



Electrochemical Synthesis of Cadmium(II) Carboxylates Compounds at Sacrificial Cadmium Anode

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Received: 13 July 2016;

Accepted: 9 September 2016;

Published online: 30 November 2016;

AJC-18156

Cadmium carboxylates and their coordination complexes are synthesized by using an electrochemical technique in the presence of different carboxylic acids (RCOOH) using cadmium and a platinum as the anode and cathode respectively and tetrabutyl ammonium chloride as a supporting electrolyte. The electrochemical oxidation of anodic cadmium in acetonitrile solution with different carboxylic acids or with 1,10-phenanthroline (phen) and 2,2'-bipyridyl (bipy) yield the complexes $\text{Cd}(\text{OOCR})_2$ and $\text{Cd}(\text{OOCR})_2\text{L}$ (L = phen or bipy), respectively. The results from spectroscopic studies FTIR, elemental analysis and physical measurements confirm the existence of bonding between the carboxylate groups of different carboxylic acids with cadmium. Current efficiencies of all these synthesized compounds are also discussed.

Keywords: Sacrificial cadmium anode, Electrochemical synthesis, Cadmium(II) carboxylates, Coordination complexes.

INTRODUCTION

Electrochemical techniques are powerful and versatile analytical techniques that offer high sensitivity, selectivity, accuracy, precision and low-cost instrumentation. This technique has been gaining extraordinary acceleration in pharmaceutical industry [1-3], chemical industry [4-8], metal industry [9,10], drug analysis [11-13] and environmental applications [14-16]. Metal(II) carboxylates have been extensively studied due to their large applications in biological samples [17], anticorrosive materials [18,19], precursors in the synthesis of metal-organic frameworks [20], semiconductor nanorods [21], in the nanoparticles [22,23] and electro-analytical analysis [24,25]. This electrochemical technique offers several advantages in inorganic synthesis: (a) the selectivity of the reaction can be influenced by the applied electrode potential; (b) the reaction rate can be controlled by the current density; (c) the electrode material and the electrolyte composition can be used as parameters for controlling the selectivity and reaction rate [26]. From our laboratory, large number of papers has been published on organic, inorganic and organometallic compounds on different metals [27-34] on zinc, mercury, antimony, bismuth, copper, aluminium, *etc.* since last three decades. So, the aim of the present communication is therefore, to synthesize and characterize a series of cadmium carboxylates and their coordination complexes to explore this electrochemical technique.

EXPERIMENTAL

All carboxylic acids (Merck) were of analytical grade and used without further purification. Tetrabutyl ammonium chloride (Sigma Aldrich) was crystallized from conductivity water, dried under reduced pressure at 100 °C and was used as a supporting electrolyte. Acetonitrile (Merck), the commercially available solvent was purified and dried over 4A molecular sieves and was kept for overnight. Then the solution was distilled in the range of 81-82 °C and collected. This distillate was kept in phosphorous pentoxide for overnight and then finally distilled again. Pure and dry acetonitrile was collected at 81.6 °C and was kept in moisture free, air tight brown coloured bottles.

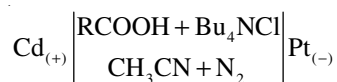
All glass H-type cell: For electrolysis, H-type cell is used which is made of pyrex glass and contains two compartments, anodic compartment (anode electrode is suspended) and cathodic compartment (cathode electrode is suspended) and are separated by a divider of sintered glass disc of G-3 porosity. Cadmium electrode having dimensions (3 cm × 10 cm × 0.2 cm) and platinum gauze (1 cm × 1 cm × 0.05 cm) was used as a sacrificial anode and inert cathode respectively. Both the compartments were fitted with guard tubes filled with calcium chloride and glass wool. The cell was incorporated into the electrolytic circuit by connecting the anode to positive terminal and cathode to negative terminal of DC power supply respectively.

Power source: Direct current for the electrochemical oxidation was supplied by electrophoresis power supply of Toshniwal make. It was regulated a voltmeter capable of indicating 0-300 volt and a milliampere capable of indicating 0-100 mA.

Magnetic stirrer: The anolyte was effectively agitated by a magnetic follower using magnetic stirrer of 'Perfit' make. The stirring increased the rate of reaction by removing the products deposited on the anodic cadmium electrode surface.

Infrared spectroscopy: Fourier transform infrared spectroscopy (FTIR) Perkin Elmer Spectrochem (RXI) in the range of 4000-400 cm^{-1} was used for the scanning of the infrared spectra of the products by using potassium bromide pellets.

Electrochemical procedure: The electrolysis system consisted of a Cd rod as the anode and platinum foil as the inert cathode in the presence of carboxylic acids, acetonitrile as a solvent and tetrabutyl ammonium chloride as the supporting electrolyte. Prior to synthesis, both anode and cathode were rinsed properly to remove any trace of organic materials on their surface. The bubbling of nitrogen gas was done throughout the reaction. The carboxylic acids (3 mL), acetonitrile (250 mL) was mixed with tetrabutyl ammonium chloride (1 g) and poured into the electrochemical cell. The electrolytic cell representation is:



where, $\text{Cd}_{(+)}$ is sacrificial cadmium anode; $\text{Pt}_{(-)}$ is inert platinum cathode.

RCOOH is carboxylic acid used in the systems (acetic acid, propanoic acid, butyric acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid and decanoic acid)

Bu_4NCl is tetrabutylammonium chloride. The reaction was performed at room temperature for 6.0 h at a constant current of 20 mA. Stirring was kept throughout the synthesis process. The electrolysis yielded solid compounds in anodic compartment and the resulting complex was then filtered and washed with warm acetonitrile, dry diethyl ether to remove the impurities and finally dried under vacuum and the product was kept in desiccator. All efforts were done to protect the product from air and moisture. For the synthesis of coordination complexes of cadmium carboxylates, 1 g of ligand 1,10-phenanthroline or 2,2'-bipyridine was also added before starting the electrolysis in addition to above substrates and

electrolysis have been done under the similar conditions. Melting point of all these products was determined using electrical device with a heating rate of 5 $^{\circ}\text{C}$ per min. Cadmium contents in electrochemically synthesized compounds were determined using oxine method [35]. Carbon, hydrogen and nitrogen (where applicable) contents in the products were determined through 'ElementorVario EL' CHNS elemental analyzer.

RESULTS AND DISCUSSION

Electrochemical synthesis of cadmium(II) carboxylates:

All the above synthesized electrochemical products are not affected by air or moisture. All these compounds are insoluble in commonly used organic solvents like acetone, benzene, ethanol, methanol, chloroform, carbon tetrachloride, N,N-dimethyl formamide, dimethyl sulfoxide and carbon disulfide. Melting point of all these products were observed that these do not melt upto 300 $^{\circ}\text{C}$, however, decompose in a temperature range of 230 to 250 $^{\circ}\text{C}$. The decomposition of the synthesized products is indicated from the change in colour of these compounds.

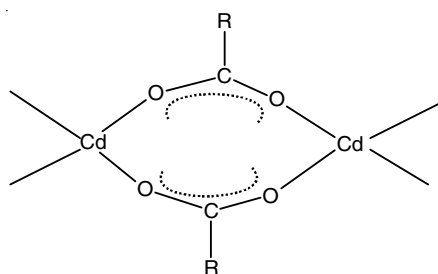
Microanalysis and IR of parent cadmium(II) carboxylates:

The elemental data of electrochemical synthesized cadmium complexes are shown in Table-1. Based on the data of elemental analysis, the composition to cadmium complexes have identified as 2:1 ratio of carboxylic acid and cadmium respectively and this ratio compete with the general formula $\text{Cd}(\text{OOCR})_2$. The infrared vibrational spectra, band positions and possible assignments of these complexes show the broad peak due to $\nu(\text{O-H})$ was not seen in the spectra of complexes *i.e.* in the region of 3300-2800 cm^{-1} due to O-H group of the carboxylic acid. It shows the deprotonation of carboxylic acids. However, major vibrational bands of these compounds appeared in the region of 1615-1556, 1435-1336 and 597-446 cm^{-1} . It is reported in literature [36,37] that $\nu(\text{C=O})$ of carboxylic groups appears in the range of 1725-1700 cm^{-1} in free carboxylic acids and in metal carboxylates $\nu(\text{COO}^-)$ asymmetric and symmetric stretching vibrations [37-39] appeared in the region of 1625-1535 and 1460-1300 cm^{-1} , respectively. In the present electrochemical products, there is no peak observed in the range of 1725-1700 cm^{-1} , which indicates that there is no free carbonyl group of carboxylic acids. It is reported [36] that in metal complexes $\nu(\text{C=O})$ peak gets lowered substantially. So, in the present work, this $\nu(\text{C=O})$ peak gets lowered and gives rise to absorption bands in the region of 1615-1556 and 1435-1336 cm^{-1} . This absorption bands were

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

System	Potential applied (V)	Product	Colour	Elemental analysis (%): Found (Calcd.)			Current efficiency (gram equivalents per Faraday)
				Cd	C	H	
Acetic acid	30	$\text{C}_4\text{H}_6\text{O}_4\text{Cd}$	White	49.05 (48.78)	21.33 (20.83)	2.45 (2.60)	0.75
Propanoic acid	35	$\text{C}_6\text{H}_{10}\text{O}_4\text{Cd}$	White	43.25 (43.49)	26.68 (27.86)	3.55 (3.86)	0.54
Butyric acid	30	$\text{C}_8\text{H}_{14}\text{O}_4\text{Cd}$	White	38.79 (39.24)	33.45 (33.51)	4.00 (4.88)	0.90
Pentanoic acid	40	$\text{C}_{10}\text{H}_{18}\text{O}_4\text{Cd}$	White	35.24 (35.75)	38.18 (38.16)	5.00 (5.72)	0.92
Hexanoic acid	45	$\text{C}_{12}\text{H}_{22}\text{O}_4\text{Cd}$	White	33.00 (32.83)	42.00 (42.06)	6.65 (6.42)	0.95
Heptanoic acid	50	$\text{C}_{14}\text{H}_{26}\text{O}_4\text{Cd}$	White	30.35 (30.34)	45.80 (45.36)	7.05 (7.02)	0.94
Octanoic acid	50	$\text{C}_{16}\text{H}_{30}\text{O}_4\text{Cd}$	White	28.00 (28.21)	48.90 (48.19)	7.55 (7.53)	0.90
Nonanoic acid	52	$\text{C}_{18}\text{H}_{34}\text{O}_4\text{Cd}$	White	26.48 (26.36)	50.60 (50.65)	7.85 (7.97)	0.88
Decanoic acid	55	$\text{C}_{20}\text{H}_{38}\text{O}_4\text{Cd}$	White	24.23 (24.73)	52.80 (52.82)	8.85 (8.36)	0.90

assigned to asymmetric and symmetric vibrations of carboxylate $\nu(\text{COO}^-)$ group. In literature, various $\nu(\text{M-O})$ vibrations in the region of $600\text{--}400\text{ cm}^{-1}$ are reported [40–42]. Survey of literature reveals [43] that $\nu(\text{Cd-O})$ stretching frequency is reported in the region of $600\text{--}450\text{ cm}^{-1}$. In present products, a strong absorption occurs in the region of $597\text{--}446\text{ cm}^{-1}$ may be assigned to $\nu(\text{Cd-O})$ vibrations. The interesting feature of these absorption bands in the region of $597\text{--}446\text{ cm}^{-1}$ is that these bands are comparatively broad showing that the bridging structure of these complexes and also conform that these compounds may be polymeric in nature. The polymeric nature of these electrochemically prepared cadmium(II) carboxylates is also supported by high melting point and insoluble behaviour of these compounds in various organic solvents. So, on the basis of above data, the present electrochemical products are characterized as unique polymeric cadmium(II) carboxylates. The plausible structure of these unique polymeric cadmium(II) carboxylates is shown in figure given below:

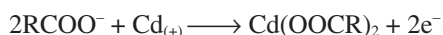


The current efficiencies of all these systems are enlisted in Table-1 which is very high. The high current efficiency shows the mechanism of formation of cadmium(II) carboxylates. The formation of cadmium(II) carboxylates is given below:

At inert cathode:



At sacrificial anode:



Coordination complexes of cadmium(II) carboxylates:

The synthesized parent cadmium(II) carboxylates have been refluxed with ligands phen or bipy in polar and non-polar solvents like methanol, ethanol, benzene and acetonitrile for 48 h in order to prepare coordination complexes of these compounds. However the analytical and IR data of these compounds showed that the ligand molecule could not be attached to this parent cadmium(II) carboxylates. It may be due to the reason that the metal atom in these cadmium(II) carboxylates have already achieved its favourable coordination number through bridging, therefore, further expansion of coordination sphere due to the addition of ligand could not be achieved. It was thus considered worthwhile that the ligand may be added to these compounds before these form carboxylate bridging and get polymerized. So, it was thought their adducts have also been prepared electrochemically by adding 1 g of ligand 1,10-phenanthroline or 2,2'-bipyridyl to above reaction mixture and the products are isolated in the anode compartment. Analytical data and elemental analysis of cadmium (by oxine method), carbon, hydrogen and nitrogen are enlisted in the Table-2. This data is best suited to the composition of 2:1:1 of carboxylic acid, cadmium and ligand respectively and

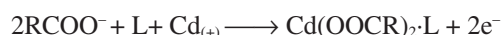
suggest the molecular formula $\text{Cd}(\text{OOCR})_2\cdot\text{L}$ (L = phen or bipy) which shows that one ligand is coordinated to metal by carboxylic group. IR spectra of these metal complexes show peaks in the range of $1530\text{--}1465$, $1620\text{--}1575$, $1437\text{--}1347$ and $648\text{--}420\text{ cm}^{-1}$. In the infrared spectra of the coordination complexes, there is also no $\nu(\text{O-H})$ peak of carboxylic acids which shows deprotonation and peak due to $\nu(\text{C=O})$ substantially gets lowered and gives rise to absorption bands in the region of $1620\text{--}1575$ and $1437\text{--}1347\text{ cm}^{-1}$. These peaks are assigned to $\nu(\text{COO}^-)$ asymmetric and $\nu(\text{COO}^-)$ symmetric stretching vibrations respectively. The characteristic bands in the region of $648\text{--}420\text{ cm}^{-1}$ are assigned to $\nu(\text{Cd-O})$ stretching frequency. IR spectra show the strong absorption of $\nu(\text{C}\cdots\text{C})/\nu(\text{C}\cdots\text{N})$ of ligand molecule [44,45] in the region of $1530\text{--}1465\text{ cm}^{-1}$ which are not present in parent cadmium(II) carboxylate. Moreover, there is appropriate shift of $\nu(\text{C}\cdots\text{C})/\nu(\text{C}\cdots\text{N})$ stretching vibrations in the lower region as compared to pure free ligands. This is due to the complex formation of ligand with cadmium metal. So, in the present products, blue shift of $\nu(\text{COO}^-)$ asymmetric and $\nu(\text{COO}^-)$ symmetric stretching vibrations and red shift in $\nu(\text{C}\cdots\text{C})/\nu(\text{C}\cdots\text{N})$ vibrations and the presence of broad bands due to $\nu(\text{Cd-O})$ vibrational modes indicate: (a) the coordination of the ligand; (b) the polymeric structure of these complexes.

Polymeric nature of these adducts have also been supported by high melting point and insoluble behaviour. Current efficiencies of all these adduct are presented in Table-2, which reveal that all these systems are associated with high current efficiencies. So, the reactions leading to the formation of coordination compounds of cadmium(II) carboxylates are the predominant reactions of these systems. Mechanism for the formation of coordination compounds of cadmium(II) carboxylates is shown below:

At inert cathode:



At sacrificial anode:



Electrochemical efficiencies/current efficiencies of cadmium(II) carboxylates: The electrochemical efficiencies (gram equivalents of metal dissolved per Faraday of electricity passed) of all these cadmium complexes were determined using Faraday's first law of electrolysis by electrolyzing the above systems for exactly 2 h at a constant current of 20 mA. After 2 h electrolysis, the anodic compartment solvent was distilled in rotary film evaporator (Buchi) till 10 mL of content was left in round bottom flask. This content were transferred to the beaker and heated to dryness. In the dry mass, the cadmium contents were determined volumetrically. The theoretical value of cadmium was calculated by using Faraday's first law of electrolysis. The ratio of experimental and theoretical cadmium content gives the electrochemical efficiency of the system. Electrochemical efficiencies of all these systems have determined and enlisted in Tables 1 and 2. All these systems have high current efficiency except for the propanoic acid, propanoic acid + 1,10-phenanthroline and butyric acid + 1,10-phenanthroline. The low value of current efficiency of these systems at cadmium anode may be due the corrosion inhibiting beha-

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

System	Potential applied (V)	Product	Colour	Elemental analysis (%): Found (calcd.)				Current efficiency (gram equivalents per Faraday)
				Cd	C	H	N	
Acetic acid + 2,2'-bipyridyl	30	C ₄ H ₆ O ₄ CdC ₁₀ H ₈ N ₂	Light cream	30.00 (29.07)	43.26 (43.45)	3.46 (3.62)	7.02 (7.24)	0.90
Propanoic acid + 2,2'-bipyridyl	35	C ₆ H ₁₀ O ₄ CdC ₁₀ H ₈ N ₂	Cream	27.99 (27.11)	45.00 (46.31)	3.94 (4.34)	7.00 (6.75)	0.76
Butyric acid + 2,2'-bipyridyl	30	C ₈ H ₁₄ O ₄ CdC ₁₀ H ₈ N ₂	Cream	25.00 (25.39)	47.76 (48.80)	5.02 (4.97)	6.00 (6.32)	0.70
Pentanoic acid + 2,2'-bipyridyl	40	C ₁₀ H ₁₈ O ₄ CdC ₁₀ H ₈ N ₂	Light yellow	24.00 (23.88)	51.00 (50.99)	6.96 (5.52)	4.62 (5.94)	0.82
Hexanoic acid + 2,2'-bipyridyl	35	C ₁₂ H ₂₂ O ₄ CdC ₁₀ H ₈ N ₂	Light yellow	23.00 (22.54)	53.00 (52.94)	6.57 (6.01)	5.00 (5.61)	0.65
Heptanoic acid + 2,2'-bipyridyl	30	C ₁₄ H ₂₆ O ₄ CdC ₁₀ H ₈ N ₂	Cream	22.00 (21.34)	54.66 (54.69)	6.67 (6.45)	5.00 (5.31)	0.80
Octanoic acid + 2,2'-bipyridyl	30	C ₁₆ H ₃₀ O ₄ CdC ₁₀ H ₈ N ₂	Cream	20.32 (20.26)	55.98 (56.25)	6.45 (6.85)	5.55 (5.04)	0.96
Nonanoic acid + 2,2'-bipyridyl	40	C ₁₈ H ₃₄ O ₄ CdC ₁₀ H ₈ N ₂	Light yellow	18.94 (19.29)	56.67 (57.67)	7.15 (7.21)	4.25 (4.81)	0.86
Decanoic acid + 2,2'-bipyridyl	35	C ₂₀ H ₃₈ O ₄ CdC ₁₀ H ₈ N ₂	Cream	18.00 (18.41)	58.02 (58.95)	7.39 (7.53)	4.50 (4.58)	0.79
Acetic acid + 1,10-phenanthroline	40	C ₄ H ₆ O ₄ CdC ₁₂ H ₈ N ₂	Cream	27.30 (27.39)	46.00 (46.78)	3.25 (3.41)	7.00 (6.82)	0.80
Propanoic acid + 1,10-phenanthroline	30	C ₆ H ₁₀ O ₄ CdC ₁₂ H ₈ N ₂	Light yellow	25.65 (25.64)	49.20 (49.27)	4.19 (4.11)	6.20 (6.39)	0.55
Butyric acid + 1,10-phenanthroline	35	C ₈ H ₁₄ O ₄ CdC ₁₂ H ₈ N ₂	Light yellow	24.00 (24.09)	51.98 (51.46)	4.66 (4.72)	6.20 (6.00)	0.60
Pentanoic acid + 1,10-phenanthroline	45	C ₁₀ H ₁₈ O ₄ CdC ₁₂ H ₈ N ₂	Light yellow	22.71 (22.73)	53.47 (53.40)	5.34 (5.26)	5.55 (5.66)	0.85
Hexanoic acid + 1,10-phenanthroline	52	C ₁₂ H ₂₂ O ₄ CdC ₁₂ H ₈ N ₂	Light yellow	21.69 (21.51)	55.70 (55.11)	5.44 (5.74)	5.82 (5.36)	0.95
Heptanoic acid + 1,10-phenanthroline	50	C ₁₄ H ₂₆ O ₄ CdC ₁₂ H ₈ N ₂	Yellow	20.59 (20.41)	56.71 (56.66)	6.40 (6.17)	5.02 (5.09)	0.75
Octanoic acid + 1,10-phenanthroline	48	C ₁₆ H ₃₀ O ₄ CdC ₁₂ H ₈ N ₂	Light yellow	19.46 (19.42)	57.87 (58.07)	6.51 (6.57)	5.00 (4.84)	0.92
Nonanoic acid + 1,10-phenanthroline	50	C ₁₈ H ₃₄ O ₄ CdC ₁₂ H ₈ N ₂	Light yellow	18.60 (18.53)	59.75 (59.34)	6.96 (6.92)	4.62 (4.62)	0.84
Decanoic acid + 1,10-phenanthroline	55	C ₂₀ H ₃₈ O ₄ CdC ₁₂ H ₈ N ₂	Light yellow	17.65 (17.71)	60.50 (60.51)	7.30 (7.25)	4.42 (4.41)	0.92

viour of these compounds to cadmium. In order to throw light on the mechanism of corrosion inhibiting nature of these compounds, current efficiencies of the reactions of propanoic acid, propanoic acid + 1,10-phenanthroline and butyric acid + 1,10-phenanthroline have been determined at different intervals of time and the relevant data is recorded in Table-3. Table-3 reveals that the current efficiencies of these systems are sufficiently high at the initial stages and decrease with the passage of time. This decrease in current efficiency with the passage of time reveals that the products of these systems form a protective layer on the cadmium surface and thus inhibits further dissolution of cadmium and shows the corrosion inhibitor behaviour of these reactants to cadmium.

Conclusion

The tremendous selectivity, high speed, extra purity, simplicity, one pot synthesis, low expense of instrument, flexibility in applications make the electrochemical technique a versatile tool for the synthesis of cadmium(II) carboxylates and their coordination complexes in the laboratory as well as at the industrial level. All the electrochemically synthesized compounds are associated with high current efficiencies, which

TABLE-3
CURRENT EFFICIENCY OF PROPANOIC ACID, PROPANOIC ACID + 1,10-PHENANTHROLINE AND BUTYRIC ACID + 1,10-PHENANTHROLINE SYSTEMS AT CADMIUM ANODE AT DIFFERENT INTERVALS OF TIME

System	Time (h)	Current efficiency (gram equivalents per Faraday)
Propanoic acid	1.0	0.75
	1.5	0.68
	2.0	0.54
Propanoic acid + 1,10-phenanthroline	1.0	0.83
	1.5	0.72
	2.0	0.55
Butyric acid + 1,10-phenanthroline	1.0	0.89
	1.5	0.79
	2.0	0.60

suggest that this electrochemical method can be used for the commercial preparations of these compounds.

ACKNOWLEDGEMENTS

This reported work is supported by UGC, New Delhi in form of MRP (Major research project).

REFERENCES

1. O.A. Farghaly, R.S. Abdel Hameed and H. Abd-Alhakeem, *Int. J. Electrochem. Sci.*, **9**, 3287 (2014).
2. I.G. Martin, C.G. Perez and M.A.B. Lopez, *Anal. Chim. Acta*, **368**, 175 (1998).
3. Y. Ni, Y. Wang and S. Kokot, *Anal. Lett.*, **37**, 3219 (2004).
4. M.A. Reynolds, T.B. Rauchfuss and S.R. Wilson, *Organometallic*, **22**, 1619 (2005).
5. J. Tian and K.D. Moeller, *Org. Lett.*, **7**, 5381 (2005).
6. N.A. Bell, W. Clegg, J.R. Creighton and E.S. Raper, *Inorg. Chim. Acta*, **303**, 12 (2000).
7. J.E. Dick and D. Chong, *Org. Chem. Curr. Res.*, **1**, 1 (2012).
8. T.H. Kim and S.M. Park, *Electrochim. Acta*, **50**, 1461 (2005).
9. M.P. Kumar, P.C. Mouli, S.J. Reddy and S.V. Mohan, *Anal. Lett.*, **38**, 463 (2005).
10. T.R. Williams, D.R. Foy and C. Benson, *Anal. Chim. Acta*, **75**, 250 (1975).
11. J.M. Kauffmann, J.C. Vire, G.J. Patriarche, L.J. Nunez-Vergara and J.A. Squella, *Electrochim. Acta*, **32**, 1159 (1987).
12. S. Shahrokhian, M. Karimi and H. Khajehsharifi, *Sens. Actuators B*, **109**, 278 (2005).
13. N. Özaltın, C. Yardımcı and I. Süslü, *J. Pharm. Biomed. Anal.*, **30**, 573 (2002).
14. E.R. Sousa, E.P. Marques, E.N. Fernandes, J. Zhang and A.L.B. Marques, *J. Braz. Chem. Soc.*, **17**, 177 (2006).
15. Y. He, Y. Zheng, M. Ramnaraine and D.C. Locke, *Anal. Chim. Acta*, **511**, 55 (2004).
16. R. Jugade and A.P. Joshi, *Acta Chim. Slov.*, **52**, 145 (2005).
17. N. Uddin, M. Sirajuddin, N. Uddin, M. Tariq, H. Ullah, S. Ali, S.A. Tirmizi and A.R. Khan, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **140**, 563 (2015).
18. L. Chen, H. Meng, L. Jiang and S. Wang, *Chem. Asian J.*, **6**, 1757 (2011).
19. S. Wang, L. Feng and L. Jiang, *Adv. Mater.*, **18**, 767 (2006).
20. G.S. Papaefstathiou and L.R. MacGillivray, *Coord. Chem. Rev.*, **246**, 169 (2003).
21. G. Mao, W. Dong, D.G. Kurth and H. Mohwald, *Nano Lett.*, **4**, 249 (2004).
22. Y.H. Kim, Y.S. Kang, W.J. Lee, B.G. Jo and J.H. Jeong, *Mol. Cryst. Liq. Cryst.*, **445**, 231 (2006).
23. A.G. Nasibulin, E.I. Kauppinen, D.P. Brown and J.K. Jokiniemi, *J. Phys. Chem. B*, **105**, 11067 (2001).
24. J.E. Halls, S.D. Ahn, D. Jiang, L.L. Keenan, A.D. Burrows and F. Marken, *J. Electroanal. Chem.*, **689**, 168 (2013).
25. O.A. Farghaly and M.A. Ghandour, *Environ. Res.*, **97**, 229 (2005).
26. P.T. Kissinger and W.R. Heineman, *Laboratory Techniques in Electroanalytical Chemistry*, Marcel Dekker Inc., New York (1996).
27. J.S. Banait and B. Singh, *J. Electrochem. Soc. India*, **46**, 215 (1997).
28. J.S. Banait and B. Singh, *J. Electrochem. Soc. India*, **45**, 103 (1996).
29. J.S. Banait, B. Singh and S. Rala, *J. Indian Chem. Soc.*, **86**, 416 (2009).
30. J.S. Banait, B. Singh and H. Kaur, *J. Indian Chem. Soc.*, **82**, 555 (2005).
31. H. Kaur and B. Singh, *E-J. Chem.*, **9**, 381 (2012).
32. B. Singh, Shavina and K. Bala, *Chem. Sci. Rev. Lett.*, **3**, 367 (2014).
33. J.S. Banait and P.K. Pahil, *Polyhedron*, **5**, 1865 (1986).
34. J.S. Banait, S.K. Deol and B. Singh, *Synth. React. Inorg. Met.-Org. Chem.*, **20**, 1331 (1990).
35. Vogel's, *Text Book of Quantitative Chemical Analysis*, Longman Group UK Ltd. (1989).
36. M. Ibrahim, A. Nada and D.E. Kamal, *Indian J. Pure Appl. Phys.*, **43**, 911 (2005).
37. S. Shahzadi, S. Ali, S. Jabeen, N. Kanwal, U. Rafique and A.N. Khan, *Russ. J. Coord. Chem.*, **34**, 38 (2008).
38. M.S. Refat, S.A. El-Korashy and M.A. Hussien, *Can. Chem. Trans.*, **2**, 24 (2014).
39. A. Kasarci, D.A. Kose, G.A. Avci and E. Avci, *Hacettepe J. Biol. Chem.*, **41**, 167 (2013).
40. K. Pachori, S. Malik and S. Wankhede, *Res. J. Chem. Sci.*, **4**, 75 (2014).
41. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds Interscience Wiley*, New York, edn 5 (1997).
42. D.A. Köse, H. Necefoglu and H. Icbudak, *J. Coord. Chem.*, **61**, 3508 (2008).
43. D.A. Köse, G. Gökce, S. Gökce and I. Uzun, *J. Therm. Anal. Calorim.*, **95**, 247 (2009).
44. A.S. Aidwayyan and F.M. Al-Jekhedab, *Int. J. Electrochem. Sci.*, **8**, 10506 (2013).
45. Z.A. Siddiqi, I.A. Ansari, F. Sama and M. Shahid, *Int. J. Innovat. Res. Sci. Eng. Technol.*, **3**, 8673 (2014).