

Available online at www.sciencedirect.com



Polyhedron 25 (2006) 1893-1900



# Synthesis, characterization and spectroscopic and electrochemical studies of new axially coordinated cobalt(III) salen (salen = N,N'-bis(salicylidene)-1,2-ethylenediamine) complexes. The crystal structure of [Co<sup>III</sup>(salen)(aniline)<sub>2</sub>]ClO<sub>4</sub>

Ali Akbar Khandar<sup>a,\*</sup>, Behrouz Shaabani<sup>a</sup>, Ferdinand Belaj<sup>b</sup>, Akbar Bakhtiari<sup>a</sup>

<sup>a</sup> Department of Inorganic Chemistry, Faculty of Chemistry, Tabriz University, Daneshgah Street, Tabriz, East Azarbaijan 51664, Iran <sup>b</sup> Institut für Chemiel Anorganische Chemie Karl-Franzens-Universität Graz, Austria

> Received 30 August 2005; accepted 1 December 2005 Available online 18 January 2006

### Abstract

Cobalt(III) complexes with some salen ligands (salen = N,N'-bis(salicylidene)-1,2-ethylenediamine) as equatorial and potentially tetradentate ligands and with different axial amine ligands (cyclohexylamine, aniline, 4-picoline and pyridine) were synthesized in situ and characterized by IR, <sup>1</sup>H NMR and elemental analysis. Electronic spectra and electrochemical properties of the complexes were studied in DMF solutions. Electronic structure calculations indicate that the absorption between 420 and 440 nm, which are the lowest energy transfers in the complexes, are attributed to metal–ligand charge transfer transitions. The cyclic voltammetry of the complexes show an irreversible reduction of Co(III) to Co(II) and a reversible reduction of Co(II) to Co(I). The axial ligands affect reduction potentials of Co(III) in the order of changes of axial ligands'  $pK_a$ . The crystal structure of [Co(salen)(aniline)<sub>2</sub>]ClO<sub>4</sub> was determined. In the [Co(salen)(aniline)<sub>2</sub>]ClO<sub>4</sub>, cobalt(III) center is six coordinated surrounded by an equatorial tetradentate salen Schiff-base ligand and two aniline axial ligands and ClO<sub>4</sub><sup>-</sup> acts as a counter ion.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Cobalt(III) complexes; Schiff-base; Axial amine ligand; Crystal structure; Electrochemistry

## 1. Introduction

Cobalt Schiff-base complexes have been used as catalysts for the oxygenation reactions, dioxygen carriers and oxygen activators [1-5] and enantioselective and asymmetric catalysis [6-8]. Modeling of transition metal coordination species existing in living systems and studying of intermediate species involved in reactions of such systems are important investigation fields that attract lots of studies [8]. In the area of bioinorganic chemistry interest in Schiff-base complexes has centered on the role of such complexes in providing synthetic models for the metal-containing sites in metallo-proteins and metallo-enzymes [9-13]. The cobalt complexes of tetradentate Schiff-base ligands have been widely used to mimic cobalamine (B<sub>12</sub>) coenzymes [14-18]. Cobalt(III) Schiff-base complexes are potent antiviral, antibacterial and antitumor agents and those containing labile axial ligands exhibit higher activities and more stability [19].

Hopping to mimic such living systems and to shed some light on binding modes and activity in this systems, we report here, the synthesis, characterization, spectroscopic and electrochemical studies of some cobalt(III) complexes of salen and its phenyl azo derivative with axial amine ligands, where salen is N,N'-bis(salicylidene)-1,2-ethylene-diamine. Moreover the crystal structure of  $[Co^{III}(salen)-(aniline)_2]ClO_4$  was determined.

<sup>\*</sup> Corresponding author. Tel.: +98 411 3393128; fax: +98 411 3340191. *E-mail address:* akhandar@yahoo.com (A.A. Khandar).

<sup>0277-5387/\$ -</sup> see front matter @ 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2005.12.001

#### 2. Experimental

#### 2.1. Materials

All of used chemicals were reagent grade. Salicylaldehyde and aniline were used after distillation under reduced pressure. Ethylenediamine and cyclohexylamine were distilled before use. The other reagents were used without further purification. 5-Phenylazo salicylaldehyde was synthesized as described in the literature [20].

#### 2.2. Physical measurements and methods

Infrared (FT-IR) spectra were recorded using KBr discs on a Bruker Tensor 27 instrument. <sup>1</sup>H NMR spectra were taken on a Bruker Spectrospin Avance 400 MHz ultrashield spectrometer. The electronic spectra in the 200-600 nm range were obtained on a Shimadzu UV-265 FW spectrophotometer and quartz cells of light pass length 1.00 cm, using solutions with the concentration of  $1 \times 10^{-5}$  in DMF. CHN elemental analyses were performed using a Heraeus CHN-O RAPID elemental analyzer. Melting points were taken using an electrothermal IA 9100 apparatus in open capillary tubes. Cyclic voltammograms were recorded using an AMEL instrument Model 2053 as potentiostat connected with AMEL Model 568 as function generator. All solutions were deoxygenated by passing a stream of argon into the solution for at least 10 min before recording the voltammogram. All potentials reported herein were measured at room temperature and referenced to the saturated Ag/AgCl electrode with ferrocene as an internal standard. A glassy carbon disc with a diameter of 3 mm was used as the working electrode and a platinum wire was used as counter electrode. Before each experiment the working electrode was polished with alumina and rinsed thoroughly with distilled water and acetone. The electrolytic medium consisted of 0.1 M LiClO<sub>4</sub> in DMF. Under these conditions the ferrocenium-ferrocene couple shows a peak separation of 89 mV. A Pentium IV computer with a 1200 MHz processor, 256 MB of RAM and the HYPER-CHEM package version 7 [21] were used for quantum chemical calculations.

#### 2.3. Synthesis of Schiff-base ligands

Schiff-base ligands were prepared in a similar manner according to the literature [22] as the following procedure: To a stirring solution of 2 mmol of appropriate aldehyde in ethanol was added a solution of 1 mmol diamine in ethanol dropwise and then refluxed for 2 h. The precipitated Schiff-base was filtered and recrystallized from hot ethanol giving N,N'-bis(5-X-salicylidene)-1,2-ethylenediamine, where X is H and N<sub>2</sub>ph (diazophenyl) that will abbreviated here as H<sub>2</sub>L<sup>1</sup> and H<sub>2</sub>L<sup>2</sup>, respectively. Some analytical and physical data of the ligands are summarized as follows.

# 2.3.1. Salen $(C_{16}H_{16}N_2O_2)$ $(H_2L^1)$

Yellow crystals, yield 78% (0.4186 g); m.p.: 168 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  13.22 (br s, 2H, OH), 8.35 (s, 2H, H<sub>e</sub>), 8.29 (m, 2H, H<sub>b</sub>), 7.22 (dd, 2H, H<sub>d</sub>), 6.94 (d, 2H, H<sub>a</sub>), 6.85 (m, 2H, H<sub>c</sub>), 3.94 (s, 4H, H<sub>f,g</sub>). FT-IR(KBr, cm<sup>-1</sup>): 3300–3400 (m, OH), 2900 (aliphatic CH), 1645 (s, imine C=N), 1200 (phenolic CO).

# 2.3.2. Bis(5-phenyl azo)salen $(C_{28}H_{24}N_6O_2)$ $(H_2L^2)$

Orange crystals, yield 92% (0.8768 g); m.p.: 229 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  13.79 (br s, 2H, OH), 8.52 (s, 2H, H<sub>e</sub>), 7.97 (dd, 2H, H<sub>b</sub>), 7.92 (d, 2H, H<sub>d</sub>), 7.84–7.87 (m, 4H, H<sub>i,m</sub>), 7.42–7.52 (m, 6H, H<sub>j,k,l</sub>), 7.07 (d, 2H, H<sub>a</sub>), 4.04 (s, 4H, H<sub>f,g</sub>). FT-IR(KBr, cm<sup>-1</sup>): 3300–3400 (m, OH), 1635 (s, imine C=N), 1185 (phenolic CO).

#### 2.4. Synthesis of the complexes

The complexes shown in Scheme 1 were synthesized as follows.

1 mmol of Co (II) acetate tetrahydrate, 1 mmol of the appropriate Schiff-base ligand, 2 mmol of axial amine and 4 mmol of LiClO<sub>4</sub> were added to 100 ml of ethanol. The obtained solution turned red rapidly upon the formation of  $Co^{(II)}$ (salen) complex. Then air was bubbled through the reaction mixture for oxidizing the  $Co^{(II)}$ (salen) and the mixture stirred and refluxed for 2 h. Then air bubbling and stirring was continued for 24 h. After which the obtained brown material was washed and recrystallized from appropriate solvent systems.

# 2.4.1. Preparation of $[CoL^{1}(cyclohexylamine)_{2}]ClO_{4}$

The complex was recrystallized from hot ethanol, yielding brown crystals. Yield 96.5% (0.6012 g). *Anal*. Calc. for  $CoC_{28}H_{40}N_4O_6Cl$ : C, 54.0; H, 6.5; N, 9.0. Found: C, 53.3; H, 6.4; N, 8.8%; m.p.: 199.2 °C. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  8.17



 $H_2L^1$  (salen) complexes: amine= pyridine, picoline, aniline, cyclohexylamine

 $H_2L^2$  (bis(5-phenylazo)salen) complex: amine= pyridine

Scheme 1. A schematic representation of the studied complexes.

(s, 2H, H<sub>e</sub>), 7.34 (dd, 2H, H<sub>d</sub>), 7.24 (m, 2H, H<sub>b</sub>), 7.10 (d, 2H, H<sub>a</sub>), 6.53 (q, 2H, H<sub>c</sub>), 3.39 (s, 4H, H<sub>f,g</sub>), 2.82 (br d, 4H, H<sub>d'</sub>), 2.21 (br m, 2H, H<sub>c'</sub>), {1.37 (m, 10H) and 0.85 (m, 10H): H<sub>a'</sub> and H<sub>b'</sub>}. FT-IR(KBr, cm<sup>-1</sup>): 3295.69 and 3245.86 (m, NH), 1629 (s, C=N), 1090 (br s,  $ClO_4^{-1}$ ).

# 2.4.2. Preparation of $[CoL^{1}(aniline)_{2}]ClO_{4}$

The complex was recrystallized from acetonitrile/ethanol (1:2 v/v) yielding brown crystals. Yield 98.2% (0.5999 g). *Anal.* Calc. for  $CoC_{28}H_{28}N_4O_6Cl$ : C, 55.1; H, 4.6; N, 9.2. Found: C, 54.3; H, 4.8; N, 8.9%; m.p.: 228.6 °C. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  7.92 (s, 2H, H<sub>e</sub>), 7.32 (m, 2H, H<sub>d</sub>), 7.16 (dd, 4H, H<sub>a'</sub>), 7.06 (m, 2H, H<sub>b</sub>), 6.90–6.94 (m, 4H, H<sub>a,c'</sub>), 6.54–6.61 (m, 6H, H<sub>c,b'</sub>), 4.52 (br s, 4H, H<sub>d'</sub>), 3.80 (s, 4H, H<sub>f,g</sub>). FT-IR(KBr, cm<sup>-1</sup>): 3234 and 3145 (m, NH), 1631 (s, C=N), 1208 (phenolic CO), 1099 (br s,  $ClO_4^{-}$ ).

#### 2.4.3. Preparation of $[CoL^{1}(4-picoline)_{2}]ClO_{4}$

The complex was recrystallized from acetonitrile/ethanol (1:2 v/v) yielding brown crystals. Yield 93.2% (0.5694 g). *Anal.* Calc. for  $CoC_{28}H_{28}N_4O_6Cl$ : C, 55.1; H, 4.6; N, 9.17. Found: C, 54.1; H, 4.7; N, 9.0%; m.p.: 249.1 °C. <sup>1</sup>H NMR(CD<sub>3</sub>CN):  $\delta$  8.39 (s, 2H, H<sub>e</sub>), 7.89 (d, 4H, H<sub>a'</sub>), 7.21–7.34 (m, 8H, H<sub>b,d,b'</sub>), 7.10 (d, 2H, H<sub>a</sub>), 6.52 (m, 2H, H<sub>c</sub>), 4.12 (s, 4H, H<sub>f,g</sub>), 2.27 (s, 6H, H<sub>c'</sub>). FT-IR(KBr, cm<sup>-1</sup>): 1626 (s, C=N), 1210 (phenolic CO), 1097 (br s,  $ClO_4^{-}$ ).

# 2.4.4. Preparation of $[CoL^{1}(pyridine)_{2}]ClO_{4}$

The complex was recrystallized from acetonitrile/ethanol (1:2 v/v) yielding brown crystals. Yield 94.0% (0.5479 g). *Anal.* Calc. for  $CoC_{26}H_{24}N_4O_6Cl$ : C, 53.6; H, 4.2; N, 9.6. Found: C, 53.4; H, 4.2; N, 9.5%; m.p.: 282.5 °C. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  8.42 (s, 2H, H<sub>e</sub>), 7.89 (d, 4H, H<sub>a'</sub>), 7.86 (m, 2H, H<sub>b</sub>), 7.22–7.42 (m, 8H, H<sub>d,b',c'</sub>), 7.12 (d, 2H, H<sub>a</sub>), 6.52 (m, 2H, H<sub>c</sub>), 4.14 (s, 4H, H<sub>f</sub>,g). FT-IR(KBr, cm<sup>-1</sup>): 1626 (s, C=N), 1210 (phenolic CO), 1093 (br s,  $ClO_4^{-}$ ).

# 2.4.5. Preparation of $[CoL^2(pyridine)_2]ClO_4$

The complex was recrystallized from acetonitrile/ethanol (1:2 v/v) yielding brown crystals. Yield 90.0% (0.7120 g). *Anal.* Calc. for  $CoC_{38}H_{32}N_8O_6Cl$ : C, 57.7; H, 4.1; N, 14.2. Found: C, 57.0; H, 4.4; N, 13.8%; m.p.: 265.1 °C. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  8.66 (s, 2H, H<sub>e</sub>), 8.14 (dd, 4H, H<sub>a'</sub>), 8.06 (d, 2H, H<sub>d</sub>), 7.87–7.94 (m, 4H, H<sub>b,c'</sub>), 7.75–7.78 (m, 4H, H<sub>i,m</sub>), 7.55 (m, 4H, H<sub>b'</sub>), 7.44–7.5 (m, 6H, H<sub>j,k,l</sub>), 7.32 (d, 2H, H<sub>a</sub>), 4.25 (s, 4H, H<sub>f,g</sub>). FT-IR(KBr, cm<sup>-1</sup>): 1628 (s, C=N), 1117 (br s, ClO<sub>4</sub><sup>-</sup>).

#### 2.5. X-ray crystallography

The red plate like single crystals of the complex  $[CoL^{1}(aniline)_{2}]ClO_{4}$  obtained by slow evaporation of solvent from acetonitrile/ethanol (1:1 v/v) solution of the complex at room temperature.

All the measurements were performed using graphite monochromatized Mo Ka radiation (0.71069 Å) at 95 K:  $C_{28}H_{28}ClCoN_4O_6$ ,  $M_r$  610.92, monoclinic, space group  $P2_1/c$ , a = 11.422(3) Å, b = 16.219(5) Å, c = 14.216(4) Å,  $\beta = 101.77(2)^\circ$ ,  $V = 2578.2(13) \text{ Å}^3$ , Z = 4,  $D_{\text{calc}} = 1.574 \text{ g/}$ cm<sup>3</sup>, absorption coefficient  $\mu = 0.822 \text{ mm}^{-1}$ . Due to the large organic ligand, the linear absorption coefficient  $(\mu)$ is only  $0.822 \text{ mm}^{-1}$  and the crystal used was small (max diameter r = 0.28 mm), so the product of  $\mu \times r$  is only 0.23 and the absorption correction was not carried out. The other crystal data and structure refinement information are as follows: crystal size:  $0.28 \times 0.18 \times 0.12$ (mm), F(000): 1264, diffractometer: Stoe, radiation source: finefocus sealed tube, scan type:  $\omega$  scans, standard reflections: 3 for every 100 reflections, intensity decay: 1.4%,  $\theta$  range for data collection: 2.51-26.00 (°), index ranges:  $-14 \leq h \leq 13$ ,  $-1 \leq k \leq 20$ ,  $-1 \leq l \leq 17$ , reflections collected/unique: 6080/5061, significant unique reflections: 4047 with  $I > 2\sigma(I)$ , R(int)/R(sigma): 0.0319/0.0635, completeness to  $\Theta = 26.0^{\circ}$ : 99.8%, refinement method: fullmatrix least-squares on  $F^2$ , data/parameters/restraints: 5061/371/2, goodness-of-fit on  $F^2$ : 1.063, final R indices [I > 2(I)]:  $R_1 = 0.0452$ ,  $wR_2 = 0.0925$ , R indices (all data):  $R_1 = 0.0647$ ,  $wR_2 = 0.1029$ , extinction expression: none, weighting scheme:  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = (F_o^2 + 2F_c^2)/3$ , weighting scheme parameters *a*, *b*: 0.0242, 2.0103, largest  $\Delta/\sigma$  in last cycle: 0.001, largest difference peak and hole  $(e/Å^3)$ : 0.401 and -0.318, structure solution program: shelxs-97 (Sheldrick, 1990), structure refinement program: SHELXL-97 (Sheldrick, 1997).

# 3. Results and discussion

#### 3.1. Crystal structure

molecular and crystal structure The of the  $[Co(salen)(aniline)_2]ClO_4$  are shown in Figs. 1 and 2, respectively. Some selected bond angles and lengths are listed in Table 1. The complex is composed of the  $[Co(salen)(aniline)_2]^+$  cation complex and the anion  $ClO_4^{-}$ . Cobalt (III) center is coordinated by two phenolate oxygens, two imine nitrogens of the salen ligand and by the two nitrogen atoms of aniline groups, which occupy the axial positions of a distorted octahedral coordination geometry. The two axial ligands are approximately normal to the salen plane. The axial bond angle N(3)-Co-N(4) is 175.92(10)° which is comparable with those of corresponding angles in similar Co(III) complexes [14,15,19]. The salen ligand has a planar coordination geometry and the Co atom lies in the best plane through the atoms O(1), O(2), N(1) and N(2)dev. 0.006 (11) Å). The Co-O (1.894(2), (max 1.911(2) A) and Co–N<sub>imine</sub> (1.895(3), 1.892(2) Å) bond lengths are in good agreement with those of similar complexes [14,15,19]. Every N(4) of ion complex is hydrogen bonded to two phenolate oxygen atoms of other symmetrically related ion complex (Table 2 and



Fig. 1. Stereoscopic ORTEP plot of  $[CoL^1(aniline)_2]ClO_4$ , showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level.



Fig. 2. bc-Plane of [CoL<sup>1</sup>(aniline)<sub>2</sub>]ClO<sub>4</sub>, viewed along the *a*-axis. Hydrogen bonds are shown as dashed lines.

Table 1

Selected bond lengths (Å), bond angles (°) and torsion angles (°) for  $[CoL^1(aniline)_2]CIO_4$ 

Bond lengths $(\mathring{A})$	
Co(1)–O(1)	1.894(2)
Co(1)–O(2)	1.911(2
Co(1) - N(1)	1.895(3
Co(1) - N(2)	1.892(2
Co(1) - N(3)	2.006(2
Co(1) - N(4)	2.002(2
O(1)–C(11)	1.322(3
C(16)–C(17)	1.434(4
C(17)–N(1)	1.289(4
N(1)-C(18)	1.477(4
C(18)–C(28)	1.500(5
O(2)–C(21)	1.320(3
C(26)–C(27)	1.427(4
C(27)–N(2)	1.290(4
N(2)-C(28)	1.466(4
N(3)–C(31)	1.455(4
N(4)-C(41)	1.432(4
Bond angles (°) and torsion angles (°)	
N(2)-Co(1)-O(1)	178.91(10
N(1)-Co(1)-O(2)	179.26(9)
N(4)-Co(1)-N(3)	175.92(10
C(11)-O(1)-Co(1)	125.25(18
C(17) - N(1) - C(18)	119.5(3)
C(17)-N(1)-Co(1)	126.6(2)
C(18) - N(1) - Co(1)	113.81(19
C(21) - O(2) - Co(1)	125.82(18
C(27)-N(2)-C(28)	119.9(2)
C(27)-N(2)-Co(1)	126.5(2)
C(28) - N(2) - Co(1)	113.37(19
C(31)-N(3)-Co(1)	118.37(18
C(41) - N(4) - Co(1)	123.48(19
N(2)-Co(1)-N(1)	85.01(11
O(2)-Co(1)-O(1)	86.67(8)
O(1)-Co(1)-N(1)	93.95(9)
O(2)-Co(1)-N(2)	94.37(10
N(1)-Co(1)-N(3)	91.60(10
N(2)-Co(1)-N(3)	87.97(10
O(1)-Co(1)-N(3)	92.39(9)
O(2)-Co(1)-N(3)	88.77(10
N(1)-Co(1)-N(4)	92.39(10
N(2)-Co(1)-N(4)	93.23(10
O(1)-Co(1)-N(4)	86.49(9)
O(2)-Co(1)-N(4)	87.25(9)
N(1)-C(18)-C(28)-N(2)	-37.4(3)
N(2)-Co(1)-O(2)-C(21)	11.3(2)
N(1)-Co(1)-O(1)-C(11)	17.5(2)
O(1)-Co(1)-N(3)-C(31)	-4.6(2)
O(1)-Co(1)-N(4)-C(41)	-135.5(2)

Fig. 2), so that two ion complexes are linked to each other by four hydrogen bonds to form a dimerized ion complex. Every N(3), also, connects to two perchlorate ions by hydrogen bonds. One of the perchlorate oxygens is hydrogen bonded to one of the N(3) of the other dimerized ion complex, so that, the dimerized ion complexes are linked together via  $\text{ClO}_4^-$  bridging group and form a ribbon along the *c*-axis. The ribbons in *bc*-plane have short contacts by the distances of less than the max sum of atomic van der walls radii.

Table 2	
Iydrogen bonds for [CoL <sup>1</sup> (aniline) <sub>2</sub> ]ClO <sub>4</sub> (Å,	°)

$D - H \cdot \cdot \cdot A$	d(D-H)	$d(H \cdot \cdot \cdot A)$	$d(\mathbf{D} \cdot \cdot \cdot \mathbf{A})$	∠(DHA)
$N(3)-H \cdot \cdot \cdot O(11)$	0.92	2.25	3.160(4)	167.9
$N(3)-H'\cdots O(12)^a$	0.92	2.25	3.161(3)	173.4
$N(4)-H\cdots O(1)^{b}$	0.92	2.16	2.898(3)	136.7
N(4)– $H'$ ···O(2) <sup>b</sup>	0.92	2.22	3.032(3)	146.9

Symmetry transformations used to generate equivalent atoms:  ${}^{a}1 - x$ , 1 - y, 1 - z;  ${}^{b}1 - x$ , 1 - y, -z.

# 3.2. Spectral characterization of the ligands and complexes

The IR and <sup>1</sup>H NMR are in accord with the proposed structures. The FT-IR spectra of all complexes, compared with those of the corresponding ligands, indicate that the v(C=N) band at 1631–1626 cm<sup>-1</sup> is shifted to lower energy by 14–19  $\text{cm}^{-1}$  for salen complexes, but 7  $\text{cm}^{-1}$  in the case of azosalen complex, indicating that the ligands are coordinated to the metal ions through the nitrogen atoms of the azomethine groups. On the other hand, the OH proton signals in <sup>1</sup>H NMR spectra of free ligands (13.2 and 13.79 ppm for H<sub>2</sub>salen and H<sub>2</sub>azosalen, respectively) disappears in the case of complexes indicating that the OH group has been deportoonated and bonded to metal ions as oxygen anion, therefore, the presence of one perchlorate counter ion for each ion-complex of Co(III) can be expected. The appearance of a broad strong band in the IR spectra of the complexes in 1090–1118 cm<sup>-1</sup> is assigned to perchlorate stretching vibrations, which are typical of non-coordinating perchlorate [24].

Comparing the <sup>1</sup>H NMR spectra of the free ligands and complexes, the imine proton resonances of the ligands (8.35 and 8.52 ppm for  $H_2L^1$  and  $H_2L^2$ , respectively) are shifted to lower fields (8.39, 8.42 and 8.66 ppm) in the case of  $[CoL^1(4\text{-picoline})_2]CIO_4$ ,  $[CoL^1(\text{pyridine})_2]CIO_4$  and  $[CoL^2(\text{pyridine})_2]CIO_4$ , respectively, and are shifted to high-field (7.92 and 8.14 ppm) in the case of  $[CoL^1(\text{aniline})_2]CIO_4$  and  $[CoL^1(\text{cyclohexylamine})_2]CIO_4$ , respectively.

Table 3 shows the electronic absorption data for ligands and complexes. The electronic absorption spectrum (>280 nm) of free salen ligand consists of an intense band centered at 316.6 nm attributable to  $\pi \rightarrow \pi^*$  transitions associated with azomethine chromophore [25]. Since such a band is seen for reduced imines too, it seems that the charge transfer from phenolate oxygens to phenyl rings

Table	3
-------	---

Electronic absorption	data for	ligands and	d complexes	in	DMF	solution
Lieutome absorption	uata 101	ingunus and	a complexes		DIMI	solution

Compound	λ (nm)				
$H_2L^1$	273.8			316.6	
$H_2L^2$	268.6			367.2	428 (sh)
[CoL <sup>1</sup> (cyclohexylamine) <sub>2</sub> ]-	268.2	300 (sh)		390.6	420 (sh)
ClO <sub>4</sub>					
$[CoL^{1}(aniline)_{2}]ClO_{4}$	267.6	300 (sh)	328 (sh)	392.2	420 (sh)
$[CoL^{1}(4-picoline)_{2}]ClO_{4}$	268.2	300 (sh)	330 (sh)	392.6	420 (sh)
[CoL <sup>1</sup> (pyridine) <sub>2</sub> ]ClO <sub>4</sub>	268.0	300 (sh)		390.0	420 (sh)
[CoL <sup>2</sup> (pyridine) <sub>2</sub> ]ClO <sub>4</sub>	267.4	300 (sh)		398.2	440 (sh)

are may be involved in this band appearance too [26]. The similar azomethine  $\pi \to \pi^*$  transitions take place at 367 nm in the case of azosalen ligand. A new band, as a shoulder, with a maximum at 428 nm appears in the UV–Vis spectrum of azosalen in contrast to salen, which is attributable to azophenyl substitute. There is some other intense band in high-energy region (about 270 nm) of the spectra of the free ligands which are related to  $\pi \to \pi^*$  transitions of phenyl rings [19].

The Co(III) complexes of these ligands exhibit absorption bands that are red shifted approximately. Complexation of this ligands with Co(III) with different axial ligands does not affect the energy of the phenyl rings  $\pi \to \pi^*$  transitions, whereas the azomethine  $\pi \to \pi^*$  transitions in complexes show red shift about 70 nm in salen complexes and 30 nm in azosalen complex. These  $\pi \to \pi^*$  azomethine transition bands, show a shoulder at 420 nm in salen complexes and at 440 nm in azosalen complex. Fig. 3 compares the electronic spectra for complexes and free ligands.

These shoulders in salen complexes spectra are attributable to metal-ligand charge transfer transitions (MLCT)  $(d \rightarrow \pi^*)$  transitions [14,19], while in azosalen complexes the shoulder can be attributed to  $\pi \rightarrow \pi^*$  intraligand charge transfer with a small contribution of MLCT. These assignments of shoulders are supported by electronic structure calculation employing Zindo/S semiempirical Hamiltonian with  $\pi$ - $\pi$  overlap weighting factor of 0.585 for structures optimized by Zindo/1 method [27–34]. The selected main atomic orbitals contributions to HOMO and LUMO of the complexes are shown in Table 4.

Azosalen spectrum bands show red shift in comparison to salen spectra due to the extended conjugated system in azosalen complexes. Different axially coordinated ligands have no effect on the energies of the electronic transitions.

#### 3.3. Electrochemical studies

By scanning in the negative direction initiated at 0.0 mV, the first and second reduction waves correspond to  $Co(III) \rightarrow Co(II)$  and  $Co(II) \rightarrow Co(I)$  processes appear in the range of (-586)-(-247) and (-1107)-(-1037) mV, respectively (Table 5). The peak separation between the related cathodic and anodic waves indicate a quasireversible and reversible redox reactions for Co(III)/Co(II) (min  $\Delta E_{\rm p} = 302 \text{ mV}$ ) and Co(II)/Co(I) (max  $\Delta E_{\rm p} = 86 \text{ mV}$ ) systems, respectively. The quasireversible redox reaction can be due to the structural changes say by elongation of axial bond lengths or losing of axial amine ligands because of the addition of one electron to  $(d_{z^2})^*$  orbital [19]. The redox peak heights increase by increasing of scan rate. Multiple scans result in nearly superposable cyclic voltammograms, i.e., the three oxidation states of cobalt involved are markedly stable.

For the cathodic process of the Co(III)  $\rightarrow$  Co(II), the observed peak potentials are strongly depend on donor strength of the appropriate axial ligands, since the electron affinity of the Co(III) complexes, decreases by



Fig. 3. The UV/Vis spectra of the ligands and complexes:  $H_2L^1$  (a),  $[CoL^1(cyclohexylamine)_2]ClO_4$  (1a),  $[CoL^1(aniline)_2]ClO_4$  (2a),  $[CoL^1(4-picoline)_2]ClO_4$  (3a),  $[CoL^1(pyridine)_2]ClO_4$  (4a),  $H_2L^2$  (b) and  $[CoL^2(pyridine)_2]ClO_4$  (1b).

increasing  $pK_a$  of the axial lewis base. The more negative cathodic potentials for Co(III)  $\rightarrow$  Co(II) process are seen in the order of cyclohexylamine > 4-picoline > pyridine > aniline, that correlates with the  $pK_a$  values order (Table 5). Fig. 4 shows the cyclic voltamogram of [CoL<sup>1</sup>(cyclohexylamine)<sub>2</sub>]ClO<sub>4</sub>.

Existing of a 5-phenylazo substitution on equatorial salen Schiff-base ligand, which acts as a good electron withdrawing group, causes a more electron affinity on cobalt

Table 4 The selected main atomic orbitals contributions to the HOMO and LUMO molecular orbitals of complexes

Complex	MO	E (eV)	Symmetry <sup>a</sup>	Contribution of AO to MO <sup>b</sup>					
				Со	C <sub>imine</sub> (average)	N <sub>imine</sub> (average)	C <sub>phenolic</sub> (average)	O <sub>phenolic</sub> (average)	N <sub>ax</sub> (average)
[CoL <sup>1</sup> (cyclohexylamine) <sub>2</sub> ]+	HOMO LUMO	$-0.39034 \\ -0.13475$	π π	0.02598 0.00575	0.00247 0.29903	0.03896 0.09717	0.07473 0.05460	0.07657 0.01048	0.00109 0.00035
[CoL <sup>1</sup> (aniline) <sub>2</sub> ]+	HOMO LUMO	$-0.38778 \\ -0.13589$	π π	$0.02304 \\ 0.00574$	0.00265 0.20332	0.02859 0.09629	0.04696 0.05517	0.10592 0.01052	$0.00086 \\ 0.00041$
[CoL <sup>1</sup> (4-picoline) <sub>2</sub> ]+	HOMO LUMO	-0.38185 -0.12131	π π	0.05220 0.00357	0.00075 0.19811	0.03886 0.09713	0.06401 0.05351	0.10796 0.01108	$0.00068 \\ 0.00058$
[CoL <sup>1</sup> (pyridine) <sub>2</sub> ]+	HOMO LUMO	$-0.38498 \\ -0.12442$	π π	0.04997 0.00312	0.00078 0.19963	0.03829 0.09672	0.06624 0.05263	$0.10403 \\ 0.01060$	0.00039 0.00159
[CoL <sup>2</sup> (pyridine) <sub>2</sub> ]+	HOMO LUMO	-0.36773 -0.12343	π π	0.00995 0.00545	0.00178 0.20040	0.01214 0.09768	0.03813 0.04764	0.04218 0.01084	0.00094 0.00119

<sup>a</sup> Since the molecular plane acts as a nodal plane, the symmetry of the orbital is  $\pi$ .

<sup>b</sup> Calculated as the sum of the squared coefficient of the 2s,  $2p_x$ ,  $2p_y$  and  $2p_z$  orbitals of C, N and O atoms and  $3d_{z^2}$ ,  $3d_{xz}$ ,  $3d_{yz}$ ,  $3d_{x^2-y^2}$ ,  $3d_{xy}$ , 4s,  $4p_x$ ,  $4p_y$  and  $4p_z$  of Co atom in the linear combination that defines the MO.

Table 5 Cyclic voltammetry data (mV)	for complexes in	n DMF solution	s (scan rate 100	mV/s) <sup>a</sup>				
Complex	$E_{\rm pc}({ m III}  ightarrow { m II})$	$E_{\rm pa}({\rm II} \rightarrow {\rm III})$	$\Delta E_{\rm p}({\rm III} \leftrightarrow {\rm II})$	$E_{\rm pc}({\rm II} \rightarrow {\rm I})$	$E_{\rm pa}({ m I}  ightarrow { m II})$	$\Delta E_{\rm p}({\rm II} \leftrightarrow {\rm I})$	$E_{1/2}(\mathrm{II}\leftrightarrow\mathrm{I})$	$pK_a$ (axial amine) <sup>b</sup>
[CoL <sup>1</sup> (cyclohexylamine) <sub>2</sub> ]ClO <sub>4</sub>	-586	27	613	-1107	-1040	67	-1073	10.64
$[CoL^1(aniline)_2]ClO_4$	-305	35	340	-1029	-1107	78	-1068	4.60
$[CoL^{1}(4-picoline)_{2}]ClO_{4}$	-327	24	351	-1105	-1043	62	-1074	6.00
[CoL <sup>1</sup> (pyridine) <sub>2</sub> ]ClO <sub>4</sub>	-319	16	335	-1107	-1029	78	-1068	5.17
[CoL <sup>2</sup> (pyridine) <sub>2</sub> ]ClO <sub>4</sub>	-247	55	302	-1037	-951	86	-994	5.17

<sup>a</sup> The ferrocenium-ferrocene couple shows a peak separation of 89 mV under the experimental conditions.

<sup>b</sup> The  $pK_a$  values (in aqueous solution) of the used axial amines are reported from Ref. [23].



Fig. 4. Cyclic voltammogram of [CoL<sup>1</sup>(cyclohexylamine)<sub>2</sub>]ClO<sub>4</sub>.

center and so a less negative cathodic peak for  $[CoL^2(pyridine)_2]ClO_4$  complex in contrast with  $[CoL^1(pyridine)_2]-ClO_4$ .

# 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 255047. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2005.12.001.

#### Acknowledgments

We are grateful to Tabriz University Research Council for the financial support of this research. Also authors are to thank prof. Dr. F. Belaj for X-ray structure determinations.

#### References

- E.C. Niederhoffer, J.H. Timmons, A.E. Martell, Chem. Rev. 84 (1984) 137.
- [2] S. Yamada, Coord. Chem. Rev. 191 (1999) 537.
- [3] N.J. Henson, P.J. Hay, A. Redondo, Inorg. Chem. 38 (1999) 1618.[4] A.E. Martell, D.T. Sawyer, Oxygen Complexes and Oxygen Activa-
- tion by Transition Metals, Plenum Press, New York, 1988.
- [5] C. Bianchini, R.W. Zoeliner, Adv. Inorg. Chem. 44 (1997) 263.
- [6] T. Nagata, K. Yorozu, T. Yamada, T. Mukaiyama, Angew. Chem. Int. Ed. Engl. 34 (1995) 2145.
- [7] E.N. Jacobsen, W. Zhang, M.L. Guler, J. Am. Chem. Soc. 113 (1991) 6703.
- [8] G.L. Estiu, A.H. Jubert, G. Costamagna, J. Vargas, Inorg. Chem. 35 (1996) 263.
- [9] P.K. Mascharak, Coord. Chem. Rev. 225 (2002) 201.
- [10] J.G. Muller, L.A. Kayser, S.J. Paikoff, V. Duarte, N. Tang, R.J. Perez, S.E. Rokita, C.J. Burrows, Coord. Chem. Rev. 185–186 (1999) 761.
- [11] D.P. Kessissoglou, Coord. Chem. Rev. 185–186 (1999) 837.
- [12] J.W. Pyrz, A.L. Roe, L.J. Stern, L. Que, J. Am. Chem. Soc. 107 (1985) 614.
- [13] V.E. Kaasjager, L. Puglisi, E. Bouwman, W.L. Driessen, J. Reedijk, Inorg. Chim. Acta 310 (2000) 183.
- [14] M. Amirnasr, K.J. Shenk, A. Gorji, R. Vafazadeh, Polyhedron 20 (2001) 695.

- [15] Y. Zhang, W. Ruan, X. Zhao, H. Wang, Z. Zho, Polyhedron 22 (2003) 1535.
- [16] M.M. Aly, J. Coord. Chem. 43 (1998) 89.
- [17] R. Cini, S.J. Moore, L.G. Marzilli, Inorg. Chem. 37 (1998) 6890.
- [18] S.M. Polson, R. Cini, C. Pifferi, L.G. Marzilli, Inorg. Chem. 36 (1997) 314.
- [19] A. Bottcher, T. Takeuchi, K.I. Hardcastle, T.J. Meade, H.B. Gray, Inorg. Chem. 36 (1997) 2498.
- [20] A.A. Khandar, Z. Rezvani, Polyhedron 18 (1998) 129.
- [21] HYPERCHEM for windows, Release version 7.
- [22] A.A. Khandar, K. Nejati, Polyhedron 19 (2000) 607.
- [23] J.A. Dean, Handbook of Organic Chemistry, Mc Graw-Hill, 1987.
- [24] A.A. Khandar, S.A. Hosseini-Yazdi, Polyhedron 22 (2003) 1481.
- [25] S.D. Bella, I. Fragala, I. Ledoux, M.A. Diaz-Garcia, T.J. Marks, J. Am. Chem. Soc. 119 (1997) 9550.
- [26] R. Klement, F. Stock, H. Elias, H. Paulus, M. Valko, M. Mazur, Polyhedron 18 (1999) 3617.
- [27] W.P. Anderson, T.R. Cundari, R.S. Drago, M.C. Zerner, Inorg. Chem. 29 (1990) 1.
- [28] D.R. Kains, M.A. Ratner, T.J. Marks, Chem. Mater. 3 (1991) 19.
- [29] W.P. Anderson, T.R. Cundari, M.C. Zerner, Int. Quantum Chem. 39 (1991) 31.
- [30] R.A. Metcalf, A.B.P. Lever, Inorg. Chem. 36 (1997) 4762.
- [31] K.K. Stavrev, M.C. Zerner, T.J. Meyer, J. Am. Chem. Soc. 117 (1995) 8684.
- [32] K.K. Stavrev, M.C. Zerner, Chem. Phys. Lett. 233 (1995) 179.
- [33] K.K. Stavrev, M.C. Zerner, Theor. Chim. Acta 3 (1996) 141.
- [34] K.K. Stavrev, M.C. Zerner, J. Chem. Phys. 102 (1995) 34.