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Research paper

# Synthesis, crystal structure, and characterization of two Cu(II) and Ni(II) complexes of a tetradentate $N_2O_2$ Schiff base ligand and their application in fabrication of a hydrazine electrochemical sensor



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# ABSTRACT

Two new Cu(II) and Ni(II) complexes of a tetradentate N<sub>2</sub>O<sub>2</sub> Schiff base ligand (H<sub>2</sub>L = *N*,*N*'-bis-(4-hydroxysalicylidene)-ethylenediamine) were synthesized. The structures of the H<sub>2</sub>L ligand and its complexes (1 and 2) were unambiguously determined by elemental analysis, FT-IR, <sup>1</sup>H NMR, and UV–Vis spectroscopy. The crystal structures of the complexes were also determined by X-ray crystallography technique. In addition, the complexes were tested as a modifier for a glassy carbon electrode (GCE) to prepare an electrochemical sensor for detection of hydrazine in real samples. The prepared sensor with Ni(II) complex showed admirable sensitivity and selectivity for determination of hydrazine at 0.55 V without any interference of other common substrates. A dynamic linear range of 0.5–150  $\mu$ M with a detection limit (LOD) of 166.66 nM and sensitivity of 0.1174  $\mu$ A  $\mu$ M<sup>-1</sup> cm<sup>-2</sup> was achieved. The obtained LOD was much lower than that specified in the U.S. Environmental Protection Agency (EPA) regulations. The prepared sensor was also successfully applied to detect hydrazine in Tehran's Jajrood river water as a real sample.

# 1. Introduction

Schiff bases are unique ligands that play an essential role in the development of coordination chemistry. They are easily synthesized and can be readily modified both electronically and sterically [1]. Schiff bases form an outstanding class of ligands due to their unique properties such as stability in different conditions, diversity of donor sites, synthetic flexibility, and formation of a wide range of complexes in various coordination geometries. Among them, salen-type Schiff base ligands are definitely appealing to coordination chemists. These are tetradentate ligands with four donor sites (N<sub>2</sub>O<sub>2</sub>), and their complexes have received much attention due to a wide range of applications such as catalysis [2], electrochemistry [3], bioscience [4], optics [5], hostguest chemistry [6], and molecular recognition [7]. As shown in Scheme 1, the salen ligand provides an ideal environment for equatorial coordination of transition metals, leaving two axial sites open for coordination of extra ligands or substrates. So far, Cu(II) and Ni(II) complexes of the salen ligand have been used as catalysts in many reactions such as oxidation of alcohols [8], epoxidation of olefins [9], alkylation [10], arylation [11], and many other industrial reactions

# [12].

Our motivation in this study was to prepare a tetradentate N<sub>2</sub>O<sub>2</sub> Schiff base ligand (H<sub>2</sub>L, Scheme 1) from 2,4-dihydroxybenzaldehyde and ethylenediamine. To investigate the coordination modes of this ligand, two new mononuclear Cu(II) and Ni(II) complexes (1 and 2) were synthesized and the structures of the ligand and its complexes were determined by appropriate techniques. Single crystal X-ray analysis confirmed the tetradentate binding mode of the H<sub>2</sub>L ligand. To study their potential application in detection of hazardous materials, the Ni(II) complex was used as a modifier for a glassy carbon electrode (GCE) to prepare an electrochemical sensor for detection of hydrazine. Hydrazine is widely used in many industries. This compound is highly toxic and is classified as a possible carcinogen with a threshold limit value (TLV) of 10 ppb (312.06 nM) according to the U.S. Environmental Protection Agency (EPA) regulations [13]. Thus, hydrazine detection is of great importance from both environmental and human health viewpoints. Incorporation of the Ni(II) complex into the glassy carbon electrode (GCE) resulted in significant improvements in detection of hydrazine in real samples.

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Scheme 1. Chemical structure of the H<sub>2</sub>L ligand.

#### Table 1

Crystal data and	structure	refinement for	complexes	1	and <b>2.</b>	
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Parameter	1	2
Empirical formula	C16H14CuN2O4·CH3CN·H2O	C16H14N2NiO4·H2O
Formula weight	420.90	375.02
Temperature (K)	100(1)	100(1)
Crystal system	Monoclinic	Monoclinic
Space group	P21/c	C2/c
Unit cell dimensions		
a (Å)	10.2793 (3)	19.5243 (8)
b (Å)	19.5904 (4)	18.6443 (7)
c (Å)	9.6778 (3)	10.1928 (4)
α (°)	90	90
β (°)	114.252 (4)	10.1928 (4)
γ (°)	90	90
V (Å <sup>3</sup> )	1776.88 (10)	3628.6 (3)
Ζ	4	8
$D_{\rm x}$ (Mg m $^{-3}$ )	1.573	1.373
$\mu$ (mm $^{-1}$ )	1.26	1.10
F (0 0 0)	868	1552
Crystal size (mm)	$0.28\times0.24\times0.21$	0.23 $\times$ 0.18 $\times$ 0.11
θ range for data collection (°)	3.1–29.1	3.0–29.0
Index ranges	$-13 \leq h \leq 14$	$-26 \leq h \leq 26$
	$-26 \leq k \leq 26$	$-24 \leq k \leq 24$
	$-13 \leq l \leq 13$	$-12 \leq l \leq 13$
Reflections collected	43,416	31,822
Independent reflections (R <sub>int</sub> )	4658 (0.044)	4678 (0.044)
Reflections with $I > 2\sigma(I)$	4054	3727
Data/restraints/ parameters	4658/0/250	4678/0/222
Goodness-of-fit on $F^2$	1.00	1.03
Final R indexes	$R_1 = 0.0274, wR_2 = 0.0633$	$R_1 = 0.0373,$
$[I > 2\sigma(I)]$	. , .	$wR_2 = 0.0875$
Final R indexes [all	$R_1 = 0.0360, wR_2 = 0.0673$	$R_1 = 0.0538$
data]	. , .	$wR_2 = 0.0939$
Largest difference in	0.396/-0.283	0.340/-0.275
peak/hole (e. Å <sup>-3</sup> )		

#### 2. Experimental

#### 2.1. Materials and instruments

All of the chemicals including 2,4-dihydroxybenzaldehyde, ethylenediamine, and hydrazine were purchased from Merck (<u>http://www. merck.com</u>) or Sigma-Aldrich (<u>http://www.sigmaaldrich.com</u>) Companies. The reagents were of analytical grade and used without further purification.

Elemental analyses were performed on a Heraeus CHN-O-Rapid elemental analyzer. FT-IR spectra were recorded on a Bruker Alpha spectrophotometer using KBr pellets over the range of 4000–400 cm<sup>-1</sup>. UV–Vis spectra were recorded on a Rayleigh UV–1800 spectrophotometer. <sup>1</sup>H NMR spectra were recorded in DMSO- $d_6$  using tetramethylsilane as internal standard on a Bruker Avance III 300 MHz spectrometer at 298 K.

All of the electrochemical measurements were carried out by a potentiostat/galvanostat,  $\mu$ -Autolab type II/FRA2 (Eco Chemie B. V,



Fig. 1. View of the molecular structure of (a) complex 1 and (b) complex 2. The solvent molecules (water and acetonitrile in 1 and water in 2) have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

# Table 2

Selected bond lengths (Å) and angles (°) for the complexes 1 and 2.

	1 (M = Cu)	<b>2</b> (M = Ni)
Bond lengths (Å)	1.9374 (13)	1.8460 (17)
M-N1		
M-N2	1.9376 (12)	1.8475 (17)
M-01	1.9284 (10)	1.8504 (14)
M-O4	1.9035 (10)	1.8676 (14)
Bond angles (°)		
N1-M-N2	84.29 (5)	85.88 (8)
N1-M-O1	93.70 (5)	95.14 (7)
N1-M-O4	167.23 (5)	179.14 (7)
N2-M-O1	170.66 (5)	177.43 (7)
N2-M-O4	93.98 (5)	94.27 (7)
O1-M-O4	89.96 (4)	84.74 (6)

#### Table 3

Hydrogen-bond geomet	ry (Å	٩, °)	in	the c	rystal	structure	of	1 a	and	2
	~ ~									

			-		
D—H…A <sup>a</sup>	D—H	Н…А	D····A	D—H…A	Symmetry
1 01 <i>W</i> —H1 <i>W</i> 1…N3 02—H2A…O1 <sup><i>i</i></sup> 03—H3A…O1 <i>W</i>	0.85 0.84 0.84	2.15 1.90 1.80	2.988 (2) 2.735 (2) 2.630 (2)	169 176 168	x, -y + 1/2, z + 1/2
<b>2</b> 02—H2A…O5 03—H3A…O4 <sup>i</sup>	0.84 0.84	1.86 1.82	2.675 (3) 2.653 (2)	162 175	x, -y + 1, z - 1/2

<sup>a</sup> D: Donor, A: Acceptor

Switzerland) driven by the Nova 2.1.2 software. A conventional threeelectrode setup consisting of a modified or unmodified GCE as a working electrode, an Ag/AgCl (3.00 M KCl) reference electrode and a Pt wire auxiliary electrode (Azar Electrode, Iran) were used. Some



Fig. 2. Arrangement of (a) complex 1 and (b) complex 2. Dashed lines represent the O-H…O hydrogen bonds that stabilized the structural architecture.

electrochemical techniques such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and amperometry techniques were used in the experiments. The EIS experiment was performed at a frequency range of 0.01 Hz to 50 kHz and a 1:1 mixture of 5 mM [Fe  $(CN)_6$ ]<sup>3@-/4-</sup> and 0.1 M KCl was utilized as the redox probe. 0.1 M NaOH was used as an electrolyte in the experiments. A pH/mV meter (Metrohm-691 pH-meter, Switzerland) was used for pH measurements.

#### 2.2. Crystal structure determination

Single-crystal X-ray data collection for the complexes 1 and 2 were performed using graphite-monochromated Mo-K $\alpha$  ( $\lambda = 0.71073$  Å) radiation on a four-circle  $\kappa$  geometry KUMA KM-4 diffractometer with a 2D CCD area detector at 100 K. The  $\omega$ -scan technique with  $\Delta\omega = 1.0^{\circ}$ 

for each image was used for data collection. One image was used as a standard after every 40 images for monitoring of the crystal stability and data collection, and no correction on the relative intensity variation was necessary. Integration, scaling of the reflections, correction for Lorenz and polarization effects and absorption corrections were performed using the CrysAlis Red program [14]. The structures were solved by direct methods using SHELXT [15] and refined using SHEXL-2018 program [15]. The hydrogen atoms were introduced in their geometrical positions and refined with isotropic displacement parameters. It was possible to localize and refine both solvent  $CH_3CN$  and  $H_2O$  molecules in crystal 1, whereas for crystal 2 was possible to localize only the water molecule as a solvent. The Checkcif Platon Raport of the cif file show additional solvent accessible VOID in the structure of the crystal 2. The correct modelling of the disordered molecules was not



Fig. 3. Projection along c-axis of molecular packing with space filling of (a) complex 1 and (b) complex 2 showing the channels along c-axis.



Fig. 4. UV–Vis spectra of (A) H<sub>2</sub>L, (B) complex 1 and (C) complex 2 (20 µM in DMSO) at room temperature. Insets show the absorption of each complex at higher wavelengths.

possible and we performed a "squeeze" treatment to remove the scattering contribution of these molecules, which could not to be satisfactory modelled. The final difference Fourier maps showed no peaks of chemical significance. The data collection parameters, crystallographic data, and final agreement parameters are collected in Table 1. The structures were visualized by using the DIAMOND 3.0 [16]. The data were deposited in Cambridge Crystallographic Data Center with deposition number CCDC 1,954,841 for  $C_{16}H_{14}CuN_2O_4$ ·CH<sub>3</sub>CN·H<sub>2</sub>O (1), and 1,954,842 for  $C_{16}H_{14}N_2NiO_4$ ·H<sub>2</sub>O (2).

#### 2.3. Synthesis

# 2.3.1. Synthesis of H<sub>2</sub>L

H<sub>2</sub>L was synthesized by condensation of ethylenediamine with 2,4dihydroxybenzaldehyde in methanol. Briefly, ethylenediamine (0.13 mL, 2.0 mmol) was added dropwise to a solution of 2,4-dihydroxybenzaldehyde (0.55 g, 4.0 mmol) in 25 mL of methanol at room temperature. The reaction mixture was then refluxed for 3 h with continuous stirring. After cooling to room temperature, the yellow precipitate was filtered and washed with methanol. Yield: 88%. <sup>1</sup>H NMR (300 MHz DMSO-*d*<sub>6</sub>, ppm); δ: 13.58 (br, 2H<sup>7</sup>), 9.80 (br, 2H<sup>5</sup>), 8.37 (s, 2H<sup>2</sup>), 7.18 (d, *J* = 8.4 Hz, 2H<sup>3</sup>), 6.28 (dd, *J* = 8.4 and 2.4 Hz, 2H<sup>4</sup>), 6.27 (d, *J* = 2.4 Hz, 2H<sup>6</sup>), 3.79 (s, 4H<sup>1</sup>). IR (KBr pellet, cm<sup>-1</sup>): 3416 (br, ν<sub>OH</sub>), 1639 (vs, ν<sub>C=N</sub>), 1234 (s, ν<sub>PhO</sub>). UV–Vis (DMSO): λ<sub>max</sub> (nm) (ε, M<sup>-1</sup> cm<sup>-1</sup>): ~280 (25750), 308 (21100), 390 (2100). Anal. Calc. for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub> (MW = 300.31 g mol<sup>-1</sup>): C, 63.99; H, 5.37; N, 9.33. Found: C, 63.87; H, 5.45; N, 9.41%.

#### 2.3.2. Synthesis of complex 1

A methanolic solution (10 mL) of  $Cu(OAc)_2H_2O$  (0.20 g, 1.0 mmol) was added dropwise to a methanolic solution (5 mL) of  $H_2L$  (0.30 g,

1.0 mmol). The yellow color of the solution was gradually faded with simultaneous precipitation of a purple microcrystalline compound. The reaction mixture was stirred for 6 h at room temperature. The crude product was then filtered off, washed with methanol and recrystallized from methanol/acetonitrile. The solvent was partially evaporated, and after three days several dark blue single crystals suitable for X-ray single crystal analysis were collected. X-ray single crystal analysis showed that the complex crystallizes as a solvate with water and acetonityle molecules, Cu(C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>)·(CH<sub>3</sub>CN)·(H<sub>2</sub>O). Yield: 0.324 g (77% based on copper). IR (KBr pellet, cm<sup>-1</sup>): 3440 (br,  $\nu_{OH}$ ), 1621 (vs,  $\nu_{C=N}$ ), 1224 (s,  $\nu_{PhO}$ ), 520 (w,  $\nu_{Cu-O}$ ), 427 (w,  $\nu_{Cu-N}$ ). UV–Vis (DMSO):  $\lambda_{max}$  (nm) ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 290 (39900), 348 (20600). Anal. Calc. for C<sub>18</sub>H<sub>19</sub>CuN<sub>3</sub>O<sub>5</sub> (MW = 420.9 gmol<sup>-1</sup>): C, 51.36; N, 9.98; Cu, 15.10; O, 19.01 and H, 4.55%. Found: C, 51.14; N, 9.90, Cu, 15.22O, 19.28 and H 4.46%.

#### 2.3.3. Synthesis of complex 2

A methanolic solution (10 mL) of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.25 g, 1.0 mmol) was added dropwise to a methanolic solution (5 mL) of H<sub>2</sub>L (0.30 g, 1 mmol). The yellow color of the solution was gradually faded with simultaneous precipitation of a dark orange microcrystalline compound. After stirring for 6 h at room temperature, the crude product was filtered off, and recrystallized from methanol. After four days several orange single crystals suitable for X-ray single crystal analysis were collected. Yield: 0.30 g (81% based on Ni(II)). IR (KBr pellet, cm<sup>-1</sup>): 3414 (br,  $\nu_{OH}$ ), 1620 (vs,  $\nu_{C=N}$ ), 1229 (s,  $\nu_{PhO}$ ), 568 (w,  $\nu_{Ni-O}$ ), 434 (w,  $\nu_{Ni-N}$ ). UV–Vis (DMSO):  $\lambda_{max}$  (nm) ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 270 (46200), 310 (16900), 392 (8400), 438 (4100). Anal. Calc. for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>NiO<sub>5</sub> (MW = 375.02 g mol<sup>-1</sup>): C, 51.24; N, 7.48, Ni, 15.65; O, 21.33 and H, 4.30%;. Found: C, 51.40; N, 7.38; Ni, 15.52; O, 21.40 and H, 4.30%.



Fig. 5. <sup>1</sup>H NMR spectrum of the H<sub>2</sub>L salen ligand in DMSO-d<sub>6</sub>.

# 2.4. Modification of the GCE with the Ni(II) complex

A bare GCE was polished on an emery paper with some alumina powder (0.05  $\mu$ m). Then, the GCE was carefully sonicated in a bath of deionized water and ethanol (1:1) to remove any absorbed particles. Finally, the washed GCE was dried at room temperature. In the next step, 1 mg of the Ni(II) complex was dispersed in 1 mL of ethanol (containing 10  $\mu$ L of nafion 0.2 wt%) for 1 h, and then 2  $\mu$ L of the obtained dispersion was dropped onto the cleaned GCE surface. The GCE modified with the Ni(II) complex, denoted as the Ni(II) complex/GCE, was air dried before use.

# 3. Results and discussion

# 3.1. Description of the crystal structures

The complexes **1** and **2** were crystallized in the monoclinic crystal system with  $P2_1/c$  and C2/c space groups, respectively (Table 1). The molecular structures of **1** and **2** are illustrated in Fig. 1. The selected bond lengths and angles are presented in Table 2. In both of the complexes, the deprotonated ligand  $L^{2-}$  is tetradentate and the central cation (Cu or Ni) is coordinated through four donor atoms to form the coordination complexes with one five-membered and two six-membered chelate rings (6–5-6). Also, the central metal ions have square-planar geometries with a slight distortion. Sum of the different angles around the metal in the complexes **1** (361.93°) and **2** (360.03°) confirms their slightly distorted square-planar geometries [17].

The O1-C1-C6-C7-N1-M and N2-C10-C11-C16-O4-M atoms form sixmembered chelate rings with the O1-M-N1 angles of 93.70° and 95.14°, and N2-M-O4 angles of 93.98° and 94.27° for the complexes 1 and 2, respectively. The N1-C8-C9-N2-M atoms form five-membered chelate rings with the N1-M-N2 angles of 84.29° and 85.88° for the complexes 1 and 2, which are smaller than their analogues in the six-membered rings [1]. The Cu<sup>2+</sup> cation is deviated by ~0.157 Å from the average plane defined by N<sub>2</sub>O<sub>2</sub> of the chelate  $L^{2-}$  ligand, whereas the deviation of Ni<sup>2+</sup> cation from this plane is only 0.039 Å. The whole complex molecule (1 and 2, without H atoms) is almost planar. The C atoms of both CH<sub>2</sub> groups, however, are displaced up and down the average plane through the all atoms of the  $L^{2-}$  excluding both C atoms of the methylene groups. The displacement of C8 and C9 atoms form the average plane of the other atoms of  $L^{2-}$  is 0.58 and -0.25 Å for the Cucomplex, and -0.22 and 0.47 Å for the Ni-complex, respectively.

Any atoms of solvent molecules or adjacent units do not coordinate to the metal (Cu, Ni) center at the axial sites, whereas the  $H_2O$  and  $CH_3CN$  solvents in crystal **1** are hydrogen bonded together via O1W—H1W1···N3 and further linked via O-H···O with the hydroxyl group of CuL complex, and in crystal **2** the water molecule acts as acceptor in the O-H··O with hydroxyl group of NiL complex (Table 3). Arrangement of molecules in the crystal **1** and **2** together with the hydrogen bonding interactions is illustrated in Fig. 2a, b, respectively. The discrete CuL in **1** and NiL in **2** chelates interact mainly by van der Waals forces and further are connected by hydrogen bonds through solvent molecules.

As can be seen from the Fig. 3, the packing of molecules in the unit cell is less compact in 2 than in 1, because crystal 2 contains channels available to the solvent. The additional solvent molecules (CH<sub>3</sub>OH) may have been partially removed from the channels because the crystals were allowed to dry at ambient temperature prior to the X-ray analysis.



Fig. 6. (a, b) SEM images of GCE and Ni(II) complex/GCE, (c) EDX pattern of Ni(II) complex/GCE, and (d) Mapping images of Ni(II) complex/GCE.

Therefore, these solvent molecules are highly disordered in channels with partial occupation, and as was mentioned in the experimental part, the correct modelling of the disordered molecules was not possible and therefore the scattering contribution of these molecules was removed by a SQUEEZE procedure. Presence of channels in the crystal structure of **2** (as a MOF) can be useful for the study of the absorption capacity of various gases or other pollutant molecules.

#### 3.2. Spectroscopic characterizations

In the FT-IR spectrum of the H<sub>2</sub>L ligand, characteristic bands of the (O–H) and (C=N)<sub>imine</sub> functional groups were observed at 3416 and 1639 cm<sup>-1</sup>, respectively. Likewise, in the FT-IR spectra of the complexes **1** and **2**, the broad peaks of the (O–H) moieties were observed at 3440 and 3414 cm<sup>-1</sup>, respectively. After complexation with Cu(II) and Ni(II), however, the (C=N) stretching vibrations of **1** and **2** were observed at 1621 and 1620 cm<sup>-1</sup>, which is a direct indication of the involvement of the azomethine nitrogen in coordination [18]. In addition, the  $\nu$ (Ph-O) was shifted to lower frequencies in both complexes, which further confirms the complexation of Cu(II) and Ni(II). Moreover, the FT-IR spectrum of complex **1** showed the  $\nu$ (Cu–O) and  $\nu$ (Cu–N) at 520 and 427 cm<sup>-1</sup>, respectively. The corresponding values for the Ni

(II) complex (2) were 568 and 434  $\text{cm}^{-1}$ , respectively.

The electronic spectra of the ligand and its complexes (H<sub>2</sub>L, 1 and 2) were recorded at room temperature (20 µM in DMSO, Fig. 4). The H<sub>2</sub>L ligand showed its characteristic absorption bands at 280, 308, and 390 nm. The high intensity bands at 280 and 308 nm are attributable to the  $\pi \to \pi^*$  and  $n \to \pi^*$  transitions of the aromatic rings and the azomethine groups, respectively. Also, the broad band at about 390 nm is attributable to the intraligand charge-transfer. Upon formation of the complexes, notably these bands were shifted to some extent, suggesting that the nitrogen atom of the azomethine group is coordinated to the metal ion. The distinct bands at 348 and 310 nm in the electronic spectra of the complexes **1** and **2** are arising from the  $n \rightarrow \pi^*$  transitions of the azomethine groups [19]. Moreover, high intensity bands at 290 and 270 nm (for 1 and 2, respectively) are associated with the aromatic  $\pi \rightarrow \pi^*$  intraligand transitions [20]. The spectrum of the complex 2 showed a band at about 392 nm which may be assigned to the MLCT transition from the metal-centered HOMO to the ligand centered LUMO (C=N( $\pi^*$ )) [21]. The Ni(II) complex is diamagnetic and the band around 440 nm could be assigned to  ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$  transition, consistent with other square-planar Ni(II) complexes [22]. Both complexes showed the anticipated *d*-*d* transitions at higher wavelengths (insets of Fig. 4), attributable to their square planar geometries [23].



**Fig. 7.** The recorded (a) CVs and (b) Nyquist plot of the GCE and Ni(II) complex/GCE in a 1:1 mixture of 5 mM [Fe(CN)<sub>6</sub>]  $^{3-}$ /[Fe(CN)<sub>6</sub>]  $^{4-}$  and 0.1 M KCl at a scan rate of 50 mV s<sup>-1</sup> in the frequency range of 0.01 Hz to 50 kHz and (c) the circuit model for Ni(II) complex/GCE.



Fig. 8. (a) CVs of the Ni(II) complex/GCE and GCE in 0.1 M NaOH in the absence and presence of 100  $\mu$ M hydrazine. Inset: the CVs of the bare GCE in the absence and presence of 100  $\mu$ M hydrazine with higher magnification and (b) CVs of the Cu(II) complex/GCE in 0.1 M NaOH in presence and the absence of 100  $\mu$ M hydrazine.

<sup>1</sup>H NMR spectra of the  $H_2L$  ligand was recorded at 298 K in DMSO- $d_6$  (Fig. 5). The broad signals at 13.58 and 9.80 ppm can be readily attributed to the phenolic OH<sup>7</sup> and OH<sup>5</sup> moieties. The aromatic protons of the salen ligand resonated in the range of 6.18–7.18 ppm, and unambiguously assigned according to their coupling constants (see experimental). The expected singlet for the proton of the imine moiety (H<sup>2</sup>) was observed at 8.37 ppm. The aliphatic protons (H<sup>1</sup>) were also observed as a singlet at 3.79 ppm.

#### 3.3. Electrochemical studies

SEM, EDX and MAP analyses were used to compare morphologies of the modified and unmodified electrodes. The SEM images are shown in Fig. 6a, b. The SEM image of the unmodified electrode is uniform, smooth, and free from any particles. On the other hand, non-uniform dispersion of particles of different sizes was observed on the surface of the modified electrode. Therefore, the SEM images show that the electrode has been modified successfully. Also, the EDX and MAP analyses reveal the presence of nitrogen, carbon, oxygen, and nickel atoms on the electrode's surface, which further confirms that the electrode was coated by the nickel complex appropriately (Fig. 6c, d).

In order to study the potential applications of the synthesized complexes, the Ni(II) complex was employed as a modifier for a glassy carbon electrode (GCE) to prepare an electrochemical sensor for detection of hydrazine. To study the properties of the modified electrode, cyclic voltammograms of the GCE and Ni(II) complex/GCE in a 1:1 mixture of 5 mM [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> and 0.1 M KCl as the redox probe were recorded. As seen in Fig. 7a, the GCE shows a pair of reversible



Fig. 9. (a) CVs recorded for the different amounts of Ni(II) complex in 0.1 M NaOH in presence of 100 µM hydrazine, and b) dependence of the Ip to the amount of the Ni(II) complex.



**Fig. 10.** (a) CVs of the Ni(II) complex/GCE in different scan rates of 10, 20, 30, 50, 70, 90, 120 and 150 mV s<sup>-1</sup> in a solution consisting of 0.1 M NaOH and 100  $\mu$ M hydrazine, (b) plot of the peak current vs square root of the scan rate, (c) anodic peak potential vs the logarithm of the scan rate and (d) variation of the scan rate normalized current (Ip/v<sup>1/2</sup>) with scan rate.

redox peaks with a peak-to-peak difference ( $\Delta E_p$ ) of 140 mV, while the Ni(II) complex/GCE represents better reversibility with a higher current and lower  $\Delta E_p$  value of 90 mV. EIS studies were used to investigate the changes in the electrochemical behavior of the modified electrode and the value of the electron transfer resistance (R<sub>ct</sub>) by monitoring of the

semicircular diameter of the curves [24,25]. To do so, the Nyquist curves of the GCE and the Ni(II) complex/GCE in the range of 0.01 Hz to 50 kHz were recorded (Fig. 7b). As expected, the semicircular diameter of the Ni(II) complex/GCE is smaller than that of the bare GCE, representing a decrease in the R<sub>ct</sub> value and an increase in the kinetics



Fig. 11. (a) Amperometric response of the Ni(II) complex/GCE in presence of different concentrations of hydrazine including 0.5, 1, 5, 10, 15, 25, 30, 40, 50, 70, 90, 100 and 150  $\mu$ M at 0.55 V in 0.1 M NaOH and (b) the relationship between the current response and hydrazine concentration.

#### Table 4

Comparison of the different electrochemical techniques for determination of hydrazine.

Modified Electrode	Technique	Sensitivity ( $\mu A \ \mu M^{-1} \ cm^{-2}$ )	LOD (µM)	Linear range (µM)	Refs.
Pd/CNF/GCE	CV	0.0012	2.9	10-4000	[30]
Mn <sub>7</sub> O <sub>13</sub> 5H <sub>2</sub> O/α-MnO <sub>2</sub> /GCE	CV	0.1096	2.1	3–2800	[31]
CoHCF-rGO/GCE	Amperometry	-	0.069	0.25-100	[32]
AuNP-GPE	Amperometry	-	3.07	25-1000	[33]
AuNPs/poly(BCP)/CNT/GCE	LSV	-	0.1	0.5–1000	[34]
Nano-Au/porous-TiO <sub>2</sub> /GCE	Amperometry	0.1722	0.5	2.5-500	[35]
GCE-CoPc-(CoTPP) <sub>4</sub>	Amperometry	-	1	0–230	[36]
FePc-linked-MPyr-SAM	CV	0.0162	11	13.2–197	[37]
ZnO/SWCNT/GCE	Amperometry	0.1	0.17	0.5–50	[38]
ZnO/Nf/Au/GCE	Amperometry	0.51	0.25	0.8-200	[39]
Ni(II) complex/GCE	Amperometry	0.1174	0.166	0.5–150	This study



Fig. 12. Amperometric current response of the Ni(II) complex/GCE against 10  $\mu$ M hydrazine and 10 mM FeSO<sub>4</sub>, FeCl<sub>2</sub>, NaCl, CuNO<sub>3</sub>, and H<sub>2</sub>O<sub>2</sub> in 0.1 M NaOH at 0.55 V and 150 s<sup>-1</sup>.

# Table 5

Determination of hydrazine in the Tehran's Jajrood river water.

Real sample	Added (µM)	Found (µM)	Recovery (%)
Tehran's Jajrood river water	25	24.1	96.40
	50	51.3	102.60
	100	98.7	98.70

of electron transfer on the electrode surface (Fig. 7c). These findings represent that the Ni(II) complex may be a good choice in the electrode modification process. Both CV and EIS techniques corroborate that the modification process was successfully done.

To investigate the electrochemical behavior of the modified electrode on the electrocatalysis of hydrazine, the CV technique was applied (Fig. 8). In the absence of hydrazine, the Ni(II) complex/GCE showed a couple of well-defined Ni(II)/Ni(III) redox peaks in the potential range of 0.2–0.8 V in 0.1 M NaOH, while there were not any redox peaks for the bare GCE. Upon addition of 100  $\mu$ M hydrazine to the electrolyte solution, the Ni(II) complex/GCE indicated a significant increase in the anodic peak current at the potential of +0.55 V and a decrease in the cathodic peak current, whereas, the bare GCE indicated no sharp signal. This behavior may be attributed to the oxidation of Ni(II) complex/GCE through the reaction between Ni species and hydrazine [26,27]. The results obtained in this study are in agreement with the previous reports on electrochemical behavior of hydrazine on the surface of the modified electrodes [26,28,29].

Electrochemical behavior of hydrazine was also investigated at the surface of the copper complex-modified electrode. Fig. 8b shows the cyclic voltammogram of the copper modified electrode in 0.1 M NaOH in presence and in the absence of hydrazine. In the absence of hydrazine, an oxidation-reduction response was observed for the copper complex, which can be related to the oxidation of Cu to Cu(I) (or Cu(II)) and reduction of the product to Cu. In presence of hydrazine, the redox potential of the copper complex was also shifted, but the difference was noticeable when compared with the nickel complex. This suggests the nickel complex as a better modifier.

Ni(II) complex  $\rightarrow Ni(III)$  complex + e<sup>-</sup>

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Ni(III) complex +  $N_2H_4 \rightarrow Ni(III)N_2H_4$  complex

 $Ni(III)N_2H_4$  complex + 4OH<sup>-</sup>  $\rightarrow$  Ni(II) complex + N<sub>2</sub> + 4H<sub>2</sub>O + 3e<sup>-</sup>

The amount of the modifier used was also investigated. The results showed that the modifier amount has no significant effect on the electrochemical behavior of hydrazine. Therefore, 2  $\mu$ L of the modifier was selected as the optimum amount of the nickel complex for modification of the glassy carbon electrode (Fig. 9).

To further study the electrocatalysis of hydrazine onto the Ni(II) complex/GCE surface, the scan rate effect was investigated by recording the CVs of the modified electrode in the range of 10–150 mV s<sup>-1</sup>. As shown in Fig. 10a, the anodic peak potentials were gradually shifted to more positive potentials upon increasing the scan rate. This behavior confirms the kinetic limitation of the electrochemical reaction onto the modified electrode surface. It was also observed that the anodic peak current of the hydrazine was linearly changed with the square root of the scan rate (Fig. 10b). These findings may be ascribed to the fact that the reaction is controlled by mass transfer, and the electrocatalytic process is controlled by diffusion of the hydrazine from the solution bulk to the modified electrode surface. Furthermore, the slope of the Tafel line can be calculated from Eq. (1) by considering the plot of the peak potential versus the logarithm of the scan rate (Fig. 10c).

$$E_p = (b \log \vartheta)/2 + \text{constant} b = \frac{2.3 RT}{(1 - \alpha)n_{\alpha}F}$$
(1)

where, all symbols have the normal meanings in the electrochemical studies. Accordingly, the slope of the Tafel line was estimated to be 0.0593 assuming a single electron transfer for the rate-determining step with the diffusion coefficient ( $\alpha$ ) equal to 0.58. The plot of the sweep rate normalized current ( $\text{Ip}/\nu^{1/2}$ ) versus sweep rate is an EC<sub>Cat</sub> catalytic process (Fig. 10d).

In order to explore the analytical performance of the modified electrode as a hydrazine sensor, different concentrations of hydrazine were injected into the electrolyte solution and the amperometric signals at the applied potential of 0.55 V were recorded. As can be seen in Fig. 11a, the sensor offers an excellent applicability for detection of hydrazine in the range of 500 nM to 150  $\mu$ M. Accordingly, there is a linear relationship between the amperometric signal and the concentration of hydrazine under the regression equation of I ( $\mu$ A) = 0.1174 [hydrazine] ( $\mu$ M) – 0.0724, with R<sup>2</sup> = 0.9886 (Fig. 11b). The limit of detection (LOD) and sensitivity values of the strategy were calculated to be 166.6 nM and 0.1174 ( $\mu$ A  $\mu$ M<sup>-1</sup> cm<sup>-2</sup>).

This fantastic low LOD value and wide dynamic linear range reflects the sensor's admirable potential in detection of hydrazine in comparison to the other reported methods in the literature (Table 4). These satisfactory results are attributed to the embedded interface sensing based on the Ni(II) complex as a modifier, and indicate its great applicability in the electrochemistry studies.

Another attractive feature of this strategy is its high operational stability for hydrazine detection, so that the signal current of the sensor does not decrease significantly after 50 repetitive cycles in the electrolyte solution (data not shown). Furthermore, to study the reproducibility of the results, five separate Ni(II) complex/GCEs were used to measure hydrazine in a known 100  $\mu$ M solution. The relative standard deviation (RSD) of the measurements was found to be 2.15%, which indicates that the sensor reproducibility is satisfactory (data not shown). Also, the repeatability of the results was checked by using the above mentioned solution for six times and a relative standard deviation (RSD) of 1.85% was obtained which indicates the good repeatability of the method for analysis of hydrazine (data not shown). An important issue in sensor studies, is to determine specificity which is a vital factor to evaluate the assay protocol.

To study this factor and to minimize the false-positive responses, several chemicals such as  $FeSO_4$ ,  $FeCl_2$ , NaCl,  $CuNO_3$  and  $H_2O_2$  were tested under the optimized sensor working conditions (Fig. 12). While a

sharp amperometric signal was obtained by injecting 10  $\mu$ M hydrazine into the electrolyte solution, none of the other compounds produced a significant signal even at a 10<sup>3</sup>-fold concentration. Thus, the Ni(II) complex/GCE can be introduced as a specific sensor for detection of hydrazine in solution.

Finally, the practicality of the Ni(II)-modified electrod was evaluated towards determination of hydrazine in three different real samples from Tehran's Jajrood river. The hydrazine concentration was determined using the standard addition technique. As listed in Table 5, the recovery values are in the range of 96.40–102.60%, corroborating that the sensor has fantastic potential in detection of hydrazine in real samples such as river water.

#### 4. Conclusion

A tetradentate  $N_2O_2$  Schiff base ligand (*N*,*N*'-bis-(4-hydroxy-salicylidene)-ethylenediamine,  $H_2L$ ) was synthesized by condensation of 2,4dihydroxybenzaldehyde and ethylenediamine. The ligand was utilized for preparation of two new mononuclear Cu(II) and Ni(II) complexes. All of the products were characterized by appropriate techniques. The Ni(II) complex was used to fabricate a Ni(II) complex/GCE as an electrochemical sensor for determination of hydrazine. The sensor presented unique features such as low LOD, broad dynamic linear range, specificity, high stability, and operational repeatability compared to the other reported hydrazine sensors. These findings may extend the potential applications of the synthesized Schiff-base complexes in various fields such as electrochemistry.

# CRediT authorship contribution statement

Tahereh Hosseinzadeh Sanatkar: Methodology, Investigation, Writing - original draft. Alireza Khorshidi: Conceptualization, Methodology, Supervision. Esmail Sohouli: Electrochemistry. Jan Janczak: Crystallography.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

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