Electrochemical synthesis of cadmium chelates at sacrificial anode

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Abstract

The synthesis of cadmium chelates through an electrochemical technique, involving the anodic oxidation of a sacrificial metallic electrode (cadmium) within an H-type cell, is reported. This process utilizes acetonitrile as a solvent with organic compounds containing abstractable hydrogen RH_2 *(nitroethane, 2-nitropropane, malononitrile and diethylmalonate) serving as the reactants. This study encompasses the coordination complexes of cadmium with ligands, 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen).*

The electrochemically synthesized products have been confirmed through various physical measurements, elemental analyses and infrared spectral studies. This one-step electrochemical technique is highly effective in obtaining metal complexes and their coordination complexes. The determination of current efficiency for these synthesized complexes serves to elucidate the underlying reaction mechanism.

Keywords: Electrochemical technique, cadmium chelates, coordination compounds, sacrificial anode.

Introduction

The electrochemical synthesis of metal complexes was pioneered by Said and Tuck[19]. In recent times, there has been a notable focus on the electrochemical synthesis of metal compounds[3,4]. The simplicity, selectivity and high product yield inherent in this technique provide a pathway to the creation of new compounds[18,24,25]. Metals are commonly abundant and typically more cost-effective than their compounds, making direct synthesis from the metal as an appealing route[6,9]. This study seeks to investigate the applicability of the electrochemical method in the synthesis of a broad spectrum of cadmium chelates. The metal chelates exihibit biological activities as antibiotic, antivirus and antitumor agents. Some metal chelates actively participate in life processes. The foremost uses of metal chelates extend to agriculture, paper pulp bleaching process, pigment and dye industries[7,15,16].

Material and Methods

Chemicals and Apparatus used: Acetonitrile (Merck), tetrabutylammonium chloride (Sigma Aldrich) and organic compounds with abstractable hydrogen (Merck) were of analytical reagent grade. The commercially available acetonitrile solvent was dried by keeping in 4A molecular sieves overnight and distilled in range of 81-82°C[23]. Tetrabutylammonium chloride, used as a supporting electrolyte, was crystallized under reduced pressure at 100°C. Direct current (D.C) was supplied by an electrophoresis power supply for the electrochemical oxidation.

During electrolysis, the mixture was stirred using a magnetic stirrer (Perfit) to enhance the reaction rate by preventing the deposition of products on the surface of the cadmium electrode. The melting points of these compounds were determined using a device with a heating rate of 5°C per minute. Carbon, hydrogen and nitrogen contents were determined by CHNS Elemental analyzer 'Elementor vario EL'. Infrared data of these products were recorded on Perkin- Elmer spectrophotometer (FTIR) in the region of 4000-400 cm^{-1} using KBr pallets.

Methodology: The electrolysis of the aforementioned organic compounds (3.0 mL) was conducted in an H-shaped cell using acetonitrile (250 mL) and tetrabutylammonium chloride (1.0 g) as the electrolyte. A cadmium rod ($2 \times 10 \times 0.02\ cm^3$) and platinum foil ($1.0 \times 1.0\ cm^2$) were dipped in anodic and cathodic compartment of the cell respectively. After establishing the proper connections with power supply, a current of 20 mA was passed through the solution. Throughout the reaction, nitrogen gas bubbling was maintained to create an inert atmosphere. The representation of cell is illustrated below:

$$Cd_{(+)} \left| \begin{array}{c} RH_2 + CH_3CN + \\ Bu_4NCl \end{array} \right| Pt_{(-)}$$

where $Cd_{(+)}$ is sacrificial cadmium anode, $Pt_{(-)}$ is inert cathode, RH_2 is organic compound having labile hydrogen and Bu_4NCl is tetrabutylammonium chloride

Electrolysis was conducted for duration of 10 hours at room temperature, utilizing a current of 20 mA, to ensure the generation of a sufficient amount of solid product separated in the anode compartment. Subsequently, the product was isolated, washed with warm acetonitrile (10 mL), dry ethyl ether (15 mL) and dried under vacuum. The products were protected from air and moisture by being stored in a desiccator.

The efforts to prepare their coordination complexes by refluxing them with ligands such as 2,2'-bipyridyl and 1,10-phenanthroline in both polar and in non-polar solvents including ethanol, acetonitrile and benzene, were unsuccessful as indicated by elemental analysis and infrared spectral studies. Therefore, coordination complexes of these products were prepared electrochemically under the similar conditions by adding 1.0 g of ligand (2,2’-bipyridyl or 1,10-phenanthroline) in addition to the aforementioned substrates.

All these prepared products are stable solid in air and all are insoluble in most commonly used organic solvents. These isolated complexes do not undergo melting upto a temperature of 250°C. However, they exhibit a colour change in a temperature range of 220°C to 230°C attributing to the decomposition of the products.

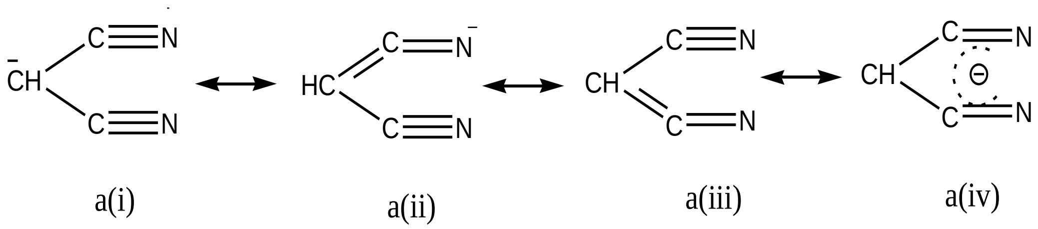
Results and Discussion

Microanalysis and IR data of cadmium (II) chelates: The synthesized compounds were confirmed by analytical and elemental analysis as well as infrared data, to illustrate their composition and complex structures. The analytical and elemental data (Cd, C, H and N) are presented in table 1, revealing that the two molecules of organic compounds with abstractable hydrogen are attached to metal, indicating a stoichiometry of 2:1. The complexes are proposed to have the general molecular formula $Cd(RH)_2$.

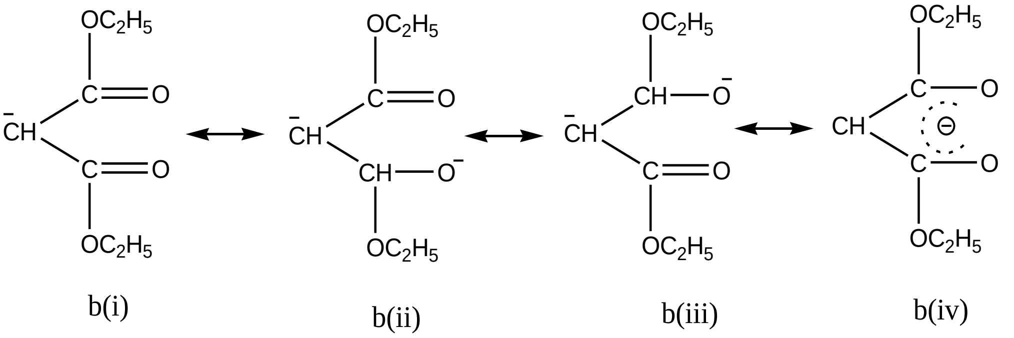
The spectral infrared (IR) data of all these synthesized complexes exhibit major vibrational bands in the region of 858-852 cm^{-1} and 467-460 cm^{-1}. A survey of literature reveals that ν(M-C) stretching bands typically appear in the range of 750-450 cm^{-1}.[1,2,12] Additionally, the literature reports the presence of the peak of ν(Cd-C) in the region of 520-450 cm^{-1}.[14,17] Thus, in the present products, only in the metal complexes of nitroethane and 2-nitropropane, broad bands at 467 cm^{-1} and 460 cm^{-1} correspond to ν(Cd-C) stretching vibrations. The appearance of the bands attributed to ν(Cd-C) suggests that these compounds may be organocadmium compounds. Moreover, these products exhibit hygroscopic properties and undergo decomposition in the presence of air like the organometallic compounds.

Thus, the combined assessment of physical characteristics and infrared spectral study of the present electrochemical products supports the characterization of these compounds as organocadmium compounds. In the literature, stretching vibrations due to ν(C-N) of nitro group in nitroalkanes are reported at 870 cm^{-1}. In our synthesized products, additional bands observed at 858 cm^{-1} and 852 cm^{-1} are attributed to ν(C-N) stretching vibrations[11].

In malononitrile and diethyl malonate, no bands are observed in the region of 520-450 cm^{-1}, signifying the absence of a ν(Cd-C) peak. This absence indicates that these products may not be organocadmium compounds. The lack of ν(Cd-C) absorption bands in infrared spectra of the electrochemical products suggests that these compounds might have formed through the resonance forms of the type a (iv) and b (iv).



Malononitrile (a)



Diethylmalonate (b)

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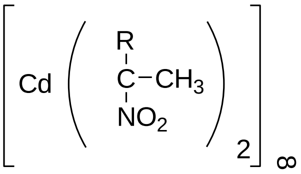
The infrared data of malononitrile and diethyl malonate revealed several vibrational bands. In malononitrile complex, a strong band appeared at 2178 cm^{-1}. Generally, $\nu(C\equiv N)$ stretching vibrations appear in the region of 2260-2240 cm^{-1} in alkyl nitriles[8,21,22]. The occurrence of $\nu(C\equiv N)$ vibrations in a significantly lower region and $\nu(C\overset{\cdots}{-}O)$ vibrations at 1462 cm^{-1} supports the conclusion that the electrochemical reaction product of malononitrile follows the resonance form a(iv). Thus, all the organic molecules (RH_2) yield cadmium (II) chelates that exhibit a polymeric nature, which is also supported by their insoluble behaviour, physical data and infrared data.

In the complex of diethylmalonate, the distinctive absorption bands appeared at 1574 cm^{-1}, 1456 cm^{-1}, 1070 cm^{-1}, 1030 cm^{-1}, 720 cm^{-1} and 400 cm^{-1}. Specifically, the bands at 1070 cm^{-1}, 1030 cm^{-1} and 1454 cm^{-1} are attributed to $\nu(C\text{-}O)Cd$ terminal, $\nu(C\text{-}O)Cd$ bridged and $\nu(C\overset{\cdots}{-}C)$ stretching vibrations respectively. Additionally, the bands at 720 cm^{-1} and 410 cm^{-1} correspond to ν (Cd-O) vibrations. The appearance of the characteristic band of the carbonyl group, $\nu(C\overset{\cdots}{-}O)$ at a sufficiently lower region around 1574 cm^{-1}, further supports the structure assignment of compounds through the resonance form b (iv).

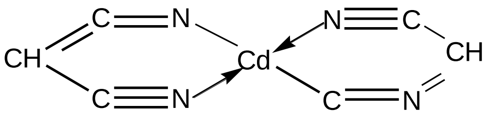
On the basis of above IR data, the plausible polymeric general formula may be:



$$\left[Cd\left(\begin{array}{c}R\\ |\\ C-CH_3\\ |\\ NO_2\end{array}\right)_2\right]_\infty$$

R = H in nitroethane and R= CH_3 in 2-nitropropane.

Structure of the malononitrile complex:



Current efficiencies of these systems have been meticulously determined and are presented in table 1. Upon perusal of the table 1, it becomes evident that the current efficiencies of all these systems are remarkably high, signifying that the reactions leading to the formation of these products are the predominant reactions with these systems. The reaction scheme may be outlined as follows. The organic compounds (RH_2) yield the carbanion on reduction at cathode:

$$2RH_2 + 2e^- \longrightarrow 2RH^- + H_2\uparrow$$

These carbanions migrate to the anode compartment under the influence of applied potential and react at the sacrificial cadmium anode, yielding cadmium (II) chelates:

$$2RH^- + Cd_{(+)} \longrightarrow Cd(RH)_2 + 2e^-$$

Microanalysis and IR data of coordination complexes of cadmium (II) chelates: The analytical and elemental analysis data encompassing Cd, C, H and N, presented in table 2, seek to identify the elemental composition of synthesized compounds. The results reveal a consistent 2:1:1 stoichiometry (representing organic compounds with abstractable hydrogen, metal and ligand) for the complexes, aligning with molecular formula $Cd(RH)_2.L$. This observation suggests the involvement of a single molecule of ligand in the complexation with the metal.

In the infrared spectra of complexes of nitroethane and 2-nitropropane with metal, the bands observed in the regions of 642-638 cm^{-1}, 423-410 cm^{-1} and 865-856 cm^{-1} in the present products can be assigned to ν(Cd–C) and ν(C-N) stretching vibrations respectively. These bands appear at the higher wavenumber than the parent cadmium (II) chelates indicating the attachment of ligand molecule with the metal. In the IR spectrum of complex of metal with diethyl malonate, the bands present at 720 cm^{-1} and 500 cm^{-1} correspond to ν(Cd-O) vibrations[10,13]. These bands are slightly broad and appear in a higher region compared to their parent compounds.

Distinct two or more bands appear in the region of 1120-980 cm^{-1}, indicating the presence of both terminal and bridged alkoxy groups in the products. The coordination of ligand results in the breaking of some alkoxy bridges, leading to the creation of terminal groups, while the presence of bridged alkoxy groups indicates the polymeric structure of these products. In the complex of metal with malononitrile, a strong band at 2180 cm^{-1} is due to ν ($C\equiv N$) vibrations. Additionally, the appearance of the bands at 1480 cm^{-1} and 1460 cm^{-1}, due to $\nu(C\overset{\cdots}{-}C)$ in the infrared spectra of malononitrile complex, supports the formation of these compounds through the resonance form of type a (iv).

The absorption bands at 1600 cm^{-1} and 1464-1460 cm^{-1} due to $\nu(C\overset{\cdots}{-}O)$ and $\nu(C\overset{\cdots}{-}C)$ respectively in the infrared spectra of the products of diethyl malonate support the formation of these compounds through the resonance form of type b (iv)[20]. In all these complexes, strong absorption bands within the region of 1538-1485 cm^{-1} are likely attributed to ν(C=C) and ν(C=N) stretching vibrations of the ligand molecules, thus confirming the attachment of ligand to the metal[5].

The presence of bands associated with the ligand molecules and observed shift of ν(Cd-O), bridged ν(C–O) Cd, terminal ν(C–O) Cd, ν(C=C), ν(C=N), $\nu(C\overset{\cdots}{-}O)$ and ν(C–N) bands towards higher wavenumbers collectively affirms the coordination of the ligand. The high melting point, insoluble behavior and the infrared data suggest that these coordination compounds may also exhibit a polymeric nature like the parent chelates. Current efficiencies for all these reactions are detailed in table 2 and they are quite high. These high current efficiencies for all systems provide the mechanism for preparation of coordination complexes

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involving organic compounds with abstractable hydrogen at sacrificial cadmium anode.

At cathode: $2RH_2 + 2e^- \longrightarrow 2RH^- + H_2\uparrow$

At anode: $2RH^- + L + Cd_{(+)} \longrightarrow Cd(RH)_2.L + 2e^-$

Conclusion

This study elucidates the facile accessibility of electrochemical methods for the one-step preparation of metal chelates, organometallic compounds and their coordination complexes, achieving high yields.

Table 1
Electrolysis characteristics, elemental analysis and other related data of electrolysis of organic compounds with abstractable hydrogen at cadmium anode

System	Potential Applied (Volts)	Product	Colour	Elemental analysis Found(Calculated)%				Current efficiency (gram equivalents per Faraday)
				Cd	C	H	N	
Nitroethane	35	$C_4H_8N_2O_4Cd$	White	43.10 (43.16)	18.38 (18.40)	3.05 (3.07)	10.70 (10.75)	0.89
2-Nitropropane	40	$C_6H_{12}N_2O_4Cd$	White	39.00 (38.97)	25.00 (24.96)	4.10 (4.16)	9.70 (9.71)	0.82
Malononitrile	30	$C_6H_2N_4Cd$	Light Brown	46.00 (46.36)	28.60 (29.70)	0.90 (0.83)	22.10 (23.10)	0.88
Diethylmalonate	30	$C_{14}H_{22}O_8Cd$	White	26.00 (26.10)	38.01 (39.03)	5.80 (5.11)	……	0.75

Table 2
Electrolysis characteristics, elemental analysis and other related data of electrolysis of organic compound with abstractable hyrdogen+ ligand systems at cadmium anode

System	Potential (Volts)	Product	Colour	Elemental analysis Found(Calculated)%				Current efficiency (gram equivalents per Faraday)
				Cd	C	H	N	
Nitroethane + 1,10-phenanthroline	30	$C_4H_8N_2O_4CdC_{12}H_8N_2$	Cream	25.00 (25.51)	43.60 (43.57)	3.60 (3.63)	12.35 (12.71)	0.92
2-Nitroopropane+ 1,10-phenanthroline	40	$C_6H_{12}N_2O_4CdC_{12}H_8N_2$	Cream	24.00 (23.98)	46.00 (46.09)	4.50 (4.27)	11.90 (11.95)	0. 80
Malononitrile+ 1,10-phenanthroline	30	$C_6H_2N_4CdC_{12}H_8N_2$	Dark Brown	26.50 (26.60)	50.00 (51.14)	2.19 (2.37)	18.17 (19.89)	0.85
Diethylmalonate+ 1,10-phenanthroline	30	$C_{14}H_{22}O_8CdC_{12}H_8N_2$	Dark Brown	18.43 (18.40)	52.00 (51.11)	4.30 (4.91)	4.70 (4.59)	0.75
Nitroethane+ 2,2’-bipyridyl	30	$C_4H_8N_2O_4CdC_{10}H_8N_2$	Cream	25.20 (26.98)	40.00 (40.33)	3.90 (3.84)	12.44 (13.44)	0.90
2-Nitropropane+ 2,2’-bipyridyl	35	$C_6H_{12}N_2O_4CdC_{10}H_8N_2$	Cream	24.28 (25.28)	44.01 (43.18)	4.50 (4.49)	13.00 (12.59)	0.86
Malononitrile+ 2,2’-bipyridyl	35	$C_6H_2N_4CdC_{10}H_8N_2$	Light Brown	28.00 (28.20)	47.50 (48.19)	2.19 (2.51)	19.02 (21.08)	0.80
Diethylmalonate+ 2,2’-bipyridyl	30	$C_{14}H_{22}O_8CdC_{10}H_8N_2$	Light Brown	20.00 (19.20)	46.70 (49.11)	4.48 (5.12)	5.20 (4.77)	0.77

The electrochemical approach demonstrated here offers an efficient mean to synthesize compounds that are often challenging to produce using traditional methods. The dynamic characteristics observed in the synthesized compounds with their prospective applications, underscore the versatility of electrochemical techniques in the field of synthetic chemistry.

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