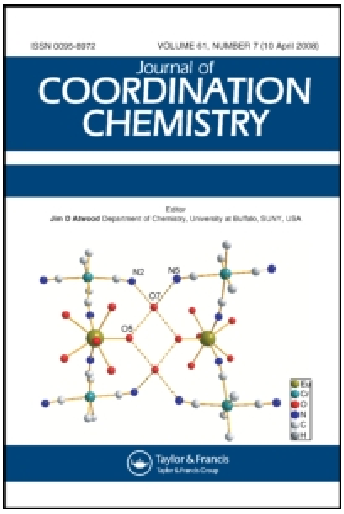

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Electrochemical synthesis and study of coordination compounds part 1: tin(II) catechol complexes

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Electrochemical synthesis and study of coordination compounds part 1: tin(II) catechol complexes

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The electrochemical synthesis of tin(II) complexes of catechols, Sn(O_2Ar) (**1a**–**9a**), have carried out using tin metal as a sacrificial anode in acetonitrile, in the presence of catechol derivatives. The cyclic voltammetric characteristics of the synthesized complexes Sn(O_2Ar) (**1a**–**9a**) have been studied at glassy carbon electrode in dichloromethane. Anodic oxidation of Sn(O_2Ar) produces a single wave which shows irreversibility. Also, the electronic effects of ligands on the redox potential of complexes **1a**–**9a** have been investigated. The synthesis of Sn(O_2Ar) species in high yields and purity has been successfully performed in an undivided cell using constant current conditions.

Keywords: Electrochemical synthesis; Sacrificial tin anode; Tin(II) catechol complex; Constant current electrolysis

1. Introduction

There is interest in the synthesis of coordination compounds by reactions with pure metals; electrochemical dissolution of sacrificial metal anodes is an attractive procedure for the preparation of a large variety of complexes. The method, which is both rapid and selective, provides pathways to new compounds. For some compounds, electrosynthesis is simpler than conventional syntheses. The diversity of products synthesized suggests that electrosynthesis using a dissolving electrode has advantages for the preparative chemist [1–8]. Metals such as thorium [9], tin [10, 11], Zn [12], Pb [13], Co, Ni and Cu [14] have been used for electrosynthesis. Catechol and its derivatives constitute an interesting class of bidentate ligands that can undergo one- or two-electron oxidations to the *o*-semiquinone or *o*-quinone [15–18], respectively, offering the possibility of preparing complexes with unusual oxidation states [11, 19]. By extension of previous work on synthesis of metal diolates [11, 19–25], we have now synthesized tin(II) complexes of substituted catechols (**1a**–**9a**). These compounds can be easily prepared electrochemically. The electrochemical oxidation of the synthesized

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complexes $Sn(O_2Ar)$ (**1a–9a**) has been studied at glassy carbon electrode in dichloromethane using cyclic voltammetry. Anodic oxidation of $Sn(O_2Ar)$ produces a single wave which shows irreversibility. Furthermore, the electronic effects of ligands on the redox potential of **1a–9a** have been investigated.

2. Experimental

2.1. *Apparatus and reagents*

Cyclic voltammetry was performed using an Autolab model PGSTAT 20 potentiostat/galvanostat. The working electrode used in the voltammetry experiment was a glassy carbon disc (1.8 mm diameter) and a platinum wire was used as counter electrode. The working electrode potentials were measured *versus* ferrocenium/ferrocene, Fc^+/Fc (all electrodes from AZAR electrode). A tin metal rod was used as anode in macroscale electrolysis and stainless steel gauze constituted the cathode. Preparative electrolysis was performed in constant current conditions using an Iran Electronic Industries 8303 DC power supply. Tin analysis was performed by using ICP-OES Integra XL, GBC instrument. ^1H NMR spectra were recorded on a JEOL NMR FX 90Q spectrometer. Infrared spectroscopy involved the use of samples as KBr discs with a Perkin Elmer instrument. All chemicals (catechols, tetrabutylammonium perchloride, acetonitrile, diethylether and dichloromethane) were reagent-grade materials from Aldrich; tin metal was 99.99% pure from E. Merck. All chemicals were used without further purification.

2.2. *Electrochemical synthesis of (1a)–(9a)*

A solution (ca 30 mL) of catechol (**1–9**) (0.50 mmol) and tetrabutylammonium perchlorate (60 mg) as supporting electrolyte was electrolyzed in an undivided cell equipped with a tin-anode (4 mm diameter and 3 cm length) and stainless steel gauze cathode at 25°C under constant current of 30 mA in 54 min. As the electrolysis proceeded, hydrogen gas evolved at the cathode, and a solid formed at the anode; this material gradually deposited in the cell, and at the end of the experiment was collected by filtration, washed with acetonitrile and then diethylether, and dried *in vacuo*. Other details are given in tables 1 and 2.

3. Results and discussion

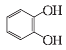
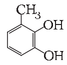
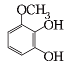
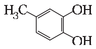
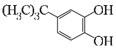
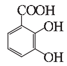
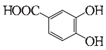
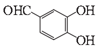
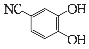
The electrochemical oxidation of tin metal, as a sacrificial anode, in the presence of the catechol derivatives in acetonitrile, led to complexes of general formula $Sn(O_2Ar)$ (**1a–9a**) where ArO_2^{2-} is the basic dianionic form of the catechol derivatives. The value of the electrochemical efficiency, E_f (defined as the number of moles of metal dissolved per Faraday of charge), close to $0.50\,mol\,F^{-1}$, and the liberation of hydrogen at the cathode are in accord with the following process (scheme 1).

$$\text{Anode:}\quad Sn - 2e \longrightarrow Sn^{2+}$$

$$\text{Cathode:}\quad Ar(OH)_2 + 2e \longrightarrow ArO^{2-}$$

$$\text{Complexation:}\quad Sn^{2+} + ArO^{2-} \longrightarrow Sn(O_2Ar)$$

Table 1. Experimental and analytical results of synthesized complexes.[a]

				Sn (%)		C (%)		H (%)	
Catechol	Compound	Color	Yield[b] (%)	Found	Calcd	Found	Calcd	Found	Calcd
	$Sn(C_6H_4O_2)$ (**1a**)	White	84	52.32	52.34	31.77	31.35	1.78	1.96
	$Sn(C_7H_6O_2)$ (**2a**)	White	85	49.30	49.29	34.91	34.55	2.51	2.53
	$Sn(C_7H_6O_3)$ (**3a**)	White	92	46.30	46.22	32.74	32.33	2.35	2.42
	$Sn(C_7H_6O_2)$ (**4a**)	White	93	49.20	46.29	34.91	34.49	2.51	2.38
	$Sn(C_{10}H_{12}O_2)$ (**5a**)	White	86	41.90	41.96	–	–	–	–
	$Sn(C_7H_4O_4)$ (**6a**)	White	99	43.80	43.83	31.05	30.68	1.49	1.65
	$Sn(C_7H_4O_4)$ (**7a**)	White	99	43.80	43.83	31.05	30.51	1.49	1.74
	$Sn(C_7H_4O_3)$ (**8a**)	Bright-green	99	46.50	46.59	32.99	32.61	1.58	1.89
	$Sn(C_7H_3NO_2)$ (**9a**)	Bright-yellow	78	47.10	47.14	–	–	–	–

[a] All compounds are stable to atmospheric exposure, to heat, and to hydrolysis; they do not melt below ca 300°C, and they are insoluble in common organic solvents.

[b] Based on metal dissolved.

Table 2. ^1H NMR, ^{13}C NMR and FT-IR data for **1a**–**9a**.

Compound	^1H NMR (DMSO-d$_6$)	^{13}C NMR (DMSO-d$_6$)	FT-IR (KBr)
$Sn(C_6H_4O_2)$ (**1a**)	6.53 (m, aromatic)	114.5, 116.1, 155.8	1581, 1479, 1255, 1188, 1105
$Sn(C_7H_6O_2)$ (**2a**)	6.31 (m, 3H, aromatic) 2.21 (s, 3H, methyl)	13.5, 113.6,115.7, 116.5, 124.5, 153.0, 155.3	1575, 1465, 1261, 1196, 1021
$Sn(C_7H_6O_3)$ (**3a**)	6.29 (m, 3H, aromatic) 3.70 (s, 3H, methoxy)	55.8, 102.7, 107.6, 109.4, 115.3, 148.5, 156.5	1586, 1469, 1291, 1246, 1091
$Sn(C_7H_6O_2)$ (**4a**)	6.40 (m, 2H, aromatic) 6.20 (m, 1H, aromatic) 2.10 (s, 3H, methyl)	16.5, 112.5, 115.3, 117.7, 122.4, 154.0, 155.2	1596, 1494, 1413, 1261, 1119
$Sn(C_{10}H_{12}O_2)$ (**5a**)	6.60 (m, 2H, aromatic) 6.40 (m, 1H, aromatic) 1.19 (s, 9H, tert-butyl)	31.7, 33.4, 110.8, 112.3, 113.5, 139.1, 147.7, 149.3	2959, 1490, 1241, 1125, 801
$Sn(C_7H_6O_4)$ (**6a**)	14.20 (s, 1H, carboxylic) 6.9–6.6 (m, 3H, aromatic)		3207, 1589, 1500, 1395, 1254
$Sn(C_7H_6O_4)$ (**7a**)	9.50 (d, 1H, carboxylic) 6.95 (q, 2H, aromatic) 6.58 (d, 1H, aromatic)	113.6, 115.0, 119.2, 120.0, 151.6, 157.9, 161.3	3224, 1568, 1494, 1428, 1268
$Sn(C_7H_6O_3)$ (**8a**)	6.44 (m, 1H, aromatic) 7.00 (d, 1H, aromatic) 7.10 (s, 1H, aromatic)	112.5, 114.2, 125.7, 126.3, 152.5, 160.4, 190.3	1659, 1486, 1437, 1271, 1116
$Sn(C_7H_5NO_2)$ (**9a**)	6.73 (q, 2H, aromatic) 6.50 (s, 1H, aromatic)		2217, 1587, 1486, 1264, 1117

The products were characterized analytically, and by IR and NMR spectroscopy (table 2). The physical properties of $Sn(O_2C_6H_4)$ prepared electrochemically are identical with those reported by Tuck [11] and Zuckerman [20] and similar to other $Sn(O_2Ar)$ compounds obtained in this work. The analytical measurements confirm that the ligand:metal formed in 1:1 ratio (table 1).

3.1. *Spectroscopic properties*

The FT-IR spectra of tin(II) complex (**1a**) between catechol (**1**) and electrochemically generated tin(II) are shown in figure 1. In comparison with the FT-IR spectrum of **1** (curve a), the bands at 3448 and 3322 cm^{-1} attributable to stretching frequency of –OH groups have disappeared (curve b), as a result of deprotonation of hydroxyl groups. Similar results were obtained in the case of the other tin(II) complexes (**2a**–**9a**). The FT-IR data for **1a**–**9a** are given in table 2.

The ^1H NMR studies also verify complex formation between catechols (**1**–**9**) and tin(II). The spectrum of **1a** (run in DMSO-d6) does not display any resonance assigned to the –OH protons (figure 2) (which in the free catechol, appear as a singlet at δ 8.80. The peak positions of other protons reveal small shifts. These observations suggest the basic dianionic form of the catechol ($C_6H_4O_2^{2-}$). Similar results were obtained in the case of the other tin(II) complexes (**2a**–**9a**). Thus, both IR and NMR data indicate synthesis of **1a**–**9a** with participation of two deprotonated hydroxyl groups. The ^{1}HNMR data for **1a**–**9a** are given in table 2.

3.2. *Electrochemical investigation*

$Sn(O_2Ar)$ complexes in dichloromethane (CH_2Cl_2) containing 0.1 M tetrabutylammonium perchlorate, as a supporting electrolyte, and pyridine (1% v/v) as a co-solvent, exhibit a single irreversible oxidation peak (A_1) (figure 3). The peak potential for this peak varied as a function of the catechol. Furthermore, E_p shifted anodically by increase in scan rate (figure 3). Also, as expected for an irreversible process, the oxidation peak remained irreversible at various temperatures as well as at all potential scan rates. Diagnostic criteria of cyclic voltammetry, and the previous reports on electrochemical oxidation of Sn(II) complexes [25–27], indicate that the overall electrooxidation reaction of $Sn(O_2Ar)$ is the generation of Sn(IV) complex (scheme 2).

$$[Sn^{II}(O_2Ar)]^0 \xrightarrow{-2e^-} [Sn^{IV}(O_2Ar)]^{2+}$$

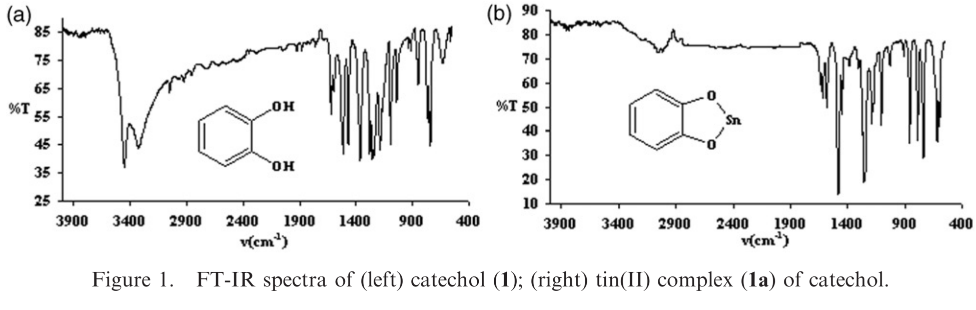


Figure 1. FT-IR spectra of (left) catechol (**1**); (right) tin(II) complex (**1a**) of catechol.

The electronic effects of the ligands on the redox potentials of complexes **1a**–**9a** have been investigated. As shown in figure 4, the peak potential (E_{pA1}) is dependent on the nature of the substituted group on the catechol ring. The presence of electron-donating groups such as *tert*-butyl or methyl on catechol causes a decrease in E_{pA1}. In contrast,

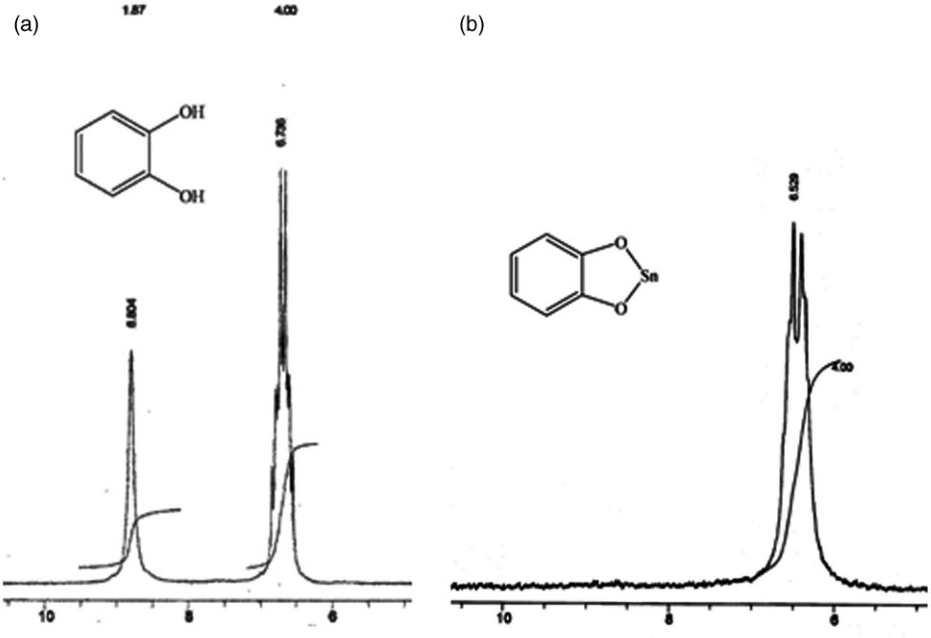


Figure 2. ^{1}H NMR spectra of (left) catechol (**1**); (right) tin(II) complex (**1a**) of catechol.

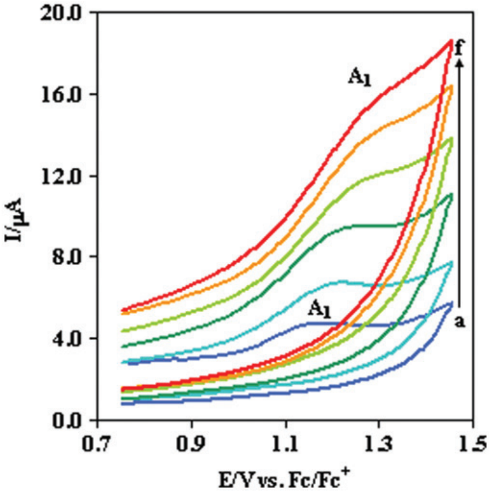


Figure 3. Typical voltammograms of saturated tin(II) complex of catechol, Sn($C_6H_4O_2$), (**1a**) in dichloromethane containing 0.1 M tetrabutylammonium perchlorate, as a supporting electrolyte and pyridine (1% v/v) as a co-solvent at a glassy carbon electrode (1.8 mm diameter) and at various scan rates. Scan rates from (a) to (f) are: 10, 15, 20, 30, 35 and 40 mV s^{-1}.

the presence of –CN, –CHO or –COOH groups with electron-withdrawing character causes an increase in E_{pA1}. In other words, electron-donating groups render oxidation easier and electron-withdrawing groups render oxidation more difficult. To correlate the variations of the redox potential of metal complexes **1a–9a** (E_{pA1}) with the electronic effects played by the substituents of catechol ring, we used the Hammett equation. The electrochemical form of the Hammett equation is [28]:

$$\Delta E^{0'} = \rho \cdot \sigma$$

where $\Delta E^{0'}$ is the difference between the redox potential of the complex containing the substituted catechol and that of the complex containing catechol, σ is Hammett parameter which assigns a numerical value to the electronic effects of the substituents [29] and ρ is constant which measures the sensitivity of the redox potential to the electronic effects of the substituents. As shown in figure 5, there is a good linear relationship between the redox potential and electronic effects of the substituents.

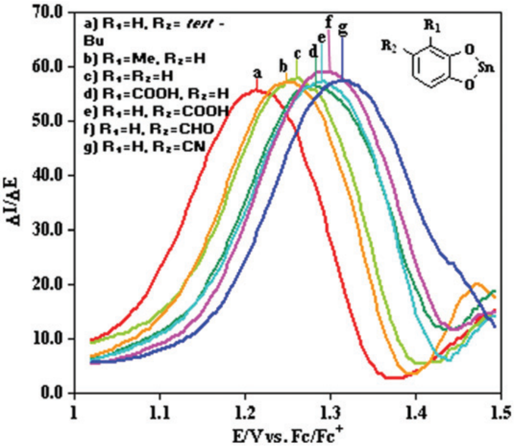


Figure 4. The first derivative, ΔI/ΔE, of linear sweep voltammogram of saturated tin(II) complex of catechols, in dichloromethane containing 0.1 M tetrabutylammonium perchlorate, as a supporting electrolyte and pyridine (1% v/v) as a co-solvent at a glassy carbon electrode (1.8 mm diameter). Scan rate: 25 mV s^{-1}.

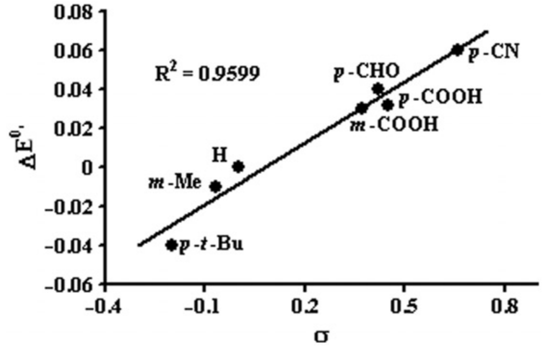


Figure 5. Hammett plot for electrochemical oxidation of tin(II) complex of catechols, $Sn(O_2Ar)$, (**1a–9a**).

4. Conclusions

This work shows that direct electrosynthesis is an efficient method to synthesize inorganic compounds. Also, this method has high atom economy with high yield and purity during short electrolysis. In addition, the effects of the substituted groups on the redox potential of the complex (Hammett plot) have been studied. And finally, although the experiments were conducted on a relatively small scale, there is little difficulty in producing larger quantities either by using larger cells or by running several cells in series.

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