

# *Structure Determination and Electric Conductivity of Phenolic Iron (III) Complexes*

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## **Abstract:**

A number of phenolic iron (III) complexes have been synthesized and characterized. The electric conductivity of these complexes was studied and the results were very promising, as they showed good levels of electric conductivity come within the semiconductors range.

**Keywords:** Phenolic iron (III), complexes, electric conductivity, semiconductors.

## **Introduction:**

The difference between a semiconductor and a good conductor is that the resistance of the latter declines rapidly as the temperature decreases, whereas the resistance of semiconductors increases notably as the temperature falls down to the absolute zero.<sup>1</sup> Phenolic iron (III) complexes have not been in great interest by researchers in the concept of electric conductivity and their use as semiconductors. However, the focus of many research groups has been on iron (III) inorganic compounds as good semiconductors and their use in manufacturing electric devices.<sup>2,3</sup> The focus on the inorganic and organic iron (III) compounds was about the use of such compounds as electrodes<sup>4</sup> and additives to improve the electric properties of some polymers and other materials.<sup>5</sup> Herein a number of organo-ferric compounds have been synthesized using an adapted literature procedure.<sup>6</sup> The resulting complexes were characterized using titration, flame test, spectroscopic methods such as atomic absorption, Uv-vis and IR.

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## Results and Discussion:

### 1 – Synthesis of Complexes:

Ferric nitrate was used instead of ferric chloride in a complexing reaction with a number of phenol ligands. The ligands were used as the corresponding sodium salts of phenol **1**, 1-naphthol **2**, *o*-cresol **3**, *m*-cresol **4**, 3-nitrophenol **5**, resorcinol **6** and hydroquinone **7**. When the reaction was first conducted, the ligands were used as phenol forms and added to an aqueous ferric nitrate at room temperature. The resulting products were soluble in water in which the precipitation of the desired complexes did not occur. However, in order to make the precipitation possible, all phenol derivatives were converted to the corresponding sodium salts (**Fig. 1**), by the treatment of the phenol derivative with 1 mole aq. NaOH.

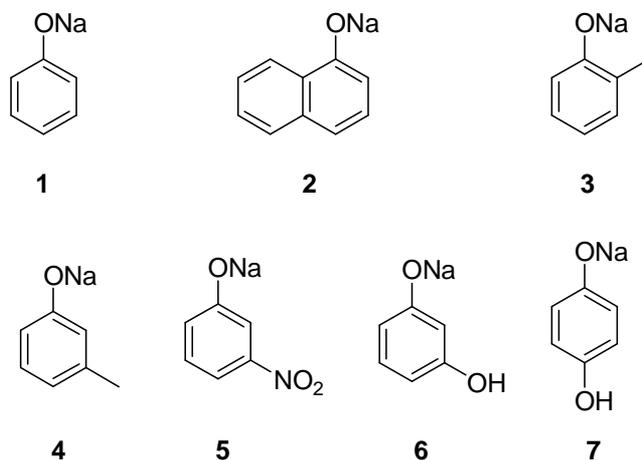
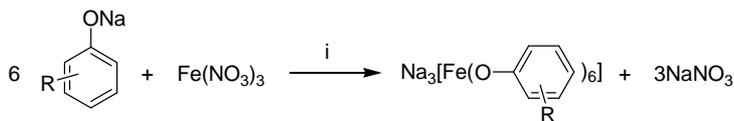


Figure 1

The resulting sodiumphenoxides were involved in the reaction with the aq. ferric nitrate at room temperature in ratio of 6:1 mole/mole. Precipitation of the desired complexes **1a** – **7a** occurred (**Scheme 1**).



Conditions: (i) aq.  $\text{Fe}(\text{NO}_3)_3$ , RT, 15 min

R	Ligand	Complex	Yield %
H	1	1a	60
	2	2a	15
2-Me	3	3a	20
3-Me	4	4a	20
3-NO <sub>2</sub>	5	5a	64
3-OH	6	6a	25
4-OH	7	7a	33

Scheme 1

Iron (III) has been found to coordinate with six monodentate ligands to form the most likely octahedral structures.<sup>7</sup> The reaction mixture was filtered; and the filtrate was titrated with 0.1 M HCl in order to determine the residual sodium phenoxide. This showed that six moles of the sodiumphenoxide were consumed in the reaction, revealing that the coordination number was six. This finding led to propose the general chemical formula of the resulting complexes as  $\text{Na}_3[\text{Fe}(\text{Ln})_6]$ . The presence of the sodium was confirmed by carrying out a flame test on the obtained complexes **1a** – **7a**. The distinctive yellow colour for the sodium ion was observed in all cases. The formation of the complexes **1a** – **7a** was further confirmed using spectrometric techniques. The uv-vis spectrometer was employed to measure the wavelengths of the resulting complexes **1a** – **7a**. The measured  $\lambda_{\text{max}}$  values were compared with those of the ligands **1** – **7**. The obtained uv-vis data showed a hypsochromic shift (a blue shift) in the absorption of the complexes. Such a blue shift could be rationalized as a result of the fluent movement of the  $n$ - and  $\pi$ -electrons in the system towards the metal ion. This electron withdrawing effect by the positively charged metal ion decreases the electronic density on the aromatic system in which the absorption takes place at lower wavelengths (**Table 1**).

**Table 1**  
Wavelength values of ligands and their iron (III) complexes

$\lambda_{\max}$ (nm)	Ligand in H <sub>2</sub> O	$\lambda_{\max}$ (nm)	Complex in EtOH
293.5	1	264.0	1a
331.5	2	295.0	2a
299.5	3	271.5	3a
297.0	4	277.5	4a
391.0	5	305.0	5a
298.0	6	264.0	6a
296.5	7	257.0	7a

It is worth mentioning that the wavelength values vary from a complex to another. This depends on the electronic nature and the position of the substituent on the aromatic ring. When the substituent was an electron-donating group at *ortho* or *para* position, as in complexes **3a** and **7a**, the electron-withdrawing effect of the metal ion increases in comparison with having electron-donating substituent at *meta* position on the aromatic ring, as in complexes **4a** and **6a**. However, the existence of an electron-withdrawing group at *meta* position on the aromatic ring, as in complex **5a**, generates a reversible electron-withdrawing effect to the metal ion electron-withdrawing effect. This allows the  $\pi$ -electrons to delocalize through the aromatic ring and the substituent raising the  $\lambda_{\max}$  value. Whereas the electronic density on the naphthyl ring, complex **2a**, is relatively high (10  $\pi$ -electrons) in comparison with the electronic capacity on the phenyl ring in the complex **1a** (6  $\pi$ -electrons). This could rationalize the fact that complex **2a** absorbs light at higher wavelength than complex **1a**.

The presence of the iron (III) ion in the complexes was also proved through measuring the atomic absorption of the Fe<sup>+3</sup>. The seven complexes showed an atomic absorption for the iron (III) ion (**Table 2**).

**Table 2**Atomic absorption of Fe<sup>+3</sup> for all complexes

Complex	Absorption of Fe <sup>+3</sup>	Concentration of Fe <sup>+3</sup> (mg/L)
<b>1a</b>	0.6501	53871.43
<b>2a</b>	0.4629	19587.99
<b>3a</b>	0.2300	24579.12
<b>4a</b>	0.5450	91703.50
<b>5a</b>	0.6980	66033.87
<b>6a</b>	0.6394	60824.68
<b>7a</b>	0.5551	92133.78

The solubility of the obtained complexes was tested in various solvents. Complex **2a** was found to be completely soluble in ethanol, methanol, *tert.*-butanol and DMF. Whereas the rest of the complexes **1a** and **3a – 7a** showed low solubility levels in these solvents.

## 2 – Conductivity of the Complexes:

Semiconductors are chemical materials in which their composition allows electrical current to pass through out. They possess electrical resistivity values ranging between  $10^{-2}$  and  $10^9$   $\Omega$ -cm at room temperature.<sup>1</sup> The resistivity  $\rho$  of the complexes **1a – 7a** could be calculated by knowing the resistance **R**, the area of the sample pellet **A** ( $\pi r^2$ ; where *r* is the radius of the sample) and the thickness of the sample pellet **l** “Eq. (1)”.<sup>8</sup> The resistivity  $\rho$  of complex **1a** was found to be  $0.702774988 \times 10^6$   $\Omega$ -cm, at room temperature. This indicates that the resistivity of complex **1a** comes within the resistivity range of the semiconductors.

$$\rho = R A/l \quad \text{“Eq. (1)”}$$

$$\text{Where } R = V/I \quad \text{“Eq. (2)”}$$

[V = applied voltage (V) and I = measured current (A)]

The experimental data (power vs current) was processed using Origin® 6.0 software. The calculations were set as second order equations for complexes **1a– 7a**. For example, the polynomial fitting (fitting as a second order equation) for the experimental data of complex **1a** revealed that 0.99657 V is the average value of voltage that led to an electric current with an average value of 2.78505

$\times 10^{-6}$  A. According to the “Eq. (2)”:

$$R = 0.99657 \text{ V} / 2.78505 \times 10^{-6} \text{ A} = 0.357828405 \times 10^6 \Omega.$$

For all complexes,  $A/l = \pi r^2/l$ ; where  $r = 0.25$  cm and  $l = 0.1$  cm. Therefore  $A/l = 1.964$  cm.

$$\rho = 0.357828405 \times 10^6 \Omega \times 1.964 \text{ cm} = 0.702774988 \times 10^6 \Omega\text{cm}$$

The conductivity  $\sigma$  of complex **1a** equals the reverse value of the resistivity<sup>8</sup> “Eq. (3)”.

$$\sigma = 1/\rho \quad \text{“Eq. (3)”}$$

$$\sigma = 1/0.702774988 \times 10^6 \Omega\text{cm} = 1.423 \times 10^{-6} (\Omega\text{-cm})^{-1}$$

The results showed that the resistivity of complex **1a** was the lowest, which led to the best conductivity of all complexes in this study. Similar calculations were carried out for complexes **2a – 7a** (Table 3).

**Table 3**

For all complexes  $A/l = 0.1964 \text{ cm}^2/0.1 \text{ cm} = 1.964 \text{ cm}$

\* The average values of voltage and current obtained from Origin® 6.0 software by fitting data as a second order equation in every case

Complex	Voltage* V	Current* A	Resistance $R \times 10^6 (\Omega)$	Resistivity $\rho \times 10^6$ ( $\Omega\text{-cm}$ )	Conductivity $\sigma (\Omega\text{-cm})^{-1}$
1a	0.99657	$2.78505 \times 10^{-6}$	0.357828405	0.702774988	$1.423 \times 10^{-6}$
2a	0.99972	$6.77806 \times 10^{-8}$	147.493531060	28.967729409	$3.452 \times 10^{-8}$
3a	0.99854	$4.63801 \times 10^{-7}$	2.152949218	4.228392263	$2.365 \times 10^{-7}$
4a	0.99968	$9.19719 \times 10^{-8}$	10.869406851	21.347515055	$4.684 \times 10^{-8}$
5a	0.99983	$6.29288 \times 10^{-8}$	15.888273732	31.204569610	$3.205 \times 10^{-8}$
6a	0.99999	$1.41524 \times 10^{-8}$	70.658686866	138.773661005	$7.206 \times 10^{-9}$
7a	0.99993	$4.1853 \times 10^{-8}$	23.891477314	46.922861445	$2.131 \times 10^{-8}$

Complex **2a** (Table 3) showed low conductivity in comparison with complex **1a** indicating that complex **2a** has higher level of resistivity. Complex **3a** (Table 3) exhibited higher conductivity [ $2.365 \times 10^{-7} (\Omega\text{-cm})^{-1}$ ] than that for complex **2a**, although it is still much smaller than the conductivity of complex **1a**. Whereas complexes **4a**, **5a** and **7a** showed levels of conductivity ranging between  $4.684 \times 10^{-8}$  and  $2.131 \times 10^{-8} (\Omega\text{-cm})^{-1}$ , within which the conductivity of complex **2a** comes. Based on these findings, complexes **1a**, **2a**, **3a**, **4a**, **5a** and **7a** could be considered as a *p*-type semiconductors as the positively charged

iron (III) ion plays a key role in transferring the  $\pi$ -electrons through the whole molecule which assist passing the electrical current throughout. However, complex **6a** showed poor electric conductivity  $7.206 \times 10^{-9} (\Omega\text{-cm})^{-1}$  because of which complex **6a** could be classified as an insulator.

The relationship between the applied voltage (V) and the measured current (A) (**Table 4**) showed that the measured current increased (resistivity falls) as the applied voltage was raised. This was observed in all cases (**Fig. 2**).

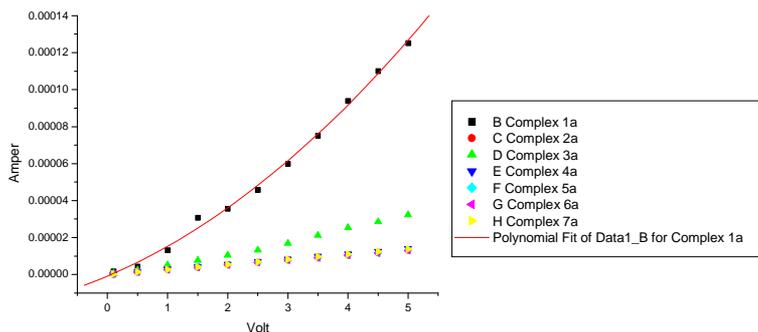
**Table 4**

The experimental data of applied voltage vs current for complexes **1a – 7a**

Voltage V	1a Current A ( $10^{-6}$ )	2a Current A ( $10^{-6}$ )	3a Current A ( $10^{-6}$ )	4a Current A ( $10^{-6}$ )	5a Current A ( $10^{-6}$ )	6a Current A ( $10^{-6}$ )	7a Current A ( $10^{-6}$ )
0.1	1.77	0.25	0.52	0.29	0.25	0.25	0.26
0.5	4.38	1.29	2.46	1.45	1.31	1.29	1.35
1.0	13.18	2.74	5.15	3.07	2.66	2.57	2.7
1.5	30.8	3.83	7.66	4.24	4.03	3.88	4.03
2.0	35.6	5.2	10.38	5.66	5.21	5.18	5.4
2.5	45.8	6.52	13.21	7.07	6.55	6.45	6.78
3.0	60	7.78	16.82	8.42	7.85	7.74	8.21
3.5	75.3	9.04	21.2	9.93	9.08	9.02	9.59
4.0	94	10.41	25.4	11.11	10.43	10.35	11.04
4.5	110.1	11.64	28.6	12.58	11.69	11.6	12.39
5.0	125.2	12.92	32.3	14.03	13.16	12.91	13.7

**Figure 2**

The relationship between applied voltage and measured current for complexes **1a – 7a**



## Conclusion:

The complexes **1a** – **7a** have been synthesized and found to exist in octahedral structures with six ligands coordinated to the iron (III) ion. These complexes, as expected, showed hypsochromic shifts (blue shifts) in their uv-vis spectra. The complexes **1a** – **7a** exhibited various levels of electric conductivity. Complex **1a** showed the lowest resistivity and the greatest electric conductivity amongst all complexes and could be classified as a *p*-type semiconductor. Complex **6a**, on the other hand, was found to be an insulator. Complexes **1a** – **7a** decomposed at around 300 °C when measuring melting points was attempted. Finally, their solubility was found to be rather poor in a number of polar organic solvents.

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## Experimental:

### Materials:

Ferric nitrate, *o*-cresol, *m*-cresol and sodium hydroxide were purchased from AVONChem., phenol and *m*-nitriphenol were purchased from BDH Chemical ltd Poole England,  $\alpha$ -naphthol was purchased from T-Baker Lab Chemical India, resorcinol and hydroquinone were purchased from Riedel-Dehaen. All chemicals were used without any further purification.

### Instrumentation:

Shimadzu uv-vis spectrophotometer – UV mini 1240, FAST Sequential Atomic Absorption Spectrometer – UARIAN – AA240FS, IR spectrophotometer JASCO-FT-IR-460 plus. Melting point apparatus CL 0301 S. No. 1144. The electrical experiments were carried out using Laboratory Power Supply EA-PS 2016-050, the applied power was measured employing Metra Max 12 IEC61010-1 with internal resistance of 5 KOhm and the current was measured using AVOMETER CEM-DT 3900.

### General Procedure for Titration:

An adapted literature procedure was followed.<sup>9</sup> The filtrate (that was collected from the filtration of the product) was titrated by 0.1 M HCl. This was carried out by adding slowly, from a burette, 0.1 M HCl to a measured volume

of the filtrate in a 250 cm<sup>3</sup> Erlenmeyer flask in the presence of one to two drops of methyl orange.

### General Procedure for the Preparation of the Complexes 1a–7a:

An adapted literature procedure was used.<sup>6</sup> The sodium phenoxide solution was prepared by dissolving the phenol derivative (6 to 6.5 mmol) in 10% NaOH aqueous solution (30–40 cm<sup>3</sup>). The resulting sodium phenoxide solution was added gradually to a stirred solution of ferric nitrate (1 mmol) in H<sub>2</sub>O (20 cm<sup>3</sup>) at room temperature. The reaction was left stirring at room temperature for around 15 min. The resulting solid product was collected by filtration, washed with water (3 × 10 cm<sup>3</sup>) and finally air-dried. Complexes: **1a** was a brown solid (60% yield),  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3567–3151 (br), 3057 (w), 1473 (m), 1435 (m), 1265 (s); **2a** was a dark brown solid (15% yield),  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3540–3100 (br), 3040 (m), 1660 (m), 1580 (s), 1260 (s); **3a** was a brown solid (20% yield),  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3480 (m), 2920 – 2820 (w), 1600 (m), 1480 (m), 1180 (w); **4a** appeared as a reddish-brown solid (20% yield),  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3548–3416 (br), 3057–2851 (w), 1605 (s), 1510 (s), 1302 (s); **5a** appeared as a reddish-brown solid (64% yield),  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3600 – 3200 (br), 3060 (w), 1580 (m), 1345 (s), 1520 (s), 1460 (s), 1240 (s); **6a** was a brown solid (25% yield),  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3400 (w), 3220 (w), 3060 (w), 1600 (w), 1480 (m), 1340 (s); **7a** appeared as a black solid (33% yield),  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3500–3220 (br), 2900 (w), 1580 (s), 1540 (s), 1380 (s).

### General Procedure for Measuring the Electric Current for Complexes 1a – 7a:

An adapted literature procedure was followed.<sup>10,11</sup> The sample (with radius of 0.25 cm) was placed between two copper discs with radius of 0.25 cm. One copper disc was connected to a power source and the other copper disc was connected respectively to an ammeter measuring the current in  $\mu$ A units. The experimental results were mentioned in (Table 4).

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