Scientific paper

The Synthesis, Characterization and Electrochemical Behavior of Transition Metal Complexes Containing Nitrogen Heterocyclic Sulphur Donor Ligand

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Abstract

1,3-di(2-methylpiperidino)propan-2-ol (**ROH**) was synthesized 1,3- dichloropropan-2-ol with 2-methlypiperidine. Potassium 1,3-di(2-methylpiperidino)propan-2-*O*-xanthate (**ROCSSK**) was obtained from the reaction of 1,3-di(2-methylpiperidino)propan-2-ol (**ROH**) with carbon disulfide and metallic potassium. All products were generally obtained in high yields. xanthate complexes of Co(II), Ni(II) and Cu(I) was synthesized in the medium water as $[CoL_2(H_2O)_2]$, $[NiL_2(H_2O)_2].2H_2O$ and $[CuL].2H_2O$. The novel xanthate ligand and its complexes were defined by FT-IR, ^1H and ^{13}C NMR spectroscopies, elemental analyses, magnetic susceptibility and TGA techniques. $[CoL_2(H_2O)_2]$ and $[NiL_2(H_2O)_2].H_2O$ complexes were subjected to cyclic voltammetry using Pt working electrode and Ag/AgCl (3 M KCl) reference electrode.

Keywords: Co(II), Ni(II) and Cu(I) complexes, xanthate, cyclic voltammetry

1. Introduction

Transition metal dithiolate complexes exhibit a rich and interesting chemistry that have been studied extensively during the last several decades.[1,2] Xanthates can form bidentate chelates or monodentate or network solids, showing a wide range of coordination behavior.[3]

Metallic xanthates are well known reagents in the flotation of minerals of transition metals such as copper, zinc, cobalt and nickel, and in the separation and quantitative determination of large number of cations.[4] Metal-xanthate complexes have low solubility products and high stability constants, and therefore xanthates are used for the removal of metal ions as complexing agents.[5] The xanthate complexes of cobalt,[6–10] nickel,[3, 10, 11–22] copper,[3, 5, 10, 23, 24] iron,[3, 25] platinum, palladium, chromium,[8] zinc,[3, 26] lead[3] have been reported. The electrochemical behavior of xanthate complexes was widely investigated.[14, 27–29]

Here we report the preparation of the complexes of Co(II), Ni(II) and Cu(I) with 1,3-di(2-methylpiperidino)propan-2-O-xanthate. Their structures were determined by elemental analysis, magnetic susceptibility, thermogravimetric analyses, FT-IR, ^1H and ^{13}C NMR spectroscopy and their electrochemical behavior was investigated by cyclic voltammetry.

2. Experimental

2. 1. General Remarks

1,3-di(2-methylpiperidino)propan-2-ol (**ROH**) and potassium 1,3-di(2-methylpiperidino) propan-2-O-xanthate (**ROCSSK**) were prepared by a reported procedure.[30] All reagents were purchased from Merck, Acros, and Fluka, companies and are chemically pure. Solvents were dried by conventional methods.

Elemental analyses (C, H, N, and S) were determined on a LECO-932 CHNSO auto elemental analysis apparatus. IR spectra were recorded on a Mattson 1000 FT-IR spectrometer as KBr pellets and NaCl window. ^1H and ^{13}C NMR spectra were recorded on Bruker DPX-400 High Performance Digital FT-NMR spectrometer operating at 400.13, 100.63 MHz, respectively. Data were recorded for solutions in $CDCl_3$ for **ROH**, and in DMSO for **ROCSSK**. The ^1H and ^{13}C chemical shifts were measured using $SiMe_4$ as an internal standard. Magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance (Model MK1) at room temperature using $Hg[Co(SCN)_4]$ as calibrant; diamagnetic corrections were calculated from Pascal's constants. Melting points were determined on a Gallenkamp melting point apparatus. The metal contents of the complexes were determined by an Ati Unicam (Model 929) Atomic Absorption Spectrophotometer, which solutions were prepared by decomposing of compounds in concentrated acid mixture [HCl : HNO_3 (3:1)] and diluted with pure water. Thermogravimetric curves were recorded on a Shimadzu TG-50 thermobalance under nitrogen atmosphere.

All the electrochemical data were taken with CH Instruments 660 B computer controlled electrochemical analyzer at room temperature using 1.05×10^{-3}M $[CoL_2(H_2O)_2]$ and 1.98×10^{-3}M $[NiL_2(H_2O)_2] \cdot H_2O$. The reference electrode, Ag/AgCl(3M KCl), was separated from the bulk of the solution with a lugin capillary and calibrated against Ferrocene/ferrocenium couple which gave perfectly reversible peaks at 0.48V against. The electro reduction and electro oxidation of the complexes $[CoL_2(H_2O)_2]$ and $[NiL_2(H_2O)_2].H_2O$ were studied with cyclic voltammetry in DMF containing 0.1 M Bu_4NBF_4 (TBAFB) supporting electrolyte using 2 mm diameter Pt disc electrode covered with teflon at a scan rate of 50 mV/s. The nickel complex was also scanned in anodic direction at a scan rate of 10 mV/s.

Synthetic Procedures:

1,3-di(2-methylpiperidino)propan-2-ol, 1,3-di(2-methylpiperidino)propan-2-O-xanthate and their transition metal complexes were synthesized as follows:

2. 2. 1,3-di(2-methylpiperidino)propan-2-ol, (ROH)

A solution of 1,3-dichloropropan-2-ol (12.9 g, 100 mmol) in toluene (10 mL) was added to a solution of 2-methylpiperidine (19,84 g, 200 mmol) and triethylamine (20.24 g, 200 mmol) in toluene (100 mL). The mixture was stirred and refluxed for 24 h. After completing the reaction, the mixture was left overnight. Triethylamine salt was separated by filtration and toluene was removed under vacuum. The product was distilled under vacuum (154 °C at 2 mm Hg) as colorless liquid (**ROH**). $C_{15}H_{30}N_2O$ (MW = 254.41). Yield: 12.75 g, 50.11%.

2. 3. 1,3-Di(2-methylpiperidino)propan-2-O-Xanthate, (ROCSSK)

Metallic potassium (0.782 g, 20 mmol) was added to a solution of 1,3-di(2-methyl piperidino)propan-2-ol (5.09 g, 20 mmol) in THF (150 mL) at 40–50 °C. It was continued until metallic potassium was reacted completely. Then the solution was cooled to –20 °C and the solution of CS_2 (1.52 g, 20 mmol) in THF (10 mL) was added dropwise to the mixture. It was reacted for 2 h. The reaction was carried out at argon atmosphere. Potassium xanthate (**ROCSSK**) was filtered off, washed with THF, diethyl ether, and petroleum ether to obtain as white crystals. Compound (**ROCSSK**) was dried under vacuum over $P_2O_5 \cdot C_{16}H_{29}KN_2OS_2$ (white).Yield 5.91 g, (80%). Decompose 170 °C.

2. 4. Transition Metal Complexes of Xanthete Ligand

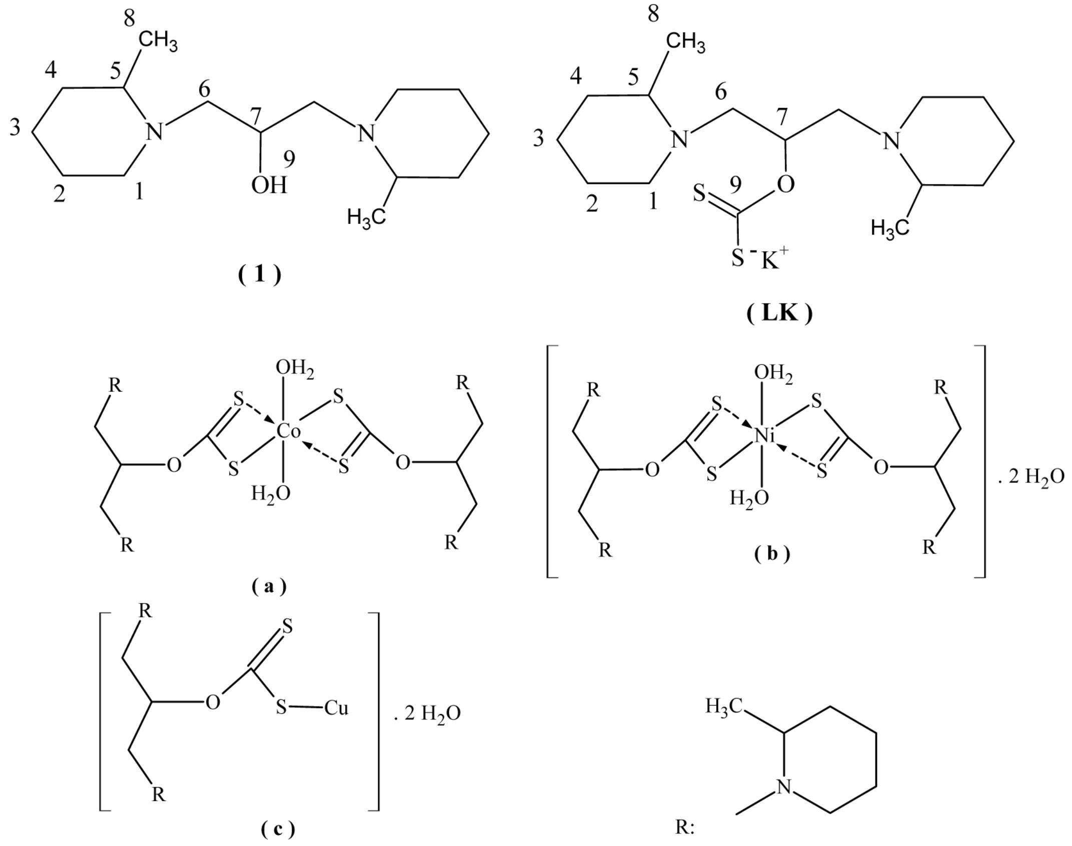
A solution of xanthate (**ROCSSK**) (0.200 g, 0,542 mmol) in water (100 mL) was added to a solution of metal salts (0.271 mmol) of [$NiCl_2.6H_2O$ (0.0642 g), $CoCl_2 \cdot 6H_2O$ (0.0645 g), $CuCl_2 \cdot 2H_20$ (0.0462 g)] in water (10 mL) by stirring at ambient temperature for 15 min. The precipitated complexes were filtered off by sintered funnel, washed with water, diethyl ether and petroleum ether several times and dried under vacuum over P_2O_5. The complexes are soluble in ethanol, methanol, acetone, DMSO, DMF and chloroform and insoluble in water, diethyl ether, petroleum ether and hexane. $[CoL_2(H_2O)_2]$ (green): Yield: 0,156 g (% 76). Decompose 258 °C. $[NiL_2(H_2O)_2] \cdot 2H_2O$ (green): Yield: 0,168 g (% 78). Decompose 218 °C. $[CuL] \cdot 2H_2O$ (brown): Yield: 0,093 g (% 80). Decompose 318 °C.

3. Results and Discussion

After deprotonation of 1,3-di(2-methylpiperidino)propan-2-ol with metallic potassium, the addition of carbon disulfide readily affords the dithiocarboxylated potassium salt of 1,3-di(2-methylpiperidino)propan-2-O-xanthate **ROCSSK** in good yield 80%. The structure of compounds **ROH**, **ROCSSK** and complexes of Co(II), Ni(II) and Cu(I) are shown in Schema 1. Carbon and hydrogen atoms were numbered for ^1H and ^{13}C NMR.

The IR spectrum (NaCl cell/cm^{-1}) of **ROH** showed four different strong and sharp peaks at 3428 ν_{OH}, 2961–2590 $\nu_{C\text{-}H\ aliphatic}$, 1470–1415 $\nu_{C\text{–}N}$ and 1076 $\nu_{C\text{-}O}$ stretching vibrations. ^1H-NMR of **ROH**: 2.57 (4H, H^1); 1.46 (4H, H^2); 1.55 (4H, H^3); 1.90 (4H, H^4); 2.60 (2H, H^5); 2.00 (4H, H^6); 3.86 (1H, H^7); 1.08 (6H, H^8). ^{13}C-NMR of **ROH**: 55.34 (C^1); 25.92 (C^2); 20.88 (C^3); 34.43 (C^4); 53.05 (C^5); 56.52 (C^6); 64.87 (C^7); 19.54 (C^8).

The IR spectrum (KBr/cm^{-1}) of **ROCSSK**: 2962-2594 $\nu_{C\text{-}H}$, 1466–1413 $\nu_{C\text{-}N}$, 1161–1072 $\nu_{C\,=\,S\text{ and }C\text{–}O\text{ asym}}$, 1043 $\nu_{C\text{–}Osym}$, 998 $\nu_{C\text{-}S}$. Anal. Calc. for $C_{16}H_{29}KN_2OS_2$



Schema 1. Structure of the compounds

(MW = 368.64): C, 52.13; H, 7.93; N, 7.60; S, 17.40. Found: C, 51.98; H, 7.58; N, 7.32; S, 16.98%. ^{1}H-NMR: 2.40 (4H, H^1); 1.46 (4H, H^2); 1.38 (4H, H^3); 1.53 (4H, H^4); 1.73 (2H, H^5); 2.66 (4H, H^6); 5.70 (1H, H^7); 0.99 (6H, H^8). ^{13}C-NMR: 53.71 (C^1); 34.68 (C^2); 20.15 (C^3); 26.88 (C^4); 55.85 (C^5); 56.32 (C^6); 76.29 (C^7); 20.14 (C^8); 229.37 (C^9).

Analatical data and IR data of the complexes were assigned down there.

$[CoL_2(H_2O)_2]$:

Anal. Calc. for $C_{32}H_{62}CoN_4O_4S_4$ (MW = 754.05): C, 50.97; H, 8.29; N, 7.43; S, 17.01. Found: C, 50.66; H, 8.30; N, 7.32; S, 16.87%. IR(KBr/cm^{-1}): 3445 ν_{H2O} 2962–2594 $\nu_{C\text{-}H}$, 1476–1440 $\nu_{C–N}$, 1185–1076 $\nu_{C\,=\,S\text{ and }C–O\text{ asym}}$, 1043 $\nu_{C–Osym}$, 1031 $\nu_{C–S}$. (BM$_{\mu eff}$):3.83

$[NiL_2(H_2O)_2] \cdot 2H_2O$:

Anal. Calc. for $C_{32}H_{66}NiN_4O_6S_4$ (MW = 789.84): C, 48.66; H, 8.42; N, 7.09; S, 16.24. Found: C, 48.54; H, 8.38; N, 7.18; S, 16.01%. IR(KBr/cm^{-1}): 3444 ν_{H2O} 2962–2594 $\nu_{C–H}$, 1470–1441 $\nu_{C–N}$, 1099–1072 $\nu_{C\,=\,S\text{ and }C–O\text{ asym}}$, 1043 $\nu_{C–Osym}$, 1030 $\nu_{C–S}$. (BM$_{\mu eff}$): 2.78

$[CuL] \cdot 2H_2O$:

Anal. Calc. for $C_{16}H_{33}CuN_2O_3S_2$ (MW = 429.12): C, 44.78; H, 7.75; N, 6.53; S, 14.94. Found: C, 44.52; H, 7.58; N, 6.32; S, 14.63 IR(KBr/cm^{-1}): 3445 ν_{H2O} 2962–2594 $\nu_{C\text{-}H}$, 1472–1427 $\nu_{C–N}$, 1154-1004 $\nu_{C\,=\,S\text{ and }C–O\text{ asym}}$, 1043 $\nu_{C–Osym}$, 1015 $\nu_{C\text{-}S}$. (BM$_{\mu eff}$): Dia

The C–N stretching bands for **ROCSSK** are wider than compound **ROH** because of new additional C–N binding The xanthates and complexes exhibit bands in the 1280-996 cm^{-1} region which are related to the vibrations of S_2COR group.[21,31] Those at approximately 1161–1072 cm^{-1} are attributable to the asymmetric stretching vibrations of the C–O–C and C=S groups, while the bands around 998 cm^{-1} belong to the υ(C–S) vibration. The C–O–C symmetric vibrations are observed around 1043 cm^{-1}.

The band observed at 998 cm^{-1} for **ROCSSK** is characteristic for the C–S bonds of the xanthates,[32,33] which is shifted to higher frequencies, indicating that the (C–S) groups take part in complexation in the complexes.[34] IR absorption of aliphatic C–H for **ROCSSK** and its metal complexes appear at 2962–2594 cm^{-1}. The presence of water molecule in the complexes of Co(II), Ni(II) and Cu(I) is supported by the existence of bending vibrations at 1647, 1667 and 1656 cm^{-1} and stretching vibrations in the 3445, 3444 and 3445 cm^{-1}, respectively.[13]

The NMR data of **ROH** and **ROCSSK** are presented above. Although Cu(I) complex is diamagnetic, its ^{1}H and ^{13}C NMR spectra couldn't be taken since the complex is insoluble in common solvents. The methyne proton next to the oxygen atom is very well characterized by the ^1H NMR spectra that show peaks at the lowest down field as multiple peak at 3.86 ppm. The OH proton peak is not observed because of hydrogen binding and solvent effect.

In order to identify structures of the xanthate ligand, ^1H and ^{13}C NMR spectra were recorded in DMSO-d_6. When compared to **ROH**, the methyne protons of **ROCSSK** is shifted to the lower down field, the signal of the methyne carbon at **ROCSSK** are also shifted to the lower down field, and the ^{13}C NMR spectra of the xanthate ligand shows an additional peak at 229.37 ppm for **ROCSSK**, supporting the authenticity of the potassium salt of the ligand **ROCSSK**.[30] The Potassium salt of the ligand **ROCSSK**, with Co(II), Ni(II) and Cu(II) salts yielded complexes corresponding to the formula $ML_{2,}$ Cu(II) is reduced to Cu(I) by xanthate ligand and Cu(I) complex is called cuprous xanthate which has linear structure Schema 1.[2,4]

Since magnetic susceptibility measurements provide sufficient information to characterize the structure of the complexes; the magnetic moments of the complexes were measured at room temperature. Co(II) and Ni(II) complexes are paramagnetic and their magnetic susceptibility values are 3.83 BM, 2.78 BM, respectively. These values suggest octahedral geometry for the Co(II) and Ni(II) complexes of **ROCSSK**.

The TGA curves were recorded in the temperature range 25–900 °C under nitrogen atmosphere. The TGA values showed that Ni(II) complex has four mole of H_2O. In TGA curves, two of these were separated from the complex in the range of 120–200 °C, which are implied as hydration water. The other two moles of water in the Co(II) and Ni(II) complexes separated from the complexes above 200 °C, which implies, in each case, that these take part as coordination water in the Co(II) and Ni(II) complexes. Two moles of water in the Cu(I) complex also removed before 200 °C. In all cases the final products are the metal sulfides. These results are in good accordance with the composition of the complexes.

The cyclic voltammograms of $[NiL_2(H_2O)_2] \cdot H_2O$ and $[CoL_2(H_2O)_2]$ complexes are given in Figures 1 and 2. The nickel complex gives an irreversible wave at 0.95 V which was attributed to the dimerization of the xanthate. This result is in accordance with the mechanism mentioned by Travnicek[14] and Dağ.[28] Ni(II) is converted into Ni(III) during the oxidation. The resulting Ni(III) rapidly converts back to Ni(II). The electron transferred in this process is used to dimerize the ligand and Ni(II) ion comes out. This dimerization process is completely irreversible.[28] The same complex is reduced at –0.70 V. This wave is also thought that belong the reduction of xanthate. Similarly, the adsorption and reduction of xanthate upon Au surface was attempted and xanthate gave a reduction peak around that potential.[27] The $–CS_2^-$ group in the structure of xanthate converts into –CHS which results in the Ni (II) coming out. The amount of water present in the structure of the complex is sufficient enough to provide the proton necessary for this reaction.[29]

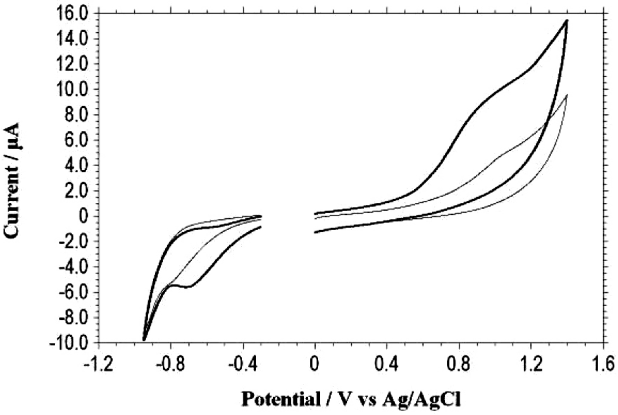


Figure 1. The cyclic Voltametric curves of Co (thin line) and Ni(solid line) complexes

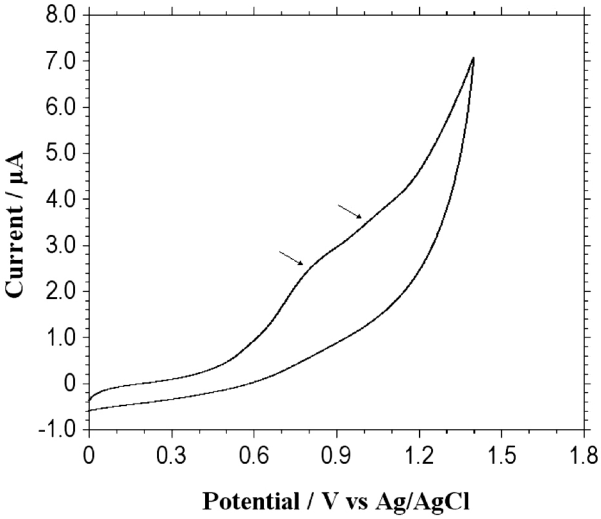


Figure 2. The anodic cyclic voltammograms of Ni complex taken at the 10 mV/s. There are two peak begin to appear (as indicated on the figure) as the scan rate is decreased.

The electrochemical investigation of $[CoL_2(H_2O)_2]$ complex gave similar results. When the complex is oxidized under the same conditions it gives an oxidation peak around 1.05 V and a reduction peak around –0.78 V. The waves obtained for Ni and Co complexes are similar but not identical (Figure 1). The main difference is that the oxidation peak of Ni complex occurs at higher potentials. This proves that the oxidation of the ligand is also dependent upon the type of the attached metal. In addition, the wave belonging to Ni complex is broad. This indicates the fact that the energies of the formation of Ni (III) and the oxidation of ligand are too close to each other as mentioned by Dağ[28] that their waves cannot be distinguished. Two different waves in the cyclic voltammograms of Ni complex at low scan rates such as the 10 mV/s were observed but they could not clearly identified (Figure 2). This result is parallel the literature datum.

4. Conclusions

Potassium 1,3-di(2-methylpiperidino)propan -2-O-xanthate was synthesized from 1,3-di(2-methylpiperidino)propan-2-ol, metallic potassium and carbon disulfide. The complexes of Co(II), Ni(II) and Cu(I) ions with potassium 1,3-di(2-methylpiperidino)propan-2-O-xanthate were prepared and characterized by FT-IR, ^{1}H and ^{13}C NMR spectroscopies, elemental analyses, magnetic susceptibility and TGA techniques. Copper(I) xanthate is diamagnetic, whereas the cobalt(II) and nickel(II) complexes are paramagnetic. The cobalt(II) and nickel(II) dithiocarbonate complexes have octahedral geometry, whereas the copper(I) dithiocarbonate complex is linear. The C–S band, which is one of the characteristic IR peaks for xanthates, is shifted to higher frequencies at the IR spectra of the complexes. The stoichiometries of the complexes were $[CoL_2(H_2O)_2]$, $[NiL_2(H_2O)_2] \cdot 2H_2O$ and $[CuL] \cdot 2H_2O$.

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6. References

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Povzetek

Pripravili smo kalijev 1,3-di(2-metilpiperidino)propan-2-*O*-ksantat (LK) in njegove komplekse z Co(II), Ni(II) in Cu(I) ioni. Komplekse s formulami $[CoL_2(H_2O)_2]$, $[NiL_2(H_2O)_2].2H_2O$ in $CuL.2H_2O$ smo karakteririzirali z FT-IR, ^1H in ^{13}C NMR spektroskopijo, elementno analizo, meritvami magnetne susceptibilnosti and TGA analizo. Ciklično voltametrijo raztopin kompleksov smo naredili s Pt delovno in Ag/AgCl (3 M KCl) referenčno elektrodo. Kompleks $[CoL_2(H_2O)_2]$ ima mireverzibilna vrha pri 0.78 in 1.05 V, $[NiL_2(H_2O)_2].H_2O$ daje širok vrh pri 0.95 V in ireverzibilen vrh pri –0.70 V.