

# The Direct Electrochemical Synthesis of Ti(II), Fe(II), Cd(II), Sn(II), and Pb(II) Complexes with N, N'-Bis(Salicylidene)-o-Phenylenediamine

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The electrochemical oxidation of anodic Ti, Fe, Cd, Sn, and Pb (=M) into acetonitrile solutions of N,N'-bis(salicylidene)-o-phenylenediamine [SalophH<sub>2</sub>] gives the corresponding M(Saloph) complexes in high yield. The mechanism of the electrochemical reactions is discussed. SalophH<sub>2</sub> forms complexes (1:1 molar ratio) with titanium, iron, cadmium, tin, and lead ions. The complexes have been characterized by elemental analyses, molar conductivity measurements, and infrared and electronic spectral data. The SalophH<sub>2</sub> complexes of iron(II) and cadmium(II) have been further identified by <sup>1</sup>H-NMR and mass spectra.

**Key Words:** Electrochemical Synthesis, N, N'-Bis(Salicylidene)-o-Phenylenediamine, metal complex.

## Introduction

A good deal of work has been reported on the synthesis and structural investigation of different types of Schiff bases and their complexes. Schiff bases and their metal complexes have exhibited biological activity as antibiotic, antiviral, and antitumor agents because of their specific structures. Tetradentate Schiff bases with a N<sub>2</sub>O<sub>2</sub> donor atom set are known to coordinate with various metal ions, and this has attracted many researchers.<sup>1-6</sup> Complexes of Schiff base ligands have been studied for their dioxygen uptake<sup>7</sup> and oxidative catalysis.<sup>8</sup> Moreover, complexes of transition metals(II), which involve derivatives of salicylaldehyde and diamine, have received considerable attention because of their potential as catalysts for the insertion of oxygen into an organic substrate.<sup>9-12</sup> The synthesis of metal complexes with the electrochemical method was introduced in 1982 by Dennis G. Tuck.<sup>13</sup> The direct electrochemical synthesis of metal complexes has been the subject of interest in recent years.<sup>14-21</sup> In the application of this technique, which involves the anodic oxidation of a metal in a non-aqueous solution of the ligand precursor, the most important advantages are the

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simplicity of the technique and high product yield. We have now extended the application of the method of direct electrochemical synthesis to the preparation of the SalophH<sub>2</sub> complexes of titanium, iron, cadmium, tin, and lead. These species are formed firstly in high yield in a one-step route by the electrochemical oxidation of the metal into an acetonitrile solution of SalophH<sub>2</sub>. The complexes have been characterized by elemental analyses, molar conductivity measurements, and infrared and electronic spectral data. SalophH<sub>2</sub> complexes of iron(II) and cadmium(II) have been further identified by <sup>1</sup>H-NMR and mass spectra.

## Experimental

All reagents used were chemically pure or analytical reagent grade. Acetonitrile was distilled from calcium hydride. C, H, and N analyses data were obtained using a Perkin-Elmer 240B elemental analysis instrument. Titanium, iron, cadmium, tin, and lead were measured by EDTA titration. All conductivity measurements were performed in absolute dimethylformamide (DMF) using a Shanghai DDS-11A conductivity apparatus at 25 °C the concentration of the solution was 10<sup>-3</sup> mol L<sup>-1</sup>. Melting points were obtained using a Beijing X<sub>4</sub> microscopic melting point apparatus. Infrared spectra were measured in KBr pellets on a Shimadzu FTIR-8400 spectrophotometer in the range 200-4000 cm<sup>-1</sup>. Electronic spectra from 200 to 800 nm were obtained in ethanol on a Perkin-Elmer Lambda 7 spectrophotometer. <sup>1</sup>H-NMR spectra of the SalophH<sub>2</sub> complexes of iron(II) and cadmium(II) were recorded in deuterated dimethylsulfoxide using a Varian XL-200 NMR spectrometer with TMS as the internal standard, whereas the mass spectra of these complexes were obtained using a VG-707 E mass spectrometer; the electron impact excitation was 70 eV.

### Preparation of the N, N'-bis(Salicylidene)-o-phenylenediamine [SalophH<sub>2</sub>]

A solution of 0.1 mol o-phenylenediamine (dissolved in 50 mL of ethanol) was slowly added to a solution of 0.2 mol of salicylaldehyde in 50 mL ethanol. After the reaction mixture was stirred for 2 h at 40-50 °C the precipitate was cooled and collected by filtration. The precipitate was purified by washing with distilled water several times, and was then washed with ethanol, followed by recrystallization in ethanol and drying at 50 °C overnight.

### Preparation of the Complexes

The electrochemical preparation essentially followed the same procedure in each case, using a cell of the form:



Details of solution composition, etc. are given in Table 1. The cell was a 100 mL tall-form beaker filled with a rubber stopper through which the electrodes were suspended. The anode was a piece of metal, approximately 2 cm<sup>2</sup>, suspended on a platinum wire. As the experiment proceeded, hydrogen was evolved at the cathode and the solution became yellow. The solid precipitated continuously throughout the electrolysis, and was subsequently collected, washed several times with acetonitrile and petroleum ether, and dried.

## Results and Discussion

The results show that complexes of titanium, iron, cadmium, tin, and lead are readily prepared by the direct electrochemical oxidation of the metal into solutions of SalophH<sub>2</sub>, with chemical yields in the 85%-95% range, based on the quantity of metal dissolved. The complexes are air-stable, non-hygroscopic colored solids, are insoluble in water, partly soluble in ethanol and methanol, and soluble in DMSO and DMF. Decomposition occurs with concentrated nitric acid and the resultant solution was used after suitable dilution for metal analysis. The elemental analysis data (Table 2) are consistent with the calculated results from the empirical formula of each compound. The results of molar conductivity measurements (Table 2) suggest that all compounds are non-electrolytes in dimethylformamide.<sup>22</sup> Because all compounds are dissociated partially in the solution, the solution has conductivity.

**Table 1.** Experimental conditions for the direct electrochemical synthesis of the complexes.

M	SalophH <sub>2</sub> (g)	CH <sub>3</sub> CN <sup>a</sup> (mL)	Initial <sup>b</sup> Voltage (V)	Time of electrolysis (h)	Metal dissolved (mg)
Ti	0.7	50	10	4.5	76
Fe	0.7	50	30	4.0	82
Cd	0.7	50	35	4.0	171
Sn	1.0	75	10	5.0	222
Pb	1.0	75	40	5.0	379

<sup>a</sup>Plus approximately 20 mg (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NClO<sub>4</sub> in each case.

<sup>b</sup>Voltage required to produce a current of 20 mA.

**Table 2.** Analytical data and some physical properties.

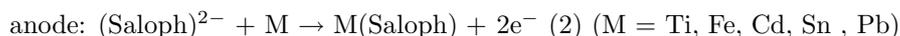
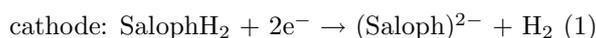
Compound (Formula)	Color	Yield (%)	Found % (Calculated %)				Conductivity (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	Melting Point(°C)
			C	H	N	M		
SalophH <sub>2</sub> (C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )	Yellow	80.0	75.78 (75.93)	5.18 (5.10)	8.81 (8.85)		1.56	159-160
Ti(Saloph) Ti(C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )	Yellow	91.5	66.20 (66.32)	3.95 (3.90)	7.69 (7.73)	13.41 (13.22)	11.35	223-224
Fe(Saloph) Fe(C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )	Orange	93.2	64.70 (64.89)	3.83 (3.81)	7.47 (7.57)	15.27 (15.09)	10.56	243-244
Cd(Saloph) Cd(C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )	Green	90.0	56.10 (56.29)	3.36 (3.31)	6.49 (6.57)	26.71 (26.34)	10.71	287-288
Sn(Saloph) Sn(C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )	Yellow	85.5	55.45 (55.47)	3.26 (3.26)	6.43 (6.47)	27.59 (27.41)	15.31	205-206
Pb(Saloph) Pb(C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )	Yellow	85.8	46.00 (46.06)	2.71 (2.71)	5.34 (5.37)	39.91 (39.71)	10.78	197-198

## Electrochemistry

The electrochemical efficiency ( $E_F$ ) defined as moles of metal dissolved per Faraday, was determined for the following systems:

Ti/SalophH <sub>2</sub>	$E_F$ 0.47 mol·F <sup>-1</sup>	Fe/SalophH <sub>2</sub>	$E_F$ 0.49 mol·F <sup>-1</sup>
Cd/SalophH <sub>2</sub>	0.51 mol·F <sup>-1</sup>	Sn/SalophH <sub>2</sub>	0.50 mol·F <sup>-1</sup>
Pb/SalophH <sub>2</sub>	0.49 mol·F <sup>-1</sup>		

The simplest mechanism compatible with these results, bearing in mind the cathodic formation of hydrogen gas, is



## Infrared Spectra

IR spectral data of the compounds and their tentative assignments are shown in Table 3. In the spectra of the ligand, the strong absorption peak at 3414 cm<sup>-1</sup> can be ascribed to the phenolic hydroxyl group,<sup>4</sup> and the characteristic absorption at 1614 cm<sup>-1</sup> and 1290 cm<sup>-1</sup> can be assigned to  $\nu_{C=N}$  and  $\nu_{(\text{phenolic}C-O)}$ , respectively.<sup>23-26</sup> Compared to SalophH<sub>2</sub>, some changes have taken place in the IR spectra of the complexes. First, the strong peak at 3414 cm<sup>-1</sup> disappeared. This suggests deprotonation of the phenolic hydroxyl group in SalophH<sub>2</sub> because of coordination with the metal ions. Second, the absorption peaks of  $\nu_{C=N}$  shifted by 10-29 cm<sup>-1</sup> to lower wave numbers, and this indicates the possibility of coordination of the imino nitrogen to the metal ions. Furthermore, some new bands have been observed between 420 and 530 cm<sup>-1</sup>. The bands in the range 518-533 cm<sup>-1</sup> are attributed to  $\nu_{M-N=C}$ , and those at 425-438 cm<sup>-1</sup> are assigned to  $\nu_{M-O}$ . All of the IR spectral information supports the idea of the coordination of the imino nitrogen and phenolic oxygen atoms to the metal ions.<sup>27</sup>

**Table 3.** Infrared spectral data of the compounds (cm<sup>-1</sup>).

Compound	$\nu(\text{OH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{phenolic C-O})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
SalophH <sub>2</sub>	3414	1614	1290		
Ti(Saloph)		1600	1332	524	432
Fe(Saloph)		1601	1398	533	435
Cd(Saloph)		1604	1299	520	438
Sn(Saloph)		1603	1305	518	430
Pb(Saloph)		1585	1312	530	425

## Electronic Spectra

The electronic spectral data of the compounds are summarized in Table 4. The bands at 318, 291, and 261 nm in SalophH<sub>2</sub> are assigned to the  $\Pi - \Pi^*$  transition and benzene  $\Pi - \Pi^*$  transition. In the spectra of the complexes, these 3 bands are blue-shift. It also indicates the coordination of the imino nitrogen to the metal ions and the influence on the conjugation system because of the ligation between the ligand and the metal ions.

**Table 4.** Electronic spectral data of the compounds.

Compound	$\lambda_{\max}(\epsilon, \text{l mol}^{-1} \text{cm}^{-1})$		
	SalophH <sub>2</sub>	261(13,900)	291(25,400)
Ti(Saloph)	252(7700)	283(12,850)	311(10,850)
Fe(Saloph)	251(12,450)	282(17,750)	309(15,750)
Cd(Saloph)	251(9350)	285(15,850)	316(9350)
Sn(Saloph)	253(900)	283(14,950)	310(12,350)
Pb(Saloph)	255(9870)	288(15,770)	315(9860)

### <sup>1</sup>H-NMR Spectra of the compounds

The <sup>1</sup>H-NMR data and assignments of the compounds are presented in Table 5. The chemical shift observed for the OH protons in SalophH<sub>2</sub> (13.07 ppm) was not observed in any of the complexes, which confirms the bonding of oxygen to the metal ions (C-O-M). The same result was confirmed by the IR spectra. The presence of a sharp singlet for the -C(H)=N proton in SalophH<sub>2</sub> clearly indicates that the magnetic environment is equivalent for all such protons, suggesting the presence of a planar ligand in these complexes.<sup>3</sup> The multiplets of aromatic protons appeared within the range 7.65-6.82 ppm, and they were not affected by chelation.

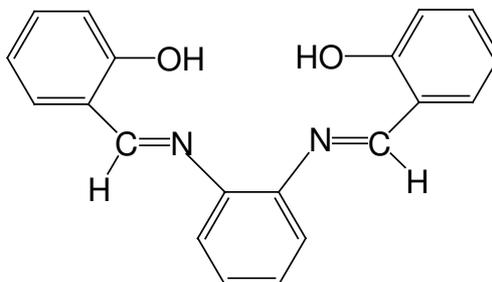
**Table 5.** <sup>1</sup>H-NMR data of the compounds (DMSO-d<sub>6</sub>).

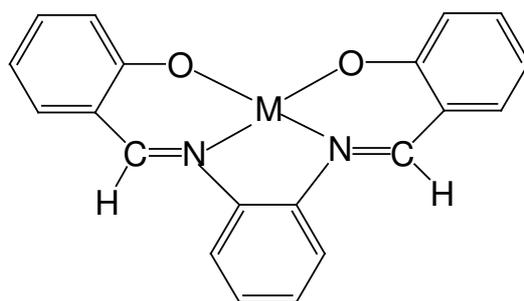
Compound	Chemical shift ( $\delta$ , ppm)		
	OH	Atom, H	C(H)=N
SalophH <sub>2</sub>	13.07(2H,s)	7.65–6.94(12H,m)	8.55(2H,s)
Fe(Saloph)		7.73–6.82(12H,m)	8.36(2H,s)
Cd(Saloph)		7.65–6.90(12H,m)	8.39(2H,s)

### Mass spectra of the compounds

The mass spectra of SalophH<sub>2</sub> and its complexes with iron and cadmium are given in Table 6 as representative examples. The molecular ion peaks are in good agreement with their empirical formula as indicated from elemental analyses. The other peaks represent fragments of the molecular ions.

On the basis of the physical and spectral data of SalophH<sub>2</sub> and the complexes discussed above, the composition of SalophH<sub>2</sub> and a general structure for the complexes are proposed as shown in Figures 1 and 2.

**Figure 1.** SalophH<sub>2</sub>.



**Figure 2.** The complexes, M: Ti(II), Fe(II), Cd(II), Sn(II), and Pb(II).

**Table 6.** Mass spectral data of the compounds.

Compound	m/e	Relative intensity (%)	Fragment
SalophH <sub>2</sub>	316	100	M <sup>+</sup> (C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )
	223	28.5	C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O
	210	59.1	C <sub>13</sub> H <sub>11</sub> N <sub>2</sub> O
	196	40.7	C <sub>13</sub> H <sub>11</sub> NO
	120	12.3	C <sub>7</sub> H <sub>7</sub> NO
	77	21.4	C <sub>6</sub> H <sub>5</sub>
Fe(SalophH <sub>2</sub> )	370	100	M <sup>+</sup> (C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> Fe)
	278	15.1	C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> OFe
	251	20.2	C <sub>13</sub> H <sub>9</sub> NOFe
	161	45	C <sub>7</sub> H <sub>5</sub> OFe
	56	83	Fe
Cd(SalophH <sub>2</sub> )	427	100	M <sup>+</sup> (C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> Cd)
	335	11.5	C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> OCd
	308	8.2	C <sub>13</sub> H <sub>9</sub> NOCd
	218	45.6	C <sub>7</sub> H <sub>5</sub> OCd
	113	29	Cd

## Conclusion

It was shown that the synthesis of metal complexes with the electrochemical method can be applied to the preparation of Schiff base metal complexes. Schiff base metal complexes were formed in high yield in a one-step route by the electrochemical oxidation of the metal into acetonitrile solution of SalophH<sub>2</sub>.

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