



Direct Electrochemical Synthesis of Nickel (II) Thiolates and their Coordination Complexes.

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ABSTRACT

Metallo organic compounds can be synthesized electrochemically by anodic generation of metal cations by using sacrificial metal anode. Bis-thiolates complexes of Nickel, $Ni(SR)_2$ have been prepared in an H-type cell by electrochemical oxidation of thiols RSH (ethanethiol, 2-propanethiol, 2-methyl-2-propanethiol, 1-butanethiol, 1-pentanethiol and thiophenol) with sacrificial Nickel (Ni) anode and inert Platinum (Pt) cathode in non-aqueous solution of acetonitrile containing tetrabutylammonium chloride (as supporting electrolyte). On refluxing with ligand (L) 2,2'-bipyridyl, these thiolates do not form coordination compounds. However, their adducts $Ni(SR)_2 \cdot L$ have been synthesized electrochemically by adding the ligand to above thiols in solution phase. All these synthesized complexes have been characterized by elemental analysis, infrared spectral data and other physical measurements. All these compounds are in the solid state with excellent yield and associated with high electrochemical efficiency.

KEYWORDS: Electrochemical Synthesis; Sacrificial Anode; Nickel (II) thiolates; Electrochemical Efficiency.



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INTRODUCTION

The complexes in which sulphur is the donor atom are of great interest because of importance of thiolate complexes in medicines[1-2], metalloproteins[3-4], catalyst[5] and chemical vapour deposition[6-7]. Nickel thiolatemetalloproteins has the ability to catalyse reversible oxidation of dihydrogen[3], proton deuterium[8] and proton tritium exchanges in the absence of electron donor or acceptors.

Electrochemical processes have wide applicability in its preventive mode (electro synthesis) and in its curative mode (elimination, recovery and recycling) as the electron (used as reagent) can be readily removed or added unlike standard chemicals[9]. Electrochemical approach to synthesis has attracted a great deal of attention in organic[10-12], inorganic[13-14], green[15] and nano chemistry[16-18], pharmaceutical[19] and chemical industries [11,20] etc. We have been doing work on this fascinating technique since last two decades for the preparation of different inorganic and organometallic compounds by using various metals like Hg, Zn, Bi, Al, Cd etc. as sacrificial electrodes [21-25]. So, in the present context, we have extended the application of direct electrochemical synthesis for the preparation of simple bis-thiolato complexes of Nickel and their adducts with bidentate ligand 2,2'-bipyridyl by anodic dissolution of zero-valentcompact Nickel. This technique is simple, selective, efficient, one-step, eco-friendly and high yielding as compared to classical chemical techniques.

GENERAL REMARKS:

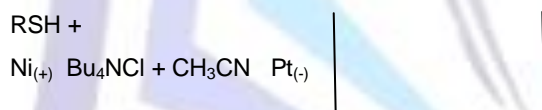
Acetonitrile was distilled from P_2O_5 and stored over 4A molecular sieves for 24 hours and then double distilled. Thiols and 2,2'-bipyridyl were used as supplied. Nickel rod (Sigma Aldrich) was washed with dilute HCl and then distilled water and dried immediately before use. Tetrabutylammonium chloride (Sigma Aldrich) was crystallized from conductivity water and dried under reduced pressure at $100^\circ C$. It was then used as supporting electrolyte.

Electrolysis has been done in an H-type cell made up of Pyrex glass in which the cathode and anode compartments were separated from each other by sintered glass disc of G-3 porosity. Platinum ($1.0 \times 1.0 \text{ cm}^2$) electrode was used as cathode and nickel rod (5cm, 0.623cm diameter) was used as sacrificial anode. Both compartments were provided with two openings: one for guard tube and other for electrode. Direct current was obtained with the help of D.C. power supply of Toshniwal make. The electrolytic solution in the anode compartment was stirred effectively using magnetic stirrer by using magnetic bead. Melting point was determined using electrical device with a heating rate of $5^\circ C$ per minute. Infrared spectrum was recorded on Perkin Elmer spectrophotometer (FTIR) in the region of $4000-400 \text{ cm}^{-1}$ using KBr pallets. Carbon, Hydrogen, Sulphur and Nitrogen (where applicable) contents were determined through 'ElementorVario EL'.

ELECTROCHEMICAL SYNTHESIS:

Electrochemical synthesis has been done by electrolysing the solution of 3 mL of thiol, 1.0g of tetrabutylammonium chloride in 250 mL of acetonitrile in an H-type cell. Nickel rod was dipped in larger compartment and platinum rod in smaller compartment and was connected to positive and negative terminal of D.C. power supply respectively.

The cell can be represented as:



Where $\text{Ni}_{(+)}$: sacrificial nickel anode

$\text{Pt}_{(-)}$: inert platinum cathode

CH_3CN : acetonitrile as solvent

Bu_4NCl : tetrabutylammonium chloride as supporting electrolyte

RSH: Ethanethiol, 2-Propanethiol, 2-Methyl-2-Propanethiol, 1-Butanethiol, 1-Pentanethiol and

Thiophenol.

Both the outlets of H-type were sealed with guard tubes filled with CaCl_2 and glass wool in order to protect the reaction mixture from moisture. The potential across the electrodes was so adjusted that a current of 20 mA passed through the solution. As the electrolysis began, H_2 gas evolved at the cathode and the colour of the solution in the anode compartment became sky blue within 5 minutes. After 20 minutes, the colour in the anode compartment changed to green and after one hour, it became brown in colour.

Electrolysis was carried out for about ten hours with continuous stirring with magnetic bead in order to avoid the product adhering on the electrode. The solid product formed in the anode compartment was filtered, washed repeatedly with hot acetonitrile and dried with diethyl ether under vacuum in the glass filtration unit of G-4 porosity.

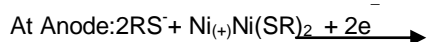
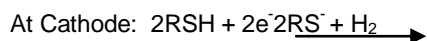
In order to synthesize adducts of these parent complexes, 1.0g of ligand (2,2'-bipyridyl) was also added in addition to the above substrates in the reaction mixture before electrolysis. The reaction pathway was determined by measuring the 'Electrochemical or Current Efficiency' (The ratio of the number of moles of metal that react to the number of moles of electrons that travels through the cell). The current efficiencies were determined by electrolysing the above systems for



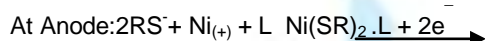
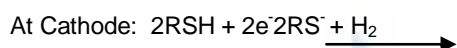
exactly 2.0 hours at constant current of 20 mA. After the electrolysis of 2.0 hours, the solution in the anode compartment was distilled in rotary film evaporator (Buchi) till 10 mL of content was left in the round bottomed flask. The contents were transferred to the beaker and heated to dryness. The nickel contents were then determined volumetrically in the dry mass by oxine method[26]. The theoretical value of nickel was calculated by using Faraday's first law of electrolysis. The ratio of the experimental nickel contents to the theoretical nickel contents gives current efficiency. This magnitude of current efficiency is indicative of the anodic process that takes place.

RESULTS AND DISCUSSION:

For each of the systems studied, we determined the electrochemical efficiency i.e. moles of metal dissolved per Faraday of charge and it ranges between 0.61 to 0.90 mole Faraday⁻¹. Together with the evolution of H₂ at cathode, this identifies the mechanism of the electrochemical reactions as:



The mechanism of coordination compounds of thiols at sacrificial nickel anode and inert platinum cathode with ligand (L) 2,2'-bipyridyl is given below:



Nickel contents in all these products were determined by oxine method which corresponds to 1:2 stoichiometry ratio of nickel and thiol respectively. This conforms to general formula Ni(SR)₂ and Ni(SR)₂·L in case of nickel thiolates and their adducts with ligand (L) respectively without change in oxidation state of metal. The relevant details are summarized in Table-I.

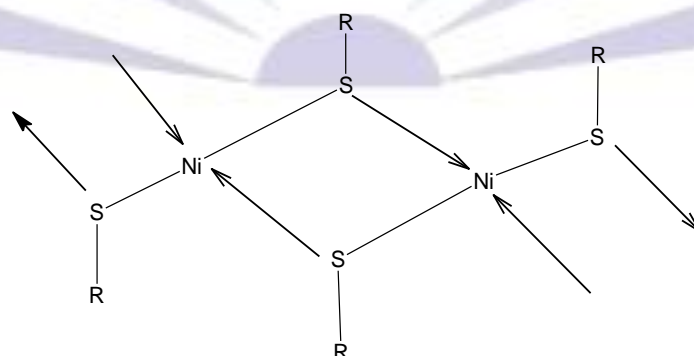
It has been observed that these products do not melt up to 300°C but decompose at a temperature of 230-250°C. The decomposition of the products is indicated from the change in colour of these compounds. These products are not much affected by air or moisture. All these compounds are insoluble in various organic solvents like methanol, ethanol, pyridine, chloroform, DMSO, DMF, acetone etc.

The analysis of IR spectra of these electrochemically synthesized products permit to conclude that there is no absorption bands corresponding to thiol group i.e. -SH group in the range of 2600-2500 cm⁻¹ which confirm that the products are completely free from thiol. However, characteristic bands appeared in the range of 608-415 cm⁻¹ and 1159-923 cm⁻¹.

It has been reported[24,27-30] in the literature that ν (M-S) and ν (C-S)M stretching vibrations appeared in the region of 600-400 cm⁻¹ and 1160-900 cm⁻¹. Thus, in the present studies, the bands appeared in the region of 608-415 cm⁻¹ may be assigned to ν (Ni-S) stretching vibration.

Review of Literature[24,29-30] also reveals that the absorption bands due to ν (C-S)M stretching vibrations in various metal thiolates exist as bridged and terminal -SR groups. Generally, terminal ν (-SR) groups show absorption bands in the region of 1150-1000 cm⁻¹ and bridged ν (-SR) groups in the region of 1000-900 cm⁻¹. Thus, in the present products, the vibrational bands appeared in the region of 1159-1020 cm⁻¹ and 1000-923 cm⁻¹ may be assigned to terminal and bridged thiolate groups respectively. Moreover, the vibrational bands due to bridged -SR groups are broader than the terminal -SR groups which indicates that these compounds may be polymeric in nature.

The plausible structure for nickel (II) thiolates is given as:



IR data of these compounds also shows that the bands appeared due to bridged thiolate groups are strong as compared to terminal groups. The band intensity of bridged thiolate groups decreases as the volume of -R group increases. This leads to lower degree of polymerization due to steric hindrance.

In case of thiophenol nickel complex, additional bands around 1576 cm⁻¹ are also observed due to ν (C=C) aromatic ring vibrations[31]. The parent nickel (II) thiolates were refluxed with 2,2'-bipyridyl in various solvents like methanol, ethanol, acetonitrile, benzene etc. for more than 48 hours. The IR data and analytical data showed that the ligand molecule could



not be attached to the parent nickel (II) thiolates. It may be due to the reason that the metal has already achieved the favourable coordination number before polymerization in these thiolates through the sulphur bridging. Therefore, further expansion of coordination sphere due to addition of ligand could not be achieved. Therefore, it was thought that the ligand may be added to these thiolates before sulphur bridging and polymerization. Therefore, these adducts have been synthesized electrochemically by simply adding 1.0g of ligand 2,2'-bipyridyl to these systems before electrolysis.

IR data of these coordination compounds show ν (Ni-S) and ν (C-S) Ni stretching vibrations[27,32] in the region of 614-420 cm^{-1} and 1173-906 cm^{-1} respectively. These stretching modes appeared slightly in higher region (+10-20 cm^{-1}) than the parent nickel (II) thiolates. Also, the bands in the region of 1620-1564 cm^{-1} and 1493-1444 cm^{-1} appeared due to ν (C=N) and ν (C=C) stretching vibrations are due to the ligand molecules[33-36] which otherwise are absent in the parent nickel thiolates, thereby confirming that the ligand molecule has been added. These coordination compounds are also insoluble in commonly used organic solvents and have high melting point indicating the polymeric nature of these thiolates.

CONCLUSION:

The electrochemical technique for the synthesis of nickel (II) thiolates and their coordination complexes is broadly applicable due to its inexpensivity, high selectivity, one pot synthesis, lower temperature requirement and environment friendly nature. The high current efficiency of all these systems offers a versatile approach for the commercial preparation of these compounds.

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Table-I: Analytical data for $\text{Ni}(\text{SR})_2$ and $\text{Ni}(\text{SR})_2\cdot\text{L}$ compounds

System	Compound	Elemental Analysis %					Current Efficiency (gram equivalents per Faraday)
		Found (Calculated)					
		Ni	C	H	N	S	
Ethanethiol	$\text{Ni}(\text{SC}_2\text{H}_5)_2$	32.0 (32.4)	25.3 (26.5)	5.2 (5.5)	---	35.2 (35.5)	0.74
2-Propanethiol	$\text{Ni}(\text{SC}_3\text{H}_7)_2$	28.1 (28.1)	27.9 (28.4)	5.5 (5.7)	---	22.8 (23.6)	0.70
1-Butanethiol	$\text{Ni}(\text{SC}_4\text{H}_9)_2$	24.3 27.0(24.8) (27.1)	39.5 (40.6)	7.2 (7.6)	---	---	0.72
2-Methyl-2-Propanethiol	$\text{Ni}(\text{SC}_4\text{H}_9)_2$	23.7 (24.8)	40.3 (40.6)	7.4 (7.6)	---	26.9 (27.1)	0.82
1-Pentanethiol	$\text{Ni}(\text{SC}_5\text{H}_{11})_2$	22.0 (22.1)	45.1 (45.3)	8.1 (8.3)	---	24.1 (24.2)	0.83
Thiophenol	$\text{Ni}(\text{SC}_6\text{H}_5)_2$	21.0 (21.2)	25.9 (26.0)	3.4 (3.6)	---	23.0 (23.1)	0.90
Ethanethiol + 2,2'-bipyridyl	$\text{Ni}(\text{SC}_2\text{H}_5)_2\cdot\text{C}_{10}\text{H}_8\text{N}_2$	16.9 (17.4)	49.3 (49.8)	5.1 (5.3)	8.1 (8.3)	18.8 (19.0)	0.61
2-Propanethiol+ 2,2'-bipyridyl	$\text{Ni}(\text{SC}_3\text{H}_7)_2\cdot\text{C}_{10}\text{H}_8\text{N}_2$	15.9 (16.1)	52.2 (52.6)	5.8 (6.0)	7.5 (7.7)	17.4 (17.6)	0.65



1-Butanethiol + 2,2'-bipyridyl	Ni(SC ₄ H ₉) ₂ C ₁₀ H ₈ N ₂	14.8 (14.9)	54.8 (55.0)	6.4 (6.6)	6.9 (7.1)	16.1 (16.3)	0.72
2-Methyl-2-Propanethiol +2,2'-bipyridyl	Ni(SC ₄ H ₉) ₂ C ₁₀ H ₈ N ₂	14.6 (14.9)	54.9 (55.0)	6.5 (6.6)	7.0 (7.1)	15.9 (16.3)	0.87
1-Pentanethiol + 2,2'-bipyridyl	Ni(SC ₅ H ₁₁) ₂ C ₁₀ H ₈ N ₂	13.7 (13.9)	59.6 (60.0)	7.0 (7.1)	6.4 (6.6)	15.0 (15.2)	0.88
Thiophenol+ 2,2'-bipyridyl	Ni(SC ₆ H ₅) ₂ C ₁₀ H ₈ N ₂	13.4 (13.5)	58.9 (61.0)	4.1 (4.2)	6.4 (6.5)	14.6 (14.8)	0.90

All these products are dark brown in colour.

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