structure of complex **4** was studied by single crystal X-ray diffraction.

The redox properties of 1-4 were studied to investigate the influence of the ligand environment on the relative stability of the species which formed in solution due to the variable oxidation states of the central metal ions (III, II and I). Besides, the electrochemical investigation, in situ spectroelectrochemical and in situ electrocolorimetric studies were firstly employed to determine the spectra and colors of the electrogenerated species of the nickel and iron complexes with N₂O₂ chelating thiosemicarbazones. It is well known that certain potential applications (e.g., in the design of an efficient catalyst and sensor) of these type complexes will require an understanding of the nature of their redox processes. It is well known that many metal N₂O₂ complexes show excellent electrocatalytic and sensor properties [16,17]. Therefore, we report here the *in situ* electrocolorimetric analysis of the complexes to determine possible application of the complexes. Because electrocolorimetry technique provides a more precise way to define color of the electro generated species, which are desired properties for the optic sensor applications [17].





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^{0020-1693/\$ -} see front matter @ 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.ica.2012.03.023



Fig. 1. (a) 2,4-Dihydroxy-benzophenone-S-methylthiosemicarbazone. (b) The complexes. M/R: Fe/Cl (1); Fe/Br (2); Ni/Cl (3); Ni/Br (4). In the nickel complex formula, *a-k* symbols indicate hydrogen atoms. For clarity, some carbon atoms labeled.

2. Experimental

2.1. Materials and physical measurements

All chemicals were of reagent grade and were used as commercially purchased without further purification. The elemental analyses were determined on a Thermo Finnigan Flash EA 1112 Series Elemental Analyser. Magnetic measurements were carried out at room temperature with an Sherwood Scientific MK I apparatus by using CuSO₄·5H₂O as calibrant. The molar conductivities of the complexes were measured in 10^{-3} M DMF solution at 25 ± 1 °C using a digital WPA CMD 750 conductivity meter. Infrared spectra were recorded as KBr discs on a Mattson 1000 FT-IR spectrophotometer in the 4000–400 cm⁻¹ range at room temperature. The NMR spectra were recorded on Bruker Avance-500 model spectrometer relative to SiMe₄ using DMSO-d₆. The ESI-MS analyses were carried out in positive and negative ion modes using a Thermo Finnigan LCQ Advantage MAX LC/MS/MS.

2.2. Synthesis of the compounds

2,4-Dihydroxy-benzophenone-S-methylthiosemicarbazone was prepared with small modifications of the literature method [18]. The colors, m.p. (°C), yields (%), elemental analysis, FT-IR (KBr disc, cm^{-1}) and NMR (ppm, 25 °C) data of the compound are as follows:

Colorless, m.p. 184.8–186.0 °C, 61%. Anal. Calc. for $C_{15}H_{15}N_3O_2S$ (301.36 g/mol): C, 59.78; H, 5.02; N, 13.94; S, 10.64. Found: C, 59.81; H, 4.98; N, 13.88; S, 10.59%. v_{max}/cm^{-1} : 3453 (2-OH), 3345 (NH)_{as}, 3172 (4-OH), 3141 (NH)_s, 1628 (C=N¹), 1597 (N²=C), 1120 (C–O), 746 (C–S). δ_H (500 MHz, DMSO-d₆, Me₄Si): 11.03, 10.46 (*cis/trans* ratio: 2/1, s, 1H, 2-OH), 9.59 (s, 1H, 4-OH), 6.64 (s, 2H, NH₂), 7.60 (d, *J* = 7.78, 1H, *f*), 7.45–7.43 (m, 2H, *d*,*h*), 7.35–7.33 (m, 2H, *eg*), 6.68 (d, *J* = 8.69, 1H, *c*), 6.31 (d, *J* = 2.29 1H, *a*), 6.24 (d, *J* = 8.69, 1H, *b*), 2.41, 2.36 (*cis/trans* ratio: 3/2, s, 3H, S–CH₃). δ_C (500 MHz, DMSO-d₆, Me₄Si): 162.98 (1), 160.69 (2), 116.08 (3), 158.78 (4), 105.51 (5), 140.99 (6), 107.23 (7), 132.02 (8), 133.35 (9), 128.45 (10,14), 129.43 (11,13), 129.99 (12), 12.91 (15). *m/z* (+c ESI): 301.42 ([M]⁺, 100%); 300.24 ([M–1]⁺, 19.33), 302.42 ([M+1]⁺, 18.12); 303.24 ([M+2]⁺, 7.20); 270.56 ([M–(–N=C(SCH₃)–NH₂)]⁺, 5.66). Complex **1** was prepared with the procedure given in previous paper [14]. 2,4-Dihydroxybenzophenone-S-methylthiosemicarbazone (1 mmol) and 2-hydroxy-benzaldehyde (1 mmol) in 10 mL absolute ethanol was added dropwise to the solution $FeCl_3 \cdot 6H_2O$ (1 mmol) in 10 mL absolute ethanol. After a week, dark brown precipitates were filtered off, washed with a mixture of ethanol and dried in vacuo over P_2O_5 . Complexes **2–4** were synthesized in similar manner. The analytical and spectroscopic data of **1–4** are below:

Complex **1**: Dark Brown, m.p. >350 °C, yield 18%, μ_{eff} : 5.8 BM, Λ_{M} : 8.3 Ω^{-1} cm² mol⁻¹. *Anal.* Calc. for C₂₂H₁₆N₃O₃SCl₂Fe (529.19 g/mol): C, 49.93; H, 3.05; N, 7.94; S, 6.06. Found: C, 49.88; H, 3.04; N, 7.92; S, 6.06%. ν_{max}/cm^{-1} : 1607 (C=N¹), 1600 (N⁴=C), 1584 (N²=C), 1161, 1123 ν (C–O)_{arom}. *m/z* (–c ESI): 529.26 ([M]⁺, 100%); 528.19 ([M–1]⁺, 14.54); 530.25 ([M+1]⁺, 35.13); 531.26 ([M+2]⁺, 23.95).

Complex **2**: Black, m.p. >350 °C, yield 24%, μ_{eff} : 5.5 BM, Λ_{M} : 1.2 Ω^{-1} cm² mol⁻¹. Anal. Calc. for $C_{22}H_{16}N_3O_3$ SBrClFe (573.64 g/ mol): C, 46.06; H, 2.81; N, 7.33; S, 5.59. Found: C, 46.00; H, 2.80; N, 7.31; S, 5.58%. ν_{max}/cm^{-1} : 1607 (C=N¹), 1604 (N⁴=C), 1576 (N²=C), 1161, 1123 ν (C-O)_{arom}. m/z (-c ESI): 573.24 ([M]⁺, 100%), 572.31 ([M-1]⁺, 22.36), 571.30 ([M-2]⁺, 75.29), 574.23 ([M+1]⁺, 29.03); 575.24 ([M+2]⁺, 26.94).

Complex **3**: Claret red, m.p. >350 °C, yield 21%, μ_{eff} : 0.30 BM, Λ_{M} : $0.06 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$. Anal. Calc. for $C_{22}H_{16}N_3O_3SCINi.C_2H_5OH$ (542.66 g/mol): C, 53.12; H, 4.09; N, 7.74; S, 5.91. Found: C, 53.05; H, 4.08; N, 7.72; S, 5.89%. v_{max}/cm⁻¹: v(C=N¹) 1615, $v(N^4=C)$ 1605, $v(N^2=C)$ 1584, $v(C-O)_{arom}$ 1161, 1130, δ_H (500 MHz, DMSO-d₆, Me₄Si): 10.25 (s, 1H, 4-OH), 8.32 (s, 1H, N⁴=CH), 7.98 (d, J = 2.44, 1H, f), 7.56-7.49 (m, 4H, d,e,g,h), 7.33-7.31 (m, 2H, *i,j*), 7.10 (d, *J* = 9.25, 1H, *k*), 6.71 (d, *J* = 9.27, 1H, *c*), 6.37 (d, J = 2.44, 1H, a), 6.17 (d, J = 9.27, 1H, b), 4.39 (s, 1H, alcohol-OH), 3.52-3.49 (q, J = 7.32, 2H, -CH₂-), 2.23 (s, 3H, S-CH₃). 1.12 (t, J = 7.32, 3H, $-CH_2-CH_3$). δ_C (500 MHz, DMSO- d_6 , Me₄Si): 167.82 (1), 159.94 (2), 113.02 (3), 157.41 (4), 104.75 (5), 137.24 (6), 108.45 (7), 131.01 (8), 133.53 (9), 128.39 (10,14), 128.97 (11,13), 129.13 (12), 15.40 (15), 167.11 (16), 124.32 (17), 164.05 (18), 121.09 (19), 135.36 (20), 135.49 (21), 120.06 (22), 56.72 (CH₃-CH₂-OH), 19.24 (CH₃-CH₂-OH). m/z (+c ESI): 496.34 ([M]⁺, 3.39%); 497.32 ([M+1]⁺, 3.22); 498.40 ([M+2]⁺, 4.13); 270.56 $(\{[(HO-C_6H_3-O)(C_6H_5)CN Ni]\}^+, 100\%).$

Complex **4**: Claret red, m.p. >350 °C, yield 26%, μ_{eff} : 0.36 BM, Λ_{M} : $0.10 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$. Anal. Calc. for $C_{22}H_{16}N_3O_3\text{SBrNi} \ C_2H_5\text{OH}$ (587.11 g/mol): C, 49.10; H, 3.78; N, 7.16; S, 5.46. Found: C, 48.97; H, 3.76; N, 7.15; S 5.44. v_{max}/cm^{-1} : $v(C=N^1)$ 1615, $v(N^4=C)$ 1607, $v(N^2=C)$ 1584, $v(C-O)_{arom}$ 1161, 1130. δ_H (500 MHz, DMSO- d_6 , Me₄Si): 10.18 (s, 1H, 4-OH), 8.25 (s, 1H, N⁴=CH), 8.03 (d, J = 2.44 Hz, 1H, f), 7.52–7.46 (m, 4H, d,e,g,h), 7.25–7.23 (m, 2H, i,j), 7.10 (d, J = 9.25 Hz, 1H, k), 6.96 (d, J = 9.27 Hz 1H, c), 6.29 (d, J = 2.44 Hz 1H, a), 6.10 (d, J = 9.27 Hz 1H, b), 4.32 (s, 1H, alcohol-OH), 3.44–3.41 (q, J = 7.32, 2H, -CH₂-), 2.15 (s, 3H, S-CH₃), 1.06 (t, $J = 7.32, 3H, -CH_2-CH_3$). δ_C (500 MHz, DMSO- d_6 , Me₄Si): 167.81 (1), 159.96 (2), 108.44, 157.40 (4), 104.75 (5), 137.24 (6), 107.23 (7), 131.02 (8), 135.36 (9), 128.39 (10,14), 128.96 (11,13), 129.13 (12), 15.40 (15), 167.30 (16), 124.64 (17), 164.06 (18), 122.04 (19), 135.48 (20), 136.82 (21), 113.03 (22), 56.72 (CH₃-CH₂-OH), 19.23 (CH₃-CH₂-OH). *m*/*z* (+c ESI): 542.18 ([M+1]⁺, 100%); 541.24 ([M]⁺, 15.07%); 540.18 ([M-2]⁺, 70.57); 118.08([(C₆H₅O)CN]⁺, 40.48). m/z (−c ESI): 540.31 ([M−1]⁺, 100%).

2.3. X-ray analysis

A red block crystal of complex **4** having approximate dimensions of $0.40 \times 0.30 \times 0.10$ mm was mounted on a glass fiber. The diffraction data was collected on a Rigaku RAXIS RAPID imaging plate area detector with graphite-monochromated Mo K α (0.7107 Å) radiation at 293 K. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied, which resulted in transmission factors ranging from 0.41 to 1.00. The data were corrected for Lorentz and polarization effects. The molecular and crystal structures were solved by direct methods using the program sir92 [19]. Hydrogen atoms were refined using the riding model and the non-hydrogen atoms were refined anisotropically. All calculations were package [20,21]. The data and refinement details of **4** are presented in Tables 1 and 2.

2.4. Electrochemistry and spectroelectrochemistry

Electrochemical and spectroelectrochemical measurements were carried out with a Gamry Reference 600 potentiostat/galvanostat utilizing a three-electrode configuration at 25 °C. For cyclic voltammetry (CV), and square wave voltammetry (SWV) measurements, the working electrode was a Pt disc with a surface area of 0.071 cm². The surface of the working electrode was polished with a diamond suspension before each run. A Pt wire served as the counter electrode. Saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Ferrocene was used as an internal reference. Tetrabuthylammonium perchlorate (TBAP) in dimethylsulfoxide (DMSO) and dichloromethane (DCM) was employed as the supporting electrolyte at a concentration of 0.10 mol dm^{-3} . High purity N₂ was used to remove dissolved O₂ at least 15 min prior to each run and to maintain a nitrogen blanket during the measurements. IR compensation was applied to the CV and SWV scans to minimize the potential control error.

UV–Vis absorption spectra and chromaticity diagrams were measured by an OceanOptics QE65000 diode array spectrophotometer. *In situ* spectroelectrochemical and *in situ* electrocolorimetric measurements were carried out by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell at 25 °C. The working electrode was Pt tulle. Pt wire counter electrode and a SCE reference electrode separated from the bulk of the solution by a double bridge were used. The standard illuminant A with 2° observer at constant temperature in a light booth designed to exclude external light was used. Prior to each set of measurements, background color coordinates (*x*, *y* and *z* values) were taken at

Table 1

The crystal data and refinement details of complex 4.

Empirical formula C	C24H22BrN3NiO4S
Formula weight 5	587.12
Temperature (K) 2	293
Wavelength (Å) 0	0.71070
Crystal dimensions (mm)	$0.40 \times 0.30 \times 0.10$
Crystal system r	monoclinic
Space group F	P121/c1
a (Å) 1	13.1091 (3)
b (Å) 2	24.2308 (3)
c (Å) 1	15.5808 (4)
α (°)	9 0
β (°) 1	102.2632 (11)
γ(°)	9 0
$V(Å^3)$	4836.2 (2)
Ζ 8	3
D_{calc} (g/cm ³) 1	1.613
λ (Mo K α) (mm ⁻¹) 2	2.582
F(000) 2	2384.0
h, k, l range -	$-18 \leqslant h \leqslant 18$
-	$-34 \leqslant k \leqslant 34$
-	$-21 \leqslant l \leqslant 21$
Reflections collected 2	279324
Unique reflections 1	14526
R _{int} 0	0.031
$R\left[I > 3\sigma(I)\right] \tag{C}$	0.118
$R_{\rm w} \left[I > 3\sigma(I) \right] \tag{C}$	0.032
Goodness-of-fit on indicator 1	1.146

open-circuit, using the electrolyte solution without complexes under study. During the measurements, readings were taken as a function of time under kinetic control.

3. Results and discussion

3.1. Synthesis and physical properties

2,4-Dihydroxy-benzophenone-S-methylthiosemicarbazone is in form of powder crystals and soluble in common solvents. Reactions of the thiosemicarbazone with 5-bromo- and 5-chloro-2-hydroxybenzaldehyde in the presence of iron(III) or nickel(II) in alcohol yielded stable solid complexes as shown in Fig. 1. The N₂O₂ complexes, **1–4**, form as fine crystal materials, very soluble in common organic solvents. The complexes are stable in air and their low molar conductances indicate non-ionic structures. The magnetic susceptibility values of **1** and **2** are compatible with high-spin d⁵ iron(III) center. Complexes **3** and **4** are in the formula [Ni(L)]--C₂H₅OH and recrystallization from alcohol to improve the quality of the crystals does not changed the composition. The low magnetic susceptibility values of **3** and **4** indicate the square planar environment of nickel(II) center in the N₂O₂ chelates.

3.2. Spectroscopic data

The template condensations of the *S*-methylthiosemicarbazones and aldehydes can be easily monitored by means of IR and ¹H NMR spectra. In the spectra of the complexes, the NH₂ and 2-OH bands of the *S*-methylthiosemicarbazone disappeared due to the condensation. Only the (OH) band of the 4-substituted hydroxyl group on the thiosemicarbazone were recorded at 3174 cm⁻¹ in the complex spectra. By the template reaction, the (C=N¹) and (N²=C) bands of the *S*-methylthiosemicarbazones shifted to lower energies *ca.* 13–20 cm⁻¹ and also a new azomethine band, (N⁴=C), appeared in 1607–1600 cm⁻¹ region due to condensation of the thioamide nitrogen (N⁴) and aldehyde.

In the ¹H and ¹³C NMR spectra of the thiosemicarbazone, the expected chemical shift values were monitored for the aromatic,

 Table 2

 Selected bond lengths (Å) and bond angles (°) for molecules A and B in the asymmetric unit of 4.

Ni1-02	1.8239 (11)	02-Ni1-03	85.98 (6)
Ni1-03	1.8399 (13)	02-Ni1-N1	95.10 (6)
Ni1-N3	1.8388 (14)	02-Ni1-N3	177.87 (6)
Ni1-N1	1.8291 (15)	03-Ni1-N1	174.43 (6)
Ni2-06	1.8399 (13)	03-Ni1-N3	94.99 (6)
Ni2-05	1.8243 (13)	N1-Ni1-N3	84.13 (6)
Ni2-N4	1.8259 (15)	N4-Ni2-N6	83.97 (6)
Ni2-N6	1.8376 (14)	05-Ni2-N6	179.14 (6)
S1-C14	1.7463 (19)	05-Ni2-06	85.64 (6)
S1-C15	1.785 (2)	05-Ni2-N4	95.24 (6)
S2-C39	1.743 (2)	06-Ni2-N6	95.16 (6)
S2-C38	1.791 (2)	S1-C14-N3	120.93 (13)
		S1-C14-N2	120.33 (14)

azomethine, S-methyl protons and even the cis–trans isomer peaks of these protons [14,18]. The ratios of signal integrations of 2-hydroxyl group are 2:1 because of cis–trans isomerism, and also Smethyl groups gave cis and trans peaks in 3:2 ratio. In the **3–4** spectra, the proton signals of 2-OH and N⁴H₂ groups of Ni(II) complexes disappear by chelation. The absence of these N⁴H₂ hydrogens indicates their deprotonation and arising the N⁴=CH signal which is a singlet and equivalent to one proton integral value confirms the template formation around nickel(II). The ¹H NMR data of the nickel templates did not show any isomer peak, probably as these moieties have been partially fixed because of the template reaction.

In the ¹³C NMR spectra, the chemical shifts of some carbon atoms of the nickel complexes are in different values compared to the thiosemicarbazone as starting material due to the formation of a new conjugated backbone by the condensation reaction. Significantly, carbon atoms of thioamide (1) and methyl (15) groups were recorded in the lower field at 2.50 and 4.84 ppm, respectively, and the chemical shift value of carbon atom (6) binding 4-OH substituent was observed at 4.84 ppm in higher field.

Characteristic peaks were observed in the ESI-mass spectra of ligand and its metal complexes. The mass spectra of iron complexes **1** and **2** revealed the protonated and deprotonated

molecular ion peaks {[M–H], [M–2H], [M+H], [M+2H], [M], etc.}. The mass spectrum of **3** and **4** showed a molecular ion (M⁺) peak at m/z 496.34 and 541.24, corresponding to the N₂O₂ chelate complexes [C₂₂H₁₆N₃O₃SClNi]⁺ and [C₂₂H₁₆N₃O₃SBrNi]⁺, respectively.

Consequently, the analytical and spectral data become evident that the chelating N1,N4-diarylidene-S-methylthiosemicarbazidato ligands are bonded to metal atom through ONNO donor set and so it can be proposed the template structures in Fig. 1.

3.3. Crystallography

Single crystal of nickel complex (**4**), suitable for X-ray diffraction studies, was grown by slow evaporation of the alcoholic solution of complex. Crystal parameters and refinement results of the complexes are summarized in Table 1. The selected bond distances and angles are presented in Table 2. An ORTEP diagram of the molecule 4, along with the atom numbering scheme, is shown in Fig. 2.

The complex is formed by chelating of a doubly deprotonated thiosemicarbazone molecule having ONNO donor set which structured in template reaction (Fig. 1). In crystal structure, each molecule (A with Ni1 and B with Ni2) in the asymmetric unit of 4, each molecules A and B is consisting by one mononuclear nickel salentype complex and one molecule of ethanol. The nickel atom lies in a four-coordinate environment and adopts a slightly distorted square-planar geometry (Fig. 2). Coordination of the symmetric [N₂O₂] ligands to the nickel atom generates three chelate rings, two of them composed by six atoms, NiONC₃ (from the keto block or salicyl aldehyde moiety) and the other one by five atoms (the isothiosemicarbazidic NiN₃C ring), in the sequence 6:5:6. In the chelate structure of 4, there are two diagonal O-Ni-N angles of 95.10 (6) and 94.99 (6) (for A), 95.24 (6) and 95.16 (6) (for B), barely deviating from linearity. The Ni–N and Ni–O bond distances are in the normal range for Ni-salen type complexes [22–24]. The Ni–N distances are 1.8291 (15), 1.8388 (14) Å for molecule A. and 1.8259 (15), 1.8376 (14) Å for molecule B and the Ni–O distances are 1.8239 (11), 1.8399 (13) Å for molecule A and 1.8243 (13), 1.8399 (13) Å for molecule B. The chelate rings [O(2)-N(1)] and [O(3)-N(3)] are approximately planar.



Fig. 2. View of the two molecules (A with Ni1 and B with Ni2) in the asymmetric unit of 4 with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.



Fig. 3. (a) CV of the complex **4** at various scan rates (inset: CV of the complex **4** at 0.100 Vs⁻¹ scan rate with different switching potentials) and (b) SWV of the complex **4** in TBAP/DCM electrolyte system on Pt working electrode (SWV parameters: pulse size = 100 mV; pulse wide = 5 mV; Frequency:25 Hz) rates (inset: Repetitive CV of the complex **4** recorded with all potential window of the electrolyte system at 0.100 Vs⁻¹ scan rate.).



Fig. 4. CV of the complex **4** at various scan rates in TBAP/DMSO electrolyte system on Pt working electrode (inset: Repetitive CV of the complex **4** recorded with all potential window of the electrolyte system at 0.100 Vs^{-1} scan rate.).



Fig. 5. (a) CV of the complex **2** at various scan rates (inset: CV of the complex **2** recorded with different negative switching potentials) in TBAP/DCM electrolyte system on Pt working electrode. (b) SWV of the complex. (SWV parameters: pulse size = 100 mV; pulse wide = 5 mV; frequency: 25 Hz).

3.4. Electrochemistry

The redox properties of the complexes (**1–4**) were studied using CV and SWV measurements in DCM and DMSO containing TBAP as supporting electrolyte on a Pt electrode (Fig. 3–8). All complexes show one 1-electron oxidation response during the anodic potential scan and two 1-electron reduction responses during the anodic potential scan. The one-electron nature of these processes has been established by comparing their current height with that of the standard ferrocene/ferrocenium couple under identical experimental conditions. Table 3 lists the assignments of the redox couples and the electrochemical parameters, which included the half-wave peak potentials ($E_{1/2}$), anodic to cathodic peak potential separation (ΔE_p), and ratio of the anodic to cathodic peak currents (I_{pa}/I_{pc}). $E_{1/2}$ values are in agreement with the reported data for redox processes in similar iron and nickel complexes in the literature [25–32].

The nickel complexes, **3** and **4**, give very similar CV and SWV responses, thus electrochemical responses of **4** is given in Fig. 3 as a representative of the nickel complexes. CV responses of **3** and **4** (Fig. 3a) indicate a metal-based 1-electron irreversible reduction (at -1.08 V for **3** and at -0.94 V for **4**) in addition to the ligand-based oxidation process (at 1.19 V for **3** and at 1.17 V for **4**) in TBAP/DCM electrolyte system. Moreover, an irreversible ligand-based reduction process is recorded with SWV at the end of the



Fig. 6. (a) CV of the complex **2** at various scan rates (inset: CV of the complex **2** recorded with different negative switching potentials) in TBAP/DMSO electrolyte system on Pt working electrode. (b) SWV with SWV parameters: pulse size = 100 mV; pulse wide = 5 mV; frequency: 25 Hz.

negative potential window of the electrolyte system. It is reported that thiosemicarbazone ligand gave a 1-electron irreversible oxidation and a 1-electron irreversible reduction processes at the end of the DCM or DMSO/TBAP electrolyte windows [33-35] and coordination of the ligands to the metal ion did not affect the redox potential of ligands considerably. Thus, the first reduction process of the complexes is easily assigned to the reduction of the central metal ions. Even though ΔE_p values of these peaks were in quasireversible range especially at very slow scan rates, very small I_{pa} $I_{\rm pc}$ values and deviation of $I_{\rm p}$ versus $v^{1/2}$ from linearity may assign the irreversible character of the redox processes to the chemical reactions succeeding the electron transfer processes. The product of the chemical reaction gives an irreversible oxidation process $(\text{Red.}_{(\text{CP})})$ at -0.13 V. When the potential is switched before the Ni^{II}/Ni^I process (from -1.0 V), Red._(CP) process disappeared, which support the existence of the chemical reaction succeeding the Ni^{II}/Ni^I process and instability of the reduced Ni^IL species (Fig. 3a inset). Similarly, the oxidation process (L/L^+) of the complex is followed with a chemical reaction, whose product gives a reduction wave at -0.43 V and an oxidation wave at 0.86 V (Fig. 3b inset). When the potential is scanned from 0.0 to -1.70 V, the complex gives a reduction couple (Ni^{II}/Ni^{I}) at -1.17 V and Red._(CP) at -0.13 V in addition to L/L⁺ process at 1.17 V during the reverse scan from -1.70 to 1.50 V (blue CV: first cycle in Fig. 3b inset). Then when the CV scans continue repeatedly, new waves are recorded at -0.43 and 0.86 V, but peak current of these waves do



Fig. 7. *In-situ* UV–Vis spectral changes of **4.** (a) $E_{app} = -1.30$ V. (b) $E_{app} = -1.80$ V. (c) Chromaticity diagram of **4.** (each symbol represents the color of electro-generated species; \Box : [Ni^{II}L], \bigcirc : [Ni^IL]⁻¹, \triangle : [Ni^IL⁻¹]]⁻².

not increases with repetitive CV cycles. These voltammetric responses indicate the presence of the chemical reaction succeeding the oxidation and also reduction processes. Besides, Red._(CP) wave disappeared when the positive potentials are scanned.

Although both oxidation and reduction of Ni^{II} center of NNS type complexes were reported in the literature [36,37], reduction of Ni^{II} to Ni^I is only recorded in this study for both nickel complexes. Moreover Ni^{II}/Ni^I reduction peak shifts to the more negative potentials with respect to the similar complexes in the literature.

It is well documented that DMSO is easily coordinated with many transition metal ions [38]. Fig. 4 illustrates the CV and SWV responses of **4** in DMSO/TBAP electrolyte system. The CV responses of **4** are approximately same in both solvents (DCM and DMSO) in cathodic potential scan, but irreversible L/L^+ wave shifts to negative potentials and get reversible in DMSO. As shown in Fig. 4b, voltammetric responses of the complex indicate presence of the chemical reaction following the L/L^+ process in DMSO during repetitive CV scans like in DCM. Differently peak current of the wave assigned to the product of the chemical reaction increases continuously during the repetitive CV scans.

The iron complexes (1 and 2) give very similar CV and SWV responses with each other. As shown in Fig. 5a, CV responses of 2 indicate a 1-electron metal-based reversible redox couple at -0.24 V in addition to the ligand-based reduction process at -1.26 V in TBAP/DCM electrolyte system. Moreover, an irreversible



Fig. 8. *In-situ* UV–Vis spectral changes of **2.** (a) $E_{app} = -0.50$ V. (b) $E_{app} = -1.70$ V. (c) Chromaticity diagram of **2.** (each symbol represents the color of electro-generated species; \Box : [Fe^{III}L], \bigcirc : [Fe^{III}L]⁻¹, \triangle : [Fe^{III}L⁻¹]⁻², [Fe^{III}L⁺¹]⁺¹.

ligand-based oxidation process is recorded at 1.33 V during the anodic potential scan. SWV measurements clearly illustrate these processes and reversibility of the first reduction process (Fig. 5b). $\Delta E_{\rm p}$ values of the Fe^{III}/Fe^{II} couple is in reversible range especially at very slow scan rates and unity of the $I_{\rm pa}/I_{\rm pc}$ ratios and linearity of $I_{\rm p}$ versus $v^{1/2}$ changes indicate the reversible character of this reduction process. As shown in Fig. 5a inset, peak character of the first reduction process does not change with different switching potentials. As compared with the similar Fe^{III} complexes in the literature [39,40], Fe^{III}/Fe^{II} reduction peak shifts to the negative potential due to the electron releasing ability of the ligand. For example, L.R. Teixeira and coworkers reported Fe^{III}/Fe^{II} reduction peak at – 0.12 V followed with a reduction process at –1.20 V for Fe^{III} complexes of N⁴-para-tolyl-thiosemicarbazones [39].

Redox properties of complex **2** change when coordinating solvent DMSO is used instead of DCM. Fig. 6 illustrates the electrochemical responses of **2** in DMSO/TBAP electrolyte system. While redox processes of **2** shift to the negative potentials, reversibility of L/L^- process increases in DMSO with respect to those in DCM. As shown in Fig. 6a (inset), different switching potentials do not also affect the electron transfer character of the redox processes in DMSO like in DCM.

3.5. Spectroelectrochemical studies

Neutral form of each complex shows several intense absorption bands in the visible and ultraviolet region in solution. The absorptions in the ultraviolet region are assigned to transitions within

the ligand orbitals and those in the visible region are probably due to metal to ligand charge-transfer (MLCT) transitions. In situ spectroelectrochemical studies were employed to determine the spectra of electrogenerated species of the complexes to perform assignments of the redox processes, and to predict the redox mechanism of the processes. The nickel complexes (3 and 4) give very similar spectroscopic changes in DCM and DMSO electrolyte under applied potentials. Fig. 7 shows in situ UV-Vis spectral changes of 4 in TBAP/DCM electrolyte as a representative of the nickel complexes during the controlled potential reductions and oxidation processes. Under the applied potential at -1.30 V, the broad MLCT band at 566 nm increases in intensity, while the intraligand transitions band at 425 nm shifts to 394 nm with increasing in intensity (Fig. 7a). These spectroscopic changes indicate a metal-based redox process and assign the couple to [Ni^{II}L]/[Ni^IL]⁻¹ process. Well-defined isosbestic points at 345, 417, and 494 nm demonstrate that the reduction proceeds to give a single reduced species under applied potential at -1.30 V. Applying 0.0 V after the first reduction process regenerate the original spectra of [Ni^{II}L] species, which indicates the chemical reversibility of the process. Isosbestic points are commonly met when electronic spectra are taken on a solution in which a reaction is in progress in which case the two absorbing components concerned are a reactant and a product and the sum of the concentrations of two principal absorbing components is constant. If absorption spectra of the types considered above intersect not at one or more isosbestic points but over progressively changing wavelength, this is prima facie evidence for the formation of a reaction intermediate in substantial concentration. Spectroscopic changes given in Fig. 7b are recorded under applied potential at -1.70 V. During this process, while the band at 394 nm shifts to 430 nm with increasing in intensity, the band at 566 nm decreases in intensity. These spectral changes are indicator of a ligand-based redox reaction. Well-defined isosbestic points at 343, 394, and 467 nm are recorded during this process. The spectrum did not return to the initial spectrum of the [Ni¹L]⁻¹ species when -1.30 V was applied to the working electrode, which indicates the irreversibility of the process chemically. Under applied potential at 1.50 V, the spectra of the complex do not change considerably. The color changes of the compounds during the redox processes were recorded using in situ colorimetric measurements. Without any potential application, the solution of $[Ni^{II}L]$ is orange (x = 0.419 and y = 0.387). As the potential is stepped from 0 to -1.30 V, the color of the neutral [Ni^{II}L] gets purple (x = 0.314 and y = 0.2824) at the end of the first reduction. Similarly color of the dianionic species are recorded as yellow (x = 0.406 and y = 0.420) at the end of the second reduction process (Fig. 7c). Measurement of the xyz coordinates allows quantification of each color of the redox species that is very important to decide their possible electrochromic application.

Fig. 8 shows in situ UV-Vis spectral changes of 2 in TBAP/DCM electrolyte as a representative of the iron complexes. Under applied potential at -0.50 V, a new band at 555 nm is recorded, while the intraligand transitions band at 300 nm decreases in intensity slightly (Fig. 8a). These spectroscopic changes indicate a metalbased redox process and assign the couple to [Fe^{III}L]/[Fe^{II}L]⁻¹ process. Well-defined isosbestic points at 284, 320, and 780 nm demonstrate that the reduction proceeds to give a single reduced species. This process is chemically reversible with in the time scale of the spectroelectrochemical measurement, since applying 0.0 V after the first reduction process regenerate the original spectra of [Fe^{III}L] species. Spectroscopic changes given in Fig. 8b are recorded under applied potential at -1.70 V. During this process, intensity of the band at 394 nm increases, whereas the band at 555 nm decreases in intensity and disappear completely. These spectral changes are indicator of a ligand-based redox reaction. Under applied potential at 1.50 V, the spectra of the complex do not change considerably. The color changes of the compounds during the redox processes were recorded using in situ colorimetric measurements and given as chromaticity diagram in Fig. 8c.

Table 3	
Voltammetric data of complexes 1-4.	

Complexes	Peak parameters	Redox processes		
		L/L ⁺	M reduction	L/L^{-}
1 (in DCM)	^a E _{1/2}	1.35 ^d	-0.22	-1.24
bΔ	${}^{\rm b}\Delta E_{\rm p}~({\rm mV})$	-	65	60
	^c I _{pa} /I _{pc}	-	0.92	0.32
2 (in DCM)	^a E _{1/2}	1.33 ^d	-0.24	-1.26
	$^{\rm b}\Delta E_{\rm p}~({\rm mV})$	-	74	97
	^c I _{pa} /I _{pc}	-	0.96	0.44
2 (in DMSO)	${}^{a}E_{1/2}$ 0	0.97 ^d	-0.32	-1.39
	$^{\rm b}\Delta E_{\rm p}~({\rm mV})$	-	66	90
	$c_{I_{pa}}/I_{pc}$	-	0.97	0.45
3 (in DCM)	${}^{a}E_{1/2}$ vs. SCE	1.21 ^d	-1.06	-1.75 ^d
	${}^{\rm b}\Delta E_{\rm p}$ (mV)	-	77	-
	^c I _{pa} /I _{pc}	-	0.34	-
4 (in DCM)	${}^{a}E_{1/2}$ (V)	1.30 ^d	-1.10	-1.79^{d}
- ()	$^{b}\Delta E_{p}$ (mV)	-	78	-
	^c I _{pa} /I _{pc}	-	0.30	-
4 (in DMSO)	^a E _{1/2}	0.71	-1.12	-1.93 ^d
· · ·	${}^{\rm b}\Delta E_{\rm p}$ (mV)	320	60	-
	^c I _{pa} /I _{pc}	0.85	0.23	-

^a $E_{1/2} = (E_{pa} + E_{pc})/2$ at 0.100 Vs⁻¹.

^b $\Delta E_{\rm p} = |E_{\rm pc} - E_{\rm pa}|.$

^c I_{pa}/I_{pc} for reduction, I_{pc}/I_{pa} for oxidation processes at 0.100 Vs⁻¹ scan rate.

^d $E_{1/2}$ values were derived from SWV measurements.

4. Conclusion

We synthesized many N₂O₂ chelate complexes of *S*-alkyl-thiosemicarbazones due to cytotoxic activities [10,11,14], antidiabetic and also protective effects on pancreas [41], in previous years. However, we could reported a limited number of crystal structure of these complexes obtained from benzophenone thiosemicarbazone because of difficulties in crystal growth [14,15]. In this paper, we present new N₂O₂ complexes of iron(III) and nickel(II) obtained from 2,4-dihydroxy-benzophenone-S-methylthiosemicarbazone (1–4), single crystal analysis of square-planar nickel complex, [Ni(L)]·C₂H₅OH (4), and first electrochemical studies of these structures in a comprehensive manner.

Voltammetric and spectroelectrochemical studies show that each complex gives a 1-electron metal-based reduction process in addition to the irreversible ligand-based ligand reduction and oxidation processes. The voltammetric data are in harmony with the reported nick-el(II) and iron(III) thiosemicarbazone complexes. The results indicate that while thiosemicarbazone ligand stabilizes both Fe^{III} and Fe^{II} form of the central metal ion, Ni^I is not stable in dichloromethane and dimethylsulfoxide solvent system. Electrochemical behaviors of iron complexes (reversible electron transfer at low negative potentials and stability of both Fe^{III} and Fe^{II}) indicate their possible electrochemical sensor applications. *In-situ* spectroelectrochemical studies were employed to determine the colors and spectra of electrogenerated species of the complexes, which give inside to possible electrochromic application of the complexes.

Acknowledgment

This present work was supported by the Research Fund of Istanbul University. Project No. BYP-12264 and 16667.

Appendix A. Supplementary material

CCDC 824761 contains the supplementary crystallographic data for [Ni(L)]-C₂H₅OH. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this

article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.ica.2012.03.023.

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