Bis(3-X, α,5-Dimethyl salicylaldehyde)ethylene Diamine Nickel(II) Complexes

Synthesis and Characterization

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A series of nickel(II) complexes with substituted Schiff bases, bis(3-X, α,5-dimethyl salycilaldehyde)ethylene diamine nickel(II) has been synthesized and characterized. The nickel(II) ion forms with ligands of this type, complexes with square planar geometry. The methods used for characterizing the free ligands and their complexes were: elemental analysis, NMR, UV-VIS, FT IR, spectroscopy and cyclic voltammetry. Cyclic voltammograms of the nickel(II) complexes have shown a quasi-reversible one-electron oxidation process of the nickel(II) $\rightleftharpoons$ nickel(III) and three reduction processes, under nitrogen gas atmosphere.

Keywords: nikel(II), Schiff bases, complexes, cyclic voltammetry

The Schiff base compounds constitute an important class of ligands that have been extensively studied in coordination chemistry, mainly due to their facile synthesis and easy tunable steric, electronic and catalytic properties [1]. The cobalt (II), manganese(II) and copper(II) complexes are able to bind reversibly molecular oxygen, being used as simplified models in the study of dioxygen binding by its natural transporters and mimic biological processes (oxidation, catalyst) [2-4]. The nickel(I) and nickel(II) complexes play an important role in the activity of several hydrogenation reactions and several catalytic redox reactions [5,6]. Although, the nickel(II) complexes with tetradentate Schiff bases derived from salicylaldehyde and aliphatic diamine have been known for a long time, their redox properties still present a high interest because of the oxidation/reduction site of the complexes that can be controlled by the aromaticity of the ligand due to its substituents [7].

This paper presents the synthesis, characterization and redox behavior of a series of nickel(II) complexes with Schiff bases derived from bis(3-X α,5-di methyl salicylaldehyde)ethylenediamine (X = H, Cl, Br, I)(fig. 1). The properties of these complexes were compared with the properties of the bis(salicylaldehyde)ethylendiamine-nickel(II) complexes, Ni(Salen) and bis(α-methyl salicylaldehyde) ethylenediamine nickel (II) complexes, Ni(dMeSalen).

Experimental part

Materials

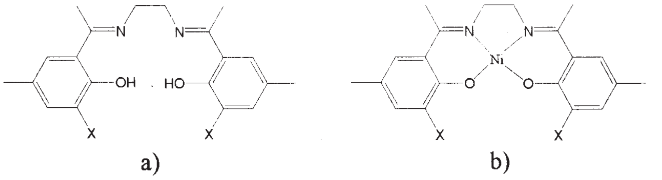
The chemicals, commercial available and of analytical purity were used without further purification. The ^1H NMR spectra of the ligands and nickel (II) complexes were performed using a Brucker AM 250 or AC 250 spectrometer, operating at 250 MHz. The spectra were obtained in $CDCl_3$ (for ligands) and DMSO (for complexes) and chemical shifts calculated in ppm with respect to TMS ($\delta = 0$). The UV-Vis spectra, in DMF solution, were taken on a DES device, operating with SAFAS program. The FT IR spectra were obtained on a Jasco FT IR 660 Plus apparatus in KBr pellets. Cyclic voltammetry experiments were performed on an Autlab apparatus. The recordings were made in DMF solution, in nitrogen atmosphere, using lithium perchlorate as electrolyte support. The working electrode was a vitreous carbon electrode (A = 4 mm^2); as reference electrode a saturated calomel electrode (SCE) and as auxiliary electrode a platinum wire were used.

Synthesis of the ligands

The Schiff bases used as ligands have been prepared by stirring for 2 h a solution of 2-OH, 3-X, 5-Methyl acetophenone and ethylenediamine, in 2/1 molar ratio, prepared in ethanol solution, at 45°C. The precipitate was collected by filtration, washed with water, ethanol-water mixture (1/1 v) and absolute ethanol, and recrystallized from methanol or ethanol. These ligands were characterized by elemental analysis, NMR, UV-VIS and IR spectroscopy.

Synthesis of the complexes

The nickel(II) complexes were synthesized using general methods, [9,10]. To a stirring solution of 1 equivalent of ligand, dissolved in 25 mL of ethanol, at 45 °C, was added by dropping 1 equivalent of $Ni(OAc)_2 \cdot 4H_2O$ dissolved in 5 mL water. For the less soluble ligands, two equivalents of



a) b)

X	Complexes
H	Ni(tMeSalen)
Cl	Ni(dCltMeSalen)
Br	Ni(dBrtMesalen)
I	Ni(dItMesalen)

Fig. 1. General formula of the ligands a) and nickel(II) complexes b)

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NaOH were added. The precipitate is deposed immediately. The mixture is further maintained stirring at 40°C for one hour. After cooling at room temperature, the solid is filtered and washed with water, ethanol-water mixture (1/1 v) and absolute ethanol. After drying *in vacuum*, the nickel complex is isolated and analysed. Elemental analysis: Ni(dMeSalen), [Ni($C_{18}H_{18}N_2O_2$)], found (calculated): C 61.11 (61.24); H 5.21 (5.14); 7.89 (7.93); Ni(tMeSalen), [Ni($C_{20}H_{20}N_2O_2$)], found (calculated): C 63.03 (62.88); H 5.82 (5.84); 7.35 (7.30); Ni(dCltMeSalen), [Ni($C_{20}H_{20}Cl_2N_2O_2$)], found (calculated): C 53.38 (53.26); H 4.48 (4.41); 6.23 (6.19); Ni(dBrtMeSalen), [Ni($C_{20}H_{20}Br_2N_2O_2$)], found (calculated): C 44.58 (44.46); H 3.74 (3.79); 5.20 (5.17); Ni(dItMeSalen), [Ni($C_{20}H_{20}Br_2N_2O_2$)], found (calculated): C 37.49 (37.34); H 3.19 (3.23); 4.43 (4.41).

Results and discussion

By condensation of the 2-OH, 3-X, 5-Methyl acetophenone (X=H, Cl, Br, I), with ethylene-diammine, in 2/1 molar ratio, resulted tetra dentate Schif bases [8,9]. Elemental analysis, ^{1}H NMR, FT IR and UV-VIS techniques confirm the structure of the ligands presented in figure 1a. Reaction of the Schiff bases with Ni(OAc)$_2$×4H$_2$O, in ethanol solution leads to nickel(II) complexes [9,10]. The formation of these compounds was also confirmed by elemental analysis, ^{1}H NMR, FT IR and UV-VIS techniques. Redox behaviour was studied by cyclic voltammetry. The magnetic studies for nickel(II) complexes show a diamagnetic behaviour. This observation indicates that there are no unpaired electrons and that the structures of the complexes are square-planar.

The ^{1}H NMR spectra of the complexes, comparatively with that of the ligands, presented significant changes due to coordination process. For example, the OH proton signal of the ligand (about 13.78 ppm) disappears upon complexation with nickel(II). The aromatic and ethylene protons are shifted, while the methyl proton does not seem to have significant change by coordination [11].

The electronic spectra of the ligands and corresponding complexes were recorded in DMF solution. The free ligands show two strong absorption bands in the UV-VIS region (300-450 nm), attributed to the π-π* and n-π* transitions [12]. The spectrum of nickel(II) – Schiff bases complex showed three absorption bands at 340-350 nm, 416-428 nm and 540-556 nm, as it is presented in table 1.

The absorption bands observed at 340-350 nm can be attributed to the O-Ni charge-transfer transition (LMCT), while the band situated at 410-430 nm can be attributed to the N-Ni charge-transfer transitions (LMCT), which are overlapping with the π-π* or n-π* transitions of the ligands. The new bands, with low intensity, observed at 540-556 nm are attributed to the d-d transitions of the divalent nickel (II) with square-planar geometry [12,13]. Sometimes the d-d transition bands are not very well defined and are present as a shoulder in the spectrum. The complex with a square-planar geometry presents a C_{2v} symmetry, and the absorption band can be attributed to the transition of one electron from A_1 or A_2 to B_1^* [14].

The FT IR spectra of the ligands show major bands around of 1600 cm^{-1} assigned to $\nu_{C=N}$, 1560 cm^{-1} and 1500 cm^{-1} assigned to rings vibration, 1280 cm^{-1} assigned to OH phenolic out of plane deformation (δ_{OH}), 1170 cm^{-1} assigned to ν_{C-N}, and 1065 cm^{-1} assigned to ν_{C-O} [15]. The FT IR spectra of the nickel(II) complexes present, the $\nu_{C=N}$ stretching mode shifted to a lower frequency and additional shifts in the bands corresponding to C-N and C-O bonds compared with free ligands, table 2.

The ligand characteristic bands for out of plane deformation, δ_{OH}, (around of 1280 cm^{-1}) are absent in the case of complexes, as a consequence of the involvement of the oxygen anion into a σ bond with the metallic centre. The formation of the metal-oxygen σ bond and metal-nitrogen π-bond determines the presence of new absorption bands in the region 420 - 664cm^{-1} [16-19]. This suggests the participation of the nitrogen atom from azomethinic group and oxygen atom of the OH group from the ligands in the coordination process with metallic ions. According to the data from UV-VIS and IR spectra, the nickel(II) complexes have a square-planar geometry shown in figure 1b.

In order to establish the appropriate conditions for our measurements some preliminary investigation were performed. It concerns mainly investigating the role of various complex concentrations and different scan rate. The obtained results of these investigations and by considering the solubility of the interest complexes as well

Table 1

ELECTRONIC SPECTRAL DATA FOR Ni (II) COMPLEXES

Compounds	λ_1, nm (ε, l/mol·cm)	λ_2, nm (ε, l/mol·cm)	λ_3, nm (ε, l/mol·cm
Ni(dMeSalen)	550 (2.11)	422 (3.22)	348 (3.14)
Ni(tMeSalen)	556 (2.32)	428 (3.25)	346 (3.16)
Ni(dCltMeSalen)	555 (1.52)	418 (2.92)	340 (3.03)
Ni(dBrtMeSalen)	542 (2.28)	416 (2.98)	342 (3.06)
Ni(dItMeSalen)	540 (2.05)	416 (3.58)	350 (3.71)

Table 2

MAIN INFRARED ABSORPTION BANDS (cm^{-1}) FOR NICKEL(II) COMPLEXES AND $N_{C=N}$ FOR LIGANDS IN BRACKETS

Compounds	$\nu_{C=N}$		ν_{Ni-O}	ν_{Ni-N}
Ni(dMeSalen)	1596	(1609)	623	457
Ni(tMeSalen)	1580	(1618)	640	433
Ni(dCltMeSalen)	1577	(1612)	615	507
Ni(dBrtMeSalen)	1607	(1612)	642	456
Ni(dItMeSalen)	1578	(1610)	664	443

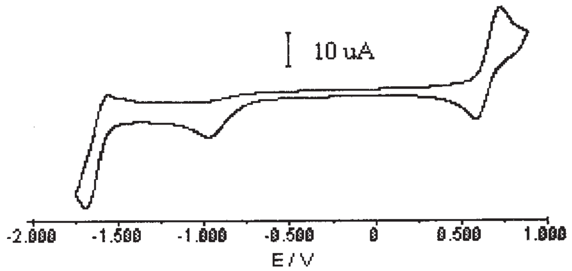
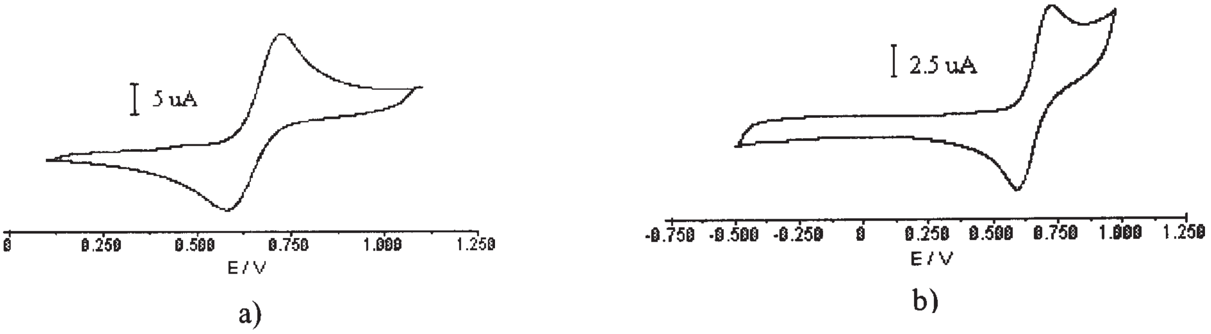


Fig. 2. Cyclic voltammogram of the 2 mM of the Ni(tMeSalen), SCE, scan rate = 100 mV/s



a)

b)

Fig. 3. Cyclic voltammograms of the 2 mM of the Ni(dMeSalen) a) and Ni(dCltMeSalen) b), in DMF, vs. SCE, scan rate = 100 mV/s

Table 3
ELECTROCHEMICAL DATA FOR THE NICKEL(II) COMPLEXES

Compounds	E_{pa} (V)	E_{pc} (V)	ΔE	$E_{1/2}$ (V)	$E'_{1/2}$ (V)
NiSalen	0.730	0.587	0.143	0.659	0.193
Ni(dMeSalen)	0.728	0.559	0.169	0.644	0.178
Ni(tMeSalen)	0.724	0.526	0.198	0.625	0.159
Ni(dCltMeSalen)	0.732	0.592	0.140	0.662	0.196
Ni(dBrtMeSalen)	0.740	0.604	0.136	0.672	0.206
Ni(dItMeSalen)	0.766	0.620	0.146	0.693	0.227

C_{NiL} = $2x10^{-3}$ M; scan rate 100mV/sec; E_{pa} and E_{pc} are the anodic and cathodic peak potentials respectively. $\Delta E = E_{pa} - E_{pc}$ in 0.1M $LiClO_4$ in DMF. $E_{1/2} = (E_{pa}+E_{pc})/2$. $E'_{1/2}$ is $E_{1/2}$ reported to the potential of the couple Fc^+/Fc, where Fc = ferrocene, $E_{Fc+/Fc}$ = 0.466 V, vs SCE.

as their electrochemical behaviour allow us to select as proper measurement conditions for the whole study, the following conditions: concentration of 2 mM for the investigated complexes and 100 mV/s as scan rate.

The cyclic voltammograms of the nickel(II) complexes exhibits one oxidation reversible process and three reduction processes, in DMF solution at room temperature, as it is shown in figure 2.

The anodic (oxidation) process (E_{pa} = 0.724V) corresponds to quasi-reversible one-electron oxidation of nickel(II) $\rightleftharpoons$ nickel(III) process, while the peaks from 0.526 mV, -900V and –1.620V correspond to quasi-reversible one-electron reduction process of nickel(III) $\rightleftharpoons$ nickel(II) and irreversible reduction processes of nickel(II) → nickel(I) and nickel(I) → nickel(0) respectively [20-22]. The other complexes of nickel(II) show similar behavior. The value of oxidation and reduction peaks for quasi-reversible processes, corresponding to nickel(II) $\rightleftharpoons$ nickel(III) depends on the nature of substituents grafted on the aromatic ring (fig. 3).

The values of the anodic and cathodic peaks (E_{pa}, E_{pc}), and halfwave-potential ($E_{1/2}$), for the nickel complexes are listed in table 3.

The $E'_{1/2}$ values correspond to $E_{1/2}$ reported to ferrocene/ferrocenium couple (+0.466 mV versus SCE). The $E_{1/2}$ values for the nickel(III)/nickel(II) couple for the complexes Ni(dMeSalen) and Ni(tMeSalen) are situated at higher negative values in comparison with those for complexes Ni(Salen), indicating that the presence of methyl group in azomethynic position determines an increase of electronic density on the metallic ion, becoming more oxidable. The presence of methyl in *para* position of the oxygen, for Ni(tMeSalen) leads to increasing of electronic density of the nickel, and the $E_{1/2}$ (also E_{pa} and E_{pc}) peaks present higher negative values. The presence of substituents (Cl, Br, I) with electronegative character in *orto* position of the oxygen, leads to more difficult oxidizing process of nickel(II) than for complexes Ni(tMeSalen). Between $E_{1/2}$ potentials of the nickel(II) complexes and electronegativity of halogens from *meta*-position toward O donor atoms is a correlation. The $E_{1/2}$ values increase with the decrease of the electronegativity of the halogens. That is in concordance with electron-attracting effect of the halogens determining the decrease of electron density on the metallic core.

Conclusions

Bis-Schiff bases form with nickel(II) ions complexes with square planar geometry. The UV-VIS and FT IR spectra evidence the coordination of ligands with nickel(II) by nitrogen and oxygen atoms. The nickel(II) complexes show a quasi-reversible behavior for nickel(II) $\rightleftharpoons$ nickel(III) processes, determined by the nature of substituents grafted on aromatic ring and in azomethynic group; also, two irreversible reduction processes to nickel(I) and nickel(0) are observed.

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