

Synthesis and Characterization of Unique Nickel(II) Carboxylates and Their Coordination Complexes

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Direct anodic dissolution of nickel metal and cathodic reduction of carboxylic acids (RCOOH) in acetonitrile has proved to be a simple and efficient one-step route to synthesize unique polymeric nickel(II) carboxylate complexes, $\{Ni(OOCR)_2\}_n$ in H-type glass Pyrex cell. When the oxidation was carried out in the presence of neutral ligands (L) such as 2,2'-bipyridyl or 1,10-phenanthroline, the complexes of type $\{Ni(OOCR)_2.L\}_n$ were obtained. Tetrabutylammonium chloride has been used as a supporting electrolyte in order to increase the electrolytic conductivity of the electrochemical system which in turn affects the current efficiency, cell voltage and energy consumption in the electrolytic cell. The complexes have been characterized by vibrational spectra, CHN elemental analysis, solubility and melting points shows a good agreement with the structure. The result also shows that the direct electrochemical synthetic technique has high current efficiency, extra purity and yield.

Keywords: Synthesis, Sacrificial anode, Electrochemical or Current efficiency, Nickel(II) carboxylate, Coordination complexes.

INTRODUCTION

Electrochemical technique in inorganic synthesis is highly selective in terms of potential, current density, electrode material and electrolyte composition for controlling the reaction rate. Electro synthesis is not only the oldest but also the simplest method for the synthesis of coordination compounds starting from the zero-valent metal. Electrochemical methods employ simple machinery and pure starting materials. The fact that the metal is employed rather than one of its salts avoids the occurrence of competitive reactions between the anion salts and the ligand to coordinate to the metal ion. Moreover, this approach allows the selective transformation of specific groups in a ligand or in a complex under very mild conditions. In the last several decades, contributions of electrochemical technique are of interest not only to inorganic [1-7], organic [8-11], organo-metallic [12], pharmaceutical [13,14] and neuroscience [15] but also it became the enabling fabrication route to grow the multi layered metallic thin films [16], nano-structures [17], nano-particles [18-20] and a high quality single crystal overlayers [21]. These new applications make the future of the research in electrochemical material science apparently quite exciting aspire. The study of transition metal carboxylates has got prime interest due to their DNA binding [22,23], catalytic [24] and anticorrosion properties [25].

EXPERIMENTAL

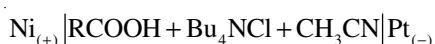
All the carboxylic acids and tetrabutylammonium chloride were purchased from Merck and Sigma Aldrich respectively and were used as received without further purification. The solvent acetonitrile was purchased from Merck and was purified using the 4A molecular sieves, dried using phosphorous pentoxide and was further distilled. Nickel electrode (Sigma Aldrich) of dimensions 0.635 mm diameter, 5 cm length was used as sacrificial anode and platinum electrode of dimensions 1 cm × 1 cm × 0.05 cm was used as inert cathode. For electrolysis, H-type pyrex glass cell was used which has two compartments anodic (larger) and cathodic (smaller) separated by sintered glass disc of G-3 porosity. Both compartments were sealed through guard tubes filled with calcium chloride and glass wool in order to protect the reaction mixture from moisture.

Electrochemical oxidation was conducted by passing the direct current supplies by electrophoresis power supply of 'Toshniwal' make indicating 0-300 V potential and 0-100 mA current. The stirring of anodic solution was done using magnetic stirrer of 'Perfit' make. The infrared spectral studies of metal complexes were realized using KBr pallets on 'Elmer FTIR spectrochem' (RXI) in the range of 4000-400 cm^{-1} . Melting points of metal complexes were determined using electrical device with a heating rate of 5 °C per min. Carbon, hydrogen

and nitrogen (where applicable) analysis were performed using 'Elementor Vario EL' CHNS elemental analyzer. The complexes were analyzed for their metal content by oxine method [26].

General procedure for synthesis of metal complexes:

Solution of 3 mL of the corresponding carboxylic acid in 250 mL of acetonitrile solvent containing tetrabutylammonium chloride as supporting electrolyte was poured into the two compartments of the H-type pyrex glass cell. The nickel electrode and platinum electrode were made sacrificial anode and inert cathode by connecting to the positive and negative terminal of electrophoresis power supply respectively. The cell was closed from both openings using guard tubes. The potential across the electrodes was so adjusted that a current of 20 mA passed through the solution. The electrolytic cell can be represented as:



where $\text{Ni}_{(+)}$ and $\text{Pt}_{(-)}$ are sacrificial nickel anode and inert platinum cathode respectively.

RCOOH is carboxylic acid used in systems (ethanoic acid, propionic acid, butyric acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid and decanoic acid).

Electrolysis was performed for 8 h with continuous stirring at constant current of 20 mA. During electrolysis, the solid compound started accumulating in the anode compartment which was filtered after the electrolysis was done. The solid product was purified by washing with hot acetonitrile and dried using dry diethyl ether. All the efforts were done to protect the product from air and moisture.

For the synthesis of coordination compounds of nickel carboxylates, the ligand (1,10-phenanthroline or 2,2'-bipyridyl) was added initially to the above substrates before electrolysis. The cell can be represented as:



RESULTS AND DISCUSSION

All the metal complexes were air stable and possessed good keeping qualities. All the complexes were insoluble in commonly used organic solvents like methanol, ethanol, benzene, dimethyl sulfoxide, dimethyl formamide, carbon disulphide and pyridine. Melting points of all these products were determined with the melting point apparatus of 5 °C rate per min. These products do not melt upto 350 °C but they show colour change in the range 230-250 °C which shows that they decompose in this temperature range. The analytical data of

these complexes are in good agreement with their formulation as given in the Table-1. The formulation of these complexes was based on elemental analysis, melting point, solubility and FTIR data. The complexes exhibited 1:2 metal-carboxylic acid stoichiometries in which the carboxylic acid moiety is coordinated to the metal ion with deprotonation in a bidentate mode.

The FTIR spectrum of the complexes consists of internal vibrations due to carboxylate group and methylene group. The spectrum is integrated by comparing with those of related complexes available in literature. The IR spectrum of the metal complexes indicates the absence of broad band in the region of 3300-3000 cm^{-1} due to -OH group of carboxylic acid which shows the deprotonation of carboxylic acid group *i.e.* metal ion is coordinated to carboxylate moiety. However, the characteristic vibrational bands appear in the region of 564-440, 942-660, 1409-1337, 1558-1552 and 2979-2851 cm^{-1} (Fig. 1).

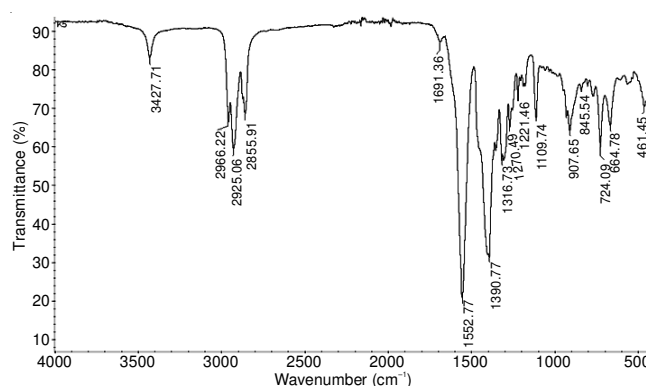


Fig. 1. IR spectrum of Ni-heptanoic acid system

It is reported in the literature [3,22,27,28] that the vibrational band due to the free $>\text{C}=\text{O}$ group of carboxylic moiety appears in the region of 1725-1700 cm^{-1} and in metal carboxylate $\nu(\text{COO}^-)$ asymmetric and symmetric stretching vibrations appeared in the region of 1610-1520 and 1460-1300 cm^{-1} . Also $\nu(\text{M}-\text{O})$ vibrational bands appeared in the region of 400-600 cm^{-1} have been reported [23,29-33] in the literature. The vibrational bands in the region of 3000-2800 cm^{-1} have been reported [3] in literature due to asymmetric and symmetric vibrations of methylene group.

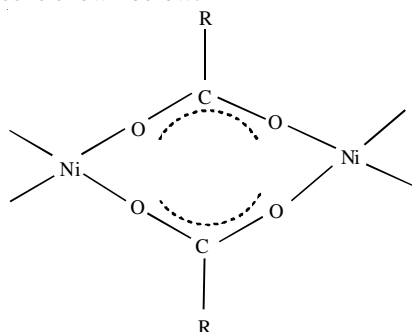
In the present products, the vibrational bands in the region of 1725-1700 cm^{-1} are absent which indicates that there is no free carbonyl group in the carboxylate moiety. This is further supported by the appearance of $\nu(\text{Ni}-\text{O})$ broad absorption

TABLE-1
ELEMENTAL ANALYSIS AND OTHER RELATED DATA OF NICKEL(II) CARBOXYLATES

System	m.f.	Elemental analysis (%): Calculated (Found)			Current efficiency (gram equivalents per Faraday)
		Ni	C	H	
Ethanoic acid	$\text{C}_4\text{H}_6\text{O}_4\text{Ni}$	33.2 (33.1)	27.2 (27.0)	3.4 (3.2)	0.68
Propionic acid	$\text{C}_6\text{H}_{10}\text{O}_4\text{Ni}$	28.7 (28.5)	35.2 (35.1)	4.9 (4.6)	0.72
Butyric acid	$\text{C}_8\text{H}_{14}\text{O}_4\text{Ni}$	25.2 (25.0)	41.2 (41.2)	6.0 (5.8)	0.61
Pentanoic acid	$\text{C}_{10}\text{H}_{18}\text{O}_4\text{Ni}$	22.5 (21.9)	46.0 (45.8)	6.9 (6.8)	0.89
Hexanoic acid	$\text{C}_{12}\text{H}_{22}\text{O}_4\text{Ni}$	20.3 (20.1)	49.9 (49.6)	7.6 (7.4)	0.77
Heptanoic acid	$\text{C}_{14}\text{H}_{26}\text{O}_4\text{Ni}$	18.5 (18.4)	53.0 (52.9)	8.2 (8.0)	0.71
Octanoic acid	$\text{C}_{16}\text{H}_{30}\text{O}_4\text{Ni}$	17.0 (16.8)	55.7 (55.5)	8.7 (8.5)	0.93
Nonanoic acid	$\text{C}_{18}\text{H}_{34}\text{O}_4\text{Ni}$	15.7 (15.4)	57.9 (57.7)	9.1 (9.0)	0.92
Decanoic acid	$\text{C}_{20}\text{H}_{38}\text{O}_4\text{Ni}$	14.6 (14.4)	59.9 (59.7)	9.5 (9.3)	0.72

bands in the region of 564-440 cm^{-1} which confirmed the coordination of the carboxylate moiety through oxygen with metal. The absorption bands in the region of 1558-1552 and 1409-1337 cm^{-1} may be assigned due to asymmetric and symmetric $\nu(\text{COO}^-)$ stretching vibrations respectively. The difference between $\nu(\text{COO}^-)$ asymmetric and symmetric is a parameter that identifies the type of bonding between the metal and carboxylate moiety. It is reported in the literature [22,34] that the value of $\Delta\nu$ above 250 cm^{-1} signify the monodentate coordination, a value in the range of 120-250 cm^{-1} signify the bridging mode while a difference below 120 cm^{-1} correspond to a chelate nature. In the present compounds the values of $\Delta\nu$ for the products lie in the range of 149-168 cm^{-1} . The value of $\Delta\nu$ suggests bridging bidentate mode due to the incarceration of interaction with both oxygen atoms of the carboxylate group. The vibrational frequencies observed in the region of 2851-2880 and 2921-2979 cm^{-1} are assigned to symmetric and asymmetric stretching vibrations of the $-\text{CH}_2$ group respectively. The bands observed in 942-660 cm^{-1} are due to the bending vibrations of the $-\text{CH}$ group. The fascinating characteristic of the bands appearing in the region of 564-440 cm^{-1} is that the bands are comparatively broad which indicates the bridging structure and polymeric nature of these compounds. Thus the broad bands, high melting points and insolubility in various organic solvents confirm that these compounds are unique polymeric nickel(II) carboxylates.

The probable structure of the unique polymeric nickel(II) carboxylates is shown below:

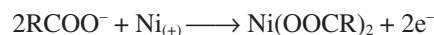


The reaction scheme for the formation of nickel(II) carboxylates is given as:

At cathode



At anode



Coordination complexes of nickel(II) carboxylates: In

order to prepare coordination complexes of nickel carboxylates, the synthesized parent nickel(II) carboxylates have been refluxed with the ligands 1,10-phenanthroline or 2,2'-bipyridyl in the solvents like methanol, ethanol, acetonitrile and benzene for 48 h. However, the analytical and IR data showed that the ligand moiety could not be attached to the parent nickel(II) carboxylates. It may be due to the reason that the metal atom in these nickel(II) carboxylates have already achieved its favourable coordination number through bridging, therefore further expansion of coordination sphere due to addition of ligand could not be achieved. However, the ligand molecule may be added to these compounds before these form carboxylate bridging and get polymerized. The coordination compounds have been prepared electrochemically by adding 1 g of ligand (1,10-phenanthroline or 2,2'-bipyridyl) to the above substrates and then electrolyzing the reaction mixture for 8 h. After electrolysis, the solid compound in the anodic compartment have been filtered, washed with hot acetonitrile and dried with dry diethyl ether. The elemental analysis data for nickel (oxine method), carbon, hydrogen and nitrogen for these adducts have been given in Table-2. The data shows that the complexes exhibit 1:2:1 stoichiometry corresponding to metal, carboxylic acid and ligand moiety respectively and conforms to the general formula $\text{Ni}(\text{OOCR})_2 \cdot \text{L}$.

IR spectra of these metal complexes shows absorption bands in the region of 598-468, 1411-1338, 1494-1442, 1579-1560 and 1615-1597 cm^{-1} . There is no absorption peak corresponding to free carbonyl group in the region of 1725-1700 cm^{-1} and the hydroxyl group in the region of 3300-3000 cm^{-1} of carboxylic acid moiety which indicates the deprotonation.

TABLE-2
ELEMENTAL ANALYSIS AND OTHER RELATED DATA OF COORDINATION COMPLEXES OF NICKEL(II) CARBOXYLATES

System	m.f.	Elemental analysis (%): Calculated (Found)				Current efficiency (gram equivalents per Faraday)
		Ni	C	H	N	
Ethanoic acid + 2,2'-bipyridyl	$\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_4\text{Ni}$	17.6 (17.4)	50.5 (50.3)	4.2 (4.0)	8.4 (8.2)	0.72
Propionic acid + 2,2'-bipyridyl	$\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_4\text{Ni}$	16.2 (16.0)	53.2 (53.0)	4.9 (4.8)	7.8 (7.7)	0.93
Butyric acid + 2,2'-bipyridyl	$\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_4\text{Ni}$	15.1 (15.0)	55.5 (55.3)	5.7 (5.6)	7.2 (7.1)	0.60
Pentanoic acid + 2,2'-bipyridyl	$\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_4\text{Ni}$	14.1 (14.0)	57.6 (57.4)	6.2 (6.0)	6.7 (6.6)	0.89
Hexanoic acid + 2,2'-bipyridyl	$\text{C}_{22}\text{H}_{30}\text{N}_2\text{O}_4\text{Ni}$	13.2 (13.0)	59.3 (59.1)	6.7 (6.6)	6.2 (6.0)	0.61
Heptanoic acid + 2,2'-bipyridyl	$\text{C}_{24}\text{H}_{34}\text{N}_2\text{O}_4\text{Ni}$	12.4 (12.1)	60.9 (60.8)	7.2 (7.0)	5.9 (5.7)	0.64
Octanoic acid + 2,2'-bipyridyl	$\text{C}_{26}\text{H}_{38}\text{N}_2\text{O}_4\text{Ni}$	11.7 (11.6)	62.3 (62.1)	7.6 (7.5)	5.6 (5.4)	0.82
Nonanoic acid + 2,2'-bipyridyl	$\text{C}_{28}\text{H}_{42}\text{N}_2\text{O}_4\text{Ni}$	11.1 (11.0)	63.5 (63.2)	7.9 (7.8)	5.3 (5.1)	0.98
Decanoic acid + 2,2'-bipyridyl	$\text{C}_{30}\text{H}_{46}\text{N}_2\text{O}_4\text{Ni}$	10.5 (10.3)	64.6 (64.4)	8.3 (8.1)	5.0 (4.9)	0.71
Ethanoic acid + 1,10-phenanthroline	$\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4\text{Ni}$	16.4 (16.2)	53.8 (53.6)	3.9 (3.6)	7.8 (7.6)	0.78
Propionic acid + 1,10-phenanthroline	$\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4\text{Ni}$	15.2 (15.0)	56.1 (55.9)	4.7 (4.6)	7.3 (7.2)	0.44
Butyric acid + 1,10-phenanthroline	$\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_4\text{Ni}$	14.2 (14.1)	58.1 (57.7)	5.3 (5.1)	6.8 (6.6)	0.81
Pentanoic acid + 1,10-phenanthroline	$\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_4\text{Ni}$	13.3 (13.2)	59.9 (59.5)	5.9 (5.7)	6.4 (6.2)	0.72
Hexanoic acid + 1,10-phenanthroline	$\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_4\text{Ni}$	12.5 (12.3)	61.4 (60.8)	6.4 (6.3)	5.9 (5.7)	0.64
Heptanoic acid + 1,10-phenanthroline	$\text{C}_{26}\text{H}_{34}\text{N}_2\text{O}_4\text{Ni}$	11.8 (11.6)	62.8 (62.6)	6.8 (6.6)	5.6 (5.4)	0.62
Octanoic acid + 1,10-phenanthroline	$\text{C}_{28}\text{H}_{38}\text{N}_2\text{O}_4\text{Ni}$	11.1 (10.8)	64.0 (63.8)	7.2 (7.1)	5.3 (5.1)	0.74
Nonanoic acid + 1,10-phenanthroline	$\text{C}_{30}\text{H}_{42}\text{N}_2\text{O}_4\text{Ni}$	10.6 (10.4)	65.1 (64.8)	7.6 (7.4)	5.1 (5.0)	0.90
Decanoic acid + 1,10-phenanthroline	$\text{C}_{32}\text{H}_{46}\text{N}_2\text{O}_4\text{Ni}$	10.1 (9.8)	66.1 (66.0)	7.9 (7.7)	4.8 (4.6)	0.83

The absorption bands appeared in the region of 598-468 cm^{-1} may be assigned due to $\nu(\text{Ni-O})$ stretching vibrations. However, the absorption bands appeared in the region of 1411-1338 and 1579-1560 cm^{-1} may be assigned due to $\nu(\text{COO}^-)$ symmetric and asymmetric stretching vibrations. All these absorption bands showed a blue shift of 10-20 cm^{-1} than the parent carboxylate complexes because of the complex formation with ligand molecule. In addition to these vibrational bands, the complexes showed the absorption bands in the region of 1494-1442 and 1615-1597 cm^{-1} due to the $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ stretching vibrations [33,35-37] which were absent in the parent nickel carboxylate and hence confirms that the ligand molecule has been attached to these nickel carboxylate complex. The peaks in the region of 598-468 cm^{-1} are comparatively broad which indicates that these compounds may be polymeric in nature (Fig. 2).

Melting points of all these compounds have been determined which were found to be higher than 350 $^{\circ}\text{C}$. These compounds are insoluble in various organic solvents like methanol, ethanol, benzene, pyridine, dimethyl sulfoxide, dimethyl formamide and carbon disulphide. High melting point, insoluble nature and broad IR peaks confirm the polymeric nature of these compounds.

The reaction scheme for the formation of adducts of nickel(II) carboxylate is given below:

At cathode



At anode



Electrochemical efficiencies or current efficiencies: The electrochemical efficiency (gram equivalents of metal dissolved per Faraday of electricity passed) is the ratio of experimental amount of metal dissolved to the theoretical amount of nickel dissolved by passing the current of 20 mA for 2 h. Theoretical amount of nickel dissolved have been determined by Faraday's First law of electrolysis. Experimental amount of nickel dissolved

have been determined by electrolyzing the above reaction mixture for exactly 2 h at constant current of 20 mA. After 2 h of electrolysis, the solution in the anodic compartment have been filtered and distilled in film evaporator (Buchi) till 10 mL solution is left. The solution was transferred to the beaker and dried to dryness. In dry mass, the nickel content was determined volumetrically by oxine method. The current efficiencies of all these systems have been determined and listed in Tables 1 and 2.

The current efficiencies of all these systems have been found to be very high except propionic acid + 1,10-phenanthroline system. Low value of current efficiency for this system is due to the corrosion inhibiting behaviour of this system to nickel anode. In order to elucidate the phenomenon of corrosion inhibition, the current efficiency of this system has been determined at different intervals of time and the data is enlisted in Table-3.

TABLE-3 CURRENT EFFICIENCIES OF PROPIONIC ACID + 1,10-PHENANTHROLINE SYSTEM AT DIFFERENT INTERVALS OF TIME		
System	Time (h)	Current efficiency
Propionic acid + 1,10-phenanthroline	1.0	0.75
	1.5	0.60
	2.0	0.44

The content in Table-3 shows that the current efficiency is high in the initial stage and then decreases with the passage of time. The decrease in current efficiency with passage of time indicates that the product of this system forms a protective layer on nickel anode which inhibits the further dissolution of metal and hence shows the corrosion inhibition phenomenon.

Conclusion

The preparative electrochemistry is an effective, single step, potential controlled, cost efficient, sustainable and selective method for the preparation of nickel complexes. The electro-

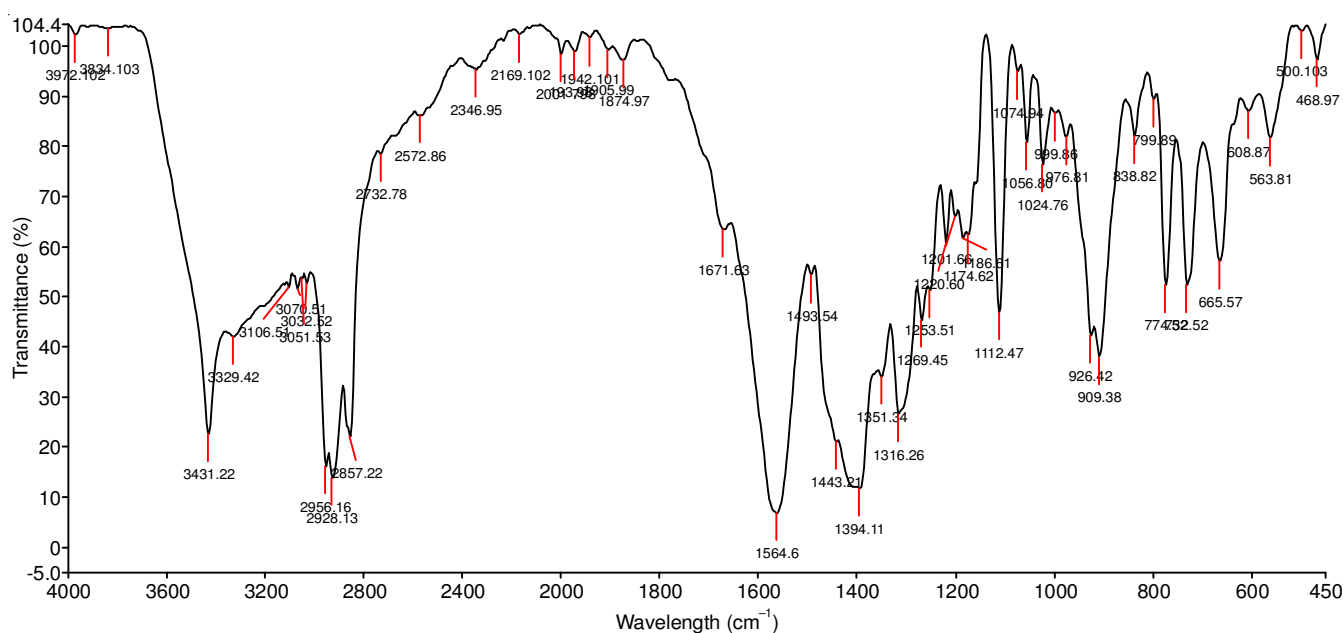


Fig. 2. IR spectrum of Ni-heptanoic acid + 2,2'-bipyridyl system

chemical synthesis is highly efficient in terms of the yield of substance and the current efficiencies are prominently higher than those in the traditional chemical synthesis. As electric current is used to drive the reactions in place of foreign oxidants or reductants so this method is highly eco-friendly for the synthesis of these unique nickel(II) carboxylates.

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