

Electrochemical Reactions at Sacrificial Electrode: Direct Electrochemical Synthesis of Cadmium(II) Thiolates and their Coordination Compounds

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Abstract: The electrochemical synthesis of sulphur containing compounds derived from thiols (Ethanethiol, 2-propanethiol, 1-butanethiol, 2-methyl-2-propanethiol, 1-pentanethiol and thiophenol) at sacrificial cadmium anode and inert platinum cathode is reported. Adducts of these compounds with 1,10 phenanthroline and 2,2'-bipyridyl (L) have also been obtained by addition of these coligands to the electrolysis phase. These compounds have been characterized by microanalysis, physical measurements and IR spectral studies. General formula conforms to $Cd(SR)_2$ and $Cd(SR)_2 \cdot L$. Current efficiencies of all these reactions are quite high.

Keywords: Electrochemical reactions, Sacrificial electrode, Cadmium(II) thiolates

Introduction

Electrochemical technique has become an attractive technique for the preparative chemists because it covers a broad spectrum of applications in organic¹⁻² and inorganic³ synthesis. Direct electrochemical synthesis has many applications to prepare 1-dimensional semiconductors, nanostructures⁴ and biosensor designing⁵. Electrochemical synthesis of transition metal sulphur complexes has been the subject of interest for their importance in the fields of metalloenzymes, material precursors and catalysts⁶.

In continuation of our interest in electrochemical synthesis of inorganic compounds⁷⁻⁹, synthesis of cadmium(II) alkoxides were reported recently from our laboratory¹⁰. The present paper reports the electrochemical synthesis of cadmium(II) thiolates and their coordination compounds with ligand 1,10-phenanthroline and 2,2'-bipyridyl. In electrochemical reactions of thiol at cadmium anode, metal thiolates is formed as a result of replacement of a proton of thiol molecule with the anodic metal. This technique is simple, high yielding, efficient, one step and as being environmentally favorable¹¹⁻¹².

Experimental

Acetonitrile was kept over phosphorus pentoxide for 24 hours and then double distilled. Freshly distilled acetonitrile was used as a solvent. Tetrabutyl ammonium chloride was

crystallized from conductivity water and dried under reduced pressure at 100 °C. Electrolysis of the solution of 3 mL of thiol (RSH) in acetonitrile (250 mL) containing tetrabutyl ammonium chloride (1.0 g) was carried out in *H*-type cell. Cadmium rod (2x10x0.2 cm³) was dipped in anode compartment and platinum foil (1.0x1.0 cm²) in cathode compartment. Outlets were sealed after fitting the guard tubes. Necessary connections were made with Toshniwal electrophoresis power supply and potential across the electrodes was then adjusted so that a current of 20 mA passed through the solution. The electrolytic solution was stirred efficiently using magnetic stirrer. The cell can be represented as:



Where Cd₍₊₎ is cadmium anode, Pt₍₋₎ is platinum cathode, Bu₄NCL is tetrabutyl ammonium chloride (supporting electrolyte) and RSH is thiol used in the systems. Electrolysis was conducted for 10 hours at a constant current of 20 mA. Solid product separated in the anode compartment was filtered and washed with hot acetonitrile, dry ether and then dried under vacuum. All efforts were done to protect the products from air and moisture.

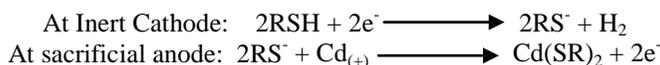
In order to synthesize the coordination compounds of these products, 1.0 g of ligand (1,10-phenanthroline or 2,2'-bipyridyl) was also added in addition to the above substrates before starting the electrolysis. The other details are same as discussed above.

Melting point of all these compounds was determined using electrical device with a heating rate of 5 °C per minute. Cadmium contents in these compounds were determined using oxine method¹³. Carbon, hydrogen, sulphur and nitrogen (where applicable) contents in the products were determined through 'Elementor vario EL' CHNS elemental analyzer.

Infra red spectra of the products have been recorded on Perkin- Elmer spectrophotometer (FTIR) in the region of 4000-400 cm⁻¹ using KBr pallets. The current efficiencies¹⁴ (gram equivalents of metal dissolved per faraday of electricity passed) of all these reactions were determined using Faraday's first law of electrolysis by electrolyzing the above systems for exactly two hours at a constant current of 20 mA.

Results and Discussion

Electrochemical reactions of thiols at sacrificial cadmium anode and inert platinum cathode yield cadmium(II) thiolates. The mechanism of the reaction is given below:

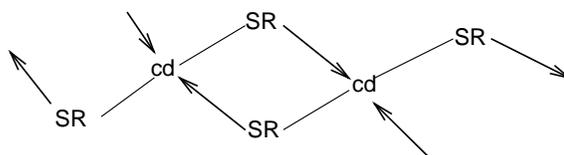


The cadmium contents (determined by oxine method) in these compounds correspond to general formula Cd(SR)₂. Melting point of all these products have been observed. It has been observed that these products don't melt upto 300 °C but decompose at a temperature of about 200- 250 °C. The decomposition of products is indicated from the change in colour of these compounds. Solubility of all these compounds has been determined in various commonly used organic solvents like chloroform, carbon tetrachloride, benzene, *N,N'*-dimethyl formamide, methanol, acetone and pyridine. All these compounds are insoluble in these solvents. The analytical data (Cadmium, carbon, hydrogen and sulphur contents in all the products) conforms to molecular formula Cd(SR)₂. All the relevant data are summarized in Table 1.

Table 1. Electrolysis characteristics, analytical and other related data of electrolytic products of thiols at cadmium anode (Potential: 50 V, current in coulombs: 720)

System	Product	Colour	Elemental analysis%					Current efficiency/ (gram equivalent/ Faraday)
			found	(calculated)	Cd	C	H	
Ethanethiol	Cd(SC ₂ H ₅) ₂	white	47.0 (47.9)	20.0 (20.4)	4.0 (4.3)	27.0 (27.3)	---	0.96
2-Propanethiol	Cd(SC ₃ H ₇) ₂	white	42.2 (42.8)	27.0 (27.4)	5.1 (5.3)	24.0 (24.4)	---	0.95
1-Butanethiol	Cd(SC ₄ H ₉) ₂	white	38.1 (38.7)	32.7 (33.0)	5.8 (6.2)	21.8 (22.0)	---	0.90
2-Methyl-2-propanethiol	Cd(SC ₄ H ₉) ₂	white	38.4 (38.7)	32.3 (33.0)	5.6 (6.2)	21.4 (22.0)	---	0.95
1-Pentanethiol	Cd(SC ₅ H ₁₁) ₂	white	35.0 (35.3)	37.1 (37.7)	6.4 (6.9)	20.0 (20.1)	---	0.92
Thiophenol	Cd(SC ₆ H ₅) ₂	white	33.8 (34.0)	43.2 (43.6)	3.0 (3.0)	19.2 (19.4)	---	0.90
Ethanethiol+1,10-phenanthroline	Cd(SC ₂ H ₅) ₂ C ₁₂ H ₈ N ₂	Dirty white	27.0 (27.1)	46.0 (46.3)	4.4 (4.3)	15.2 (15.4)	6.5 (6.7)	0.90
2-Propanethiol+1,10-phenanthroline	Cd(SC ₃ H ₇) ₂ C ₁₂ H ₈ N ₂	Dirty white	25.1 (25.4)	48.5 (48.8)	4.8 (4.9)	14.2 (14.4)	6.0 (6.3)	0.92
1-Butanethiol+1,10-phenanthroline	Cd(SC ₄ H ₉) ₂ C ₁₂ H ₈ N ₂	Dirty white	23.2 (23.8)	50.0 (50.9)	5.4 (5.5)	13.2 (13.6)	5.5 (5.9)	0.82
2-Methyl-2-propanethiol+1,10-phenanthroline	Cd(SC ₄ H ₉) ₂ C ¹² H ₈ N ₂	Dirty white	23.2 (23.8)	50.6 (50.9)	5.4 (5.5)	13.4 (13.6)	5.6 (5.9)	0.85
1-Pentanethiol+1,10-phenanthroline	Cd(SC ₅ H ₁₁) ₂ C ₁₂ H ₈ N ₂	Dirty white	22.2 (22.5)	52.8 (52.9)	6.0 (6.0)	12.4 (12.8)	5.4 (5.6)	0.87
Thiophenol+1,10-phenanthroline	Cd(SC ₆ H ₅) ₂ C ₁₂ H ₈ N ₂	Dirty white	22.0 (22.0)	56.2 (56.4)	3.5 (3.5)	12.4 (12.5)	5.6 (5.5)	0.83
Ethanethiol+ 2,2'-bipyridyl	Cd(SC ₂ H ₅) ₂ C ₁₀ H ₈ N ₂	white	7.3 (28.7)	42.9 (43.1)	4.3 (4.6)	16.1 (16.4)	7.0 (7.2)	0.85
2-propanethiol+ 2,2'-bipyridyl	Cd(SC ₃ H ₇) ₂ C ₁₀ H ₈ N ₂	white	26.3 (26.8)	45.1 (45.8)	4.9 (5.2)	15.0 (15.3)	6.2 (6.6)	0.82
1-Butanethiol+ 2,2'-bipyridyl	Cd(SC ₄ H ₉) ₂ C ₁₀ H ₈ N ₂	white	25.1 (25.2)	48.0 (48.3)	5.1 (5.8)	14.0 (14.3)	6.0 (6.3)	0.85
2-Methyl-2-propanethiol+ 2,2'-bipyridyl	Cd(SC ₄ H ₉) ₂ C ₁₀ H ₈ N ₂	white	25.0 (25.2)	48.1 (48.3)	5.5 (5.8)	14.1 (14.3)	6.0 (6.3)	0.90
1-Pentanethiol+ 2,2'-bipyridyl	Cd(SC ₅ H ₁₁) ₂ C ₁₀ H ₈ N ₂	white	23.0 (23.7)	50.1 (50.5)	6.1 (6.3)	13.2 (13.5)	5.5 (5.9)	0.92
Thiophenol+ 2,2'-bipyridyl	Cd(SC ₆ H ₅) ₂ C ₁₀ H ₈ N ₂	white	23.0 (23.1)	54.0 (54.2)	3.4 (3.7)	13.2 (13.1)	5.6 (5.7)	0.88

Infrared spectra of these products reveal¹⁵ that there is no absorption bands corresponding to thiol group *i.e.* in the region of 2600-2499 cm^{-1} which shows that the product is completely free from thiol and proton of thiol has been replaced by cadmium. Characteristic bands appeared in the region of 614-420 cm^{-1} and 1180-967 cm^{-1} . Survey of literature reveals¹⁶⁻¹⁹ that $\nu(\text{M-S})$ and $\nu(\text{C-S})$ M stretching vibrations appear in the region of 600-400 cm^{-1} and 1160-950 cm^{-1} . Thus in the present products, bands appeared in the region of 614-420 cm^{-1} and 1180-967 cm^{-1} may be assigned to $\nu(\text{Cd-S})$ and $\nu(\text{C-S})\text{Cd}$ stretching vibrations respectively. Review of literature also reveals¹⁶⁻¹⁹ that the absorption bands due to $\nu(\text{C-S})\text{M}$ stretching vibrations in the region of 1160-950 cm^{-1} in various metal thiolates exist as bridged and terminal SR groups, an analogy to transition metal alkoxides¹⁰ that exist as polymers.. The plausible structure of these metal thiolates is given below:



Infrared spectra of the present electrochemical products show appearance of two/ three broad bands in the region of 1040-967 cm^{-1} can be attributed to bridged SR groups thereby showing their polymeric nature which is also supported by high melting point and insoluble nature of these compounds in various solvents. Infrared spectra of these compounds also reveals¹⁶⁻¹⁹ that the bands appeared due to bridged thiolates groups are strong as compared to terminal $\nu(\text{C-S})\text{Cd}$ stretching vibrations (in the region of 1180-1040 cm^{-1}). As the size of the alkyl group in thiol increases the relative intensity of the bands due to bridged thiolate groups decreases, indicating that degree of polymerization decreases. In case of thiophenol cadmium complex additional band around 1600 cm^{-1} is also observed due to $\nu(\text{C}=\text{C})$ aromatic ring vibrations²⁰.

Thus, analytical and IR data show that cadmium(II) thiolates conforming to general formula, $\text{Cd}(\text{SR})_2$, have been synthesized electrochemically. The cadmium(II) thiolates prepared have been refluxed with 1,10-phenanthroline and 2,2'-bipyridyl separately in solvents like methanol ethanol, benzene and acetonitrile for 48 hours in order to prepare coordination compounds of these thiolates. However, analytical and infrared spectral data of these products show that the ligand molecule could not rupture the sulphur bridges in these cadmium(II) thiolates to form their coordination compounds. It may be due to the reason that the metal in these thiolates has already achieved the favorable coordination number through sulphur bridging, therefore further expansion of coordination sphere due to addition of ligand could not be achieved. It was, therefore, thought that the ligand may be added to these thiolates before these form sulphur bridges and get polymerized. Therefore in addition to thiol (RSH) and supporting electrolyte, 1.0 g of ligand was also added to these systems and then solution was electrolyzed at cadmium anode and inert platinum cathode for 10 hours.

The analytical data (cadmium, carbon, hydrogen, sulphur and nitrogen contents in all the products) conform to general molecular formula, $\text{Cd}(\text{SR})_2 \cdot \text{L}$. All the relevant data are summarized in Table 1.

Infrared spectra of these coordination compounds show $\nu(\text{C-S})\text{Cd}$ and $\nu(\text{Cd-S})$ modes like their parent thiolates in the respective regions with only difference that these bands appear slightly in the higher region (+10 to 20 cm^{-1}). Moreover $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ modes due to ligand molecules²⁰ are also present in the adduct around 1600-1590 cm^{-1} , which otherwise

are absent in the parent thiolates, thereby confirming that the ligand molecule has been added. These coordination compounds are also insoluble in commonly used organic solvents like their parent metal thiolates and do not melt up to 300 °C indicating their polymeric nature.

Current efficiencies of all these systems have also been determined and are quite high (in the range of 0.82 to 0.96 gram equivalents per Faraday) thereby showing that the reaction leading to the formation of cadmium(II) thiolates and their coordination compounds are the predominant reactions of these systems.

Conclusion

This electrochemical procedure associated with high current efficiency and is simple, direct and one pot method that allows the synthesis of cadmium(II) thiolates and their coordination complexes in one step and offers a versatile approach for the commercial preparation of these compounds.

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