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Properties and Synthesis of the Cr(III)-Salen/Salophen Complexes Containing Triphenylamine Core

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# Properties and Synthesis of the Cr(III)-Salen/Salophen Complexes Containing Triphenylamine Core

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Two triphenylamine derivatives bearing 4-aminobenzoic acid and 5-aminoisophthalic acid were synthesized. Then, the prepared triphenylamine derivatives were reacted with new Cr(III) complexes involving two tetradenta Schiff bases N,N-bis(salicylidene)ethylenediamine or bis(salicylidene)-ophenylenediamine. The structures of these compounds were characterized by elemental analysis, FT-IR, TG, <sup>1</sup>H NMR, and <sup>13</sup>C NMR techniques and magnetic susceptibility measurement. The complexes can also be characterized as low-spin distorted octahedral Cr(III) bridged by carboxylic acids. The carboxylic acids play a role as bridges for weak antiferromagnetic intramolecular exchange. Also, the UV spectra of these derivatives revealed that the maximum wavelengths of the complexes are shifted, compared with the ligands.

Keywords complexation, Schiff base, synthesis, triphenylamin

#### INTRODUCTION

Investigation on metal organic complexes represents one of the most active areas of materials science and chemical research. Major advances have been made in these materials due to their interesting properties and potential in various applications (e.g., electrical conductivity, magnetism, hostguest chemistry, ion exchange, catalysis, nonlinear optics).<sup>[1–3]</sup> Synthesis of new Schiff bases and their metal complexes still the aim of many recent investigations. Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. They show interesting properties such as their ability to reversibly bind oxygen,<sup>[4]</sup> catalytic activity in hydrogenation of olefins<sup>[5]</sup> and transfer of an amino group,<sup>[6]</sup> photochromic properties,<sup>[7]</sup> and complexing ability towards toxic metals.<sup>[8]</sup>

In the present article, we report the synthesis of novel triphenylamine derivatives containing mono- and dicarboxylic acid groups by using 4-aminobenzoic acid and 5-aminoisophthalic acid reagents and the preparation of their mono- and dinuclear Cr(III)(Salen/Salophen) complexes. The structure of the compounds was characterized using elemental analysis, FT-

IR, TGA, <sup>1</sup>H NMR, and <sup>13</sup>C NMR techniques and magnetic

Condensation of salicylaldehydes or salicylaldehyde derivatives with 1,2-diamines leads to the formation of one extremely important class of ligands, generally known as Salens (accordingly with *o*-phenylenediamine, Salophen). Salen-type and Salophen-type ligands with N and O donor atoms are important because their metal complexes find widespread applications as homogeneous and heterogeneous catalysts in various organic transformation reactions.<sup>[9]</sup> For example, a Schiff base complex of chromium(III), [Cr(Salen)(OH<sub>2</sub>)<sub>2</sub>]<sup>+</sup>, was found to enhance insulin activity and insulin derivatized with the same was found to exhibit higher activity in glucose metabolism in animal models when compared to either free insulin or other derivatives.<sup>[10,11]</sup> The bridged complexes of Salen-Salophen are especially attractive by lastest studies in inorganic chemistry.<sup>[12–14]</sup> Triphenylamine (TPA) has been known as a hole-transporting

as well as thermally and photolytically stable material.<sup>[15]</sup> TPA and its derivatives have been widely utilized as a functional building block in the fabrication of the organic photoconductors, nonlinear optical materials, and photorefractive materials in OLEDs owing to their excellent solubility, stability and the excellent hole-transporting capability (the electron-donating properties).<sup>[16-22]</sup> Triarylamines (TAAs) having various substituents at their para positions have been widely known to give the corresponding very stable cation radicals upon chemical or electrochemical one electron oxidation,<sup>[23]</sup> serving as stable positive charge and spin bearing units. During the past decade, this salient feature has been utilized for the synthesis of a number of p-extended TAA-based oligomers as models for positively charged purely organic high-spin entities<sup>[24]</sup> as well as for organic mixed-valence molecular systems.<sup>[25]</sup> Very recently, Bushby et al. reported a triarylamine-based ligand with a 4pyridyl unit and its manganese complex.<sup>[26]</sup> Yano and coworkers<sup>[27]</sup> designed and prepared a starburst-shaped ligand, 4,4'4"tris[N, N-bis(2-pyridylmethyl) aminomethyl] triphenylamine, and its palladium and copper trinuclear complexes.

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susceptibility measurement. Also, the magnetic and physical properties of the synthesized complexes are reported and their ultraviolet visible spectrum (UV-vis) was recorded.

#### **EXPERIMENTAL**

#### Materials and Methods

All starting materials and reagents used were of standard analytical grade from Fluka, Merck as well as from Aldrich and used without further purification. [ $\{Cr(Salen)_2\}O$ ] and  $[{Cr(Salophen)_2}O]$  were prepared according to previously published methods.<sup>[28-30]</sup> Melting points were measured using a Buchi B-540 melting point apparatus. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian 400 MHz spectrometer at room temperature. Thermal gravimetric analysis (TG) was carried out with Seteram thermogravimetric analyzer. The sample weight was 12-15 mg. Analysis was performed from room temperature to 900°C at heating rate of 15°C/min in argon atmosphere with a gas flow rate of 20 mL/min. The elemental analysis for the ligand and the bridged complexes were carried out at on a Hewlett-Packard 185 analyzer. UV-vis spectra were obtained on a PerkinElmer Lambda 25 UV/Vis System. FT-IR spectra were recorded on a PerkinElmer Spectrum 100 as KBr pellets. Magnetic susceptibilities of metal complexes were determined using a Sherwood Scientific MX Gouy magnetic susceptibility apparatus carried out using the Gouy method with Hg[Co(SCN)<sub>4</sub>] as calibrant. The effective magnetic moments,  $\mu$  eff, per metal atom was calculated from the expression:  $\mu_{\rm eff.} = 2.84.(\chi_{\rm M})^{1/2}$ where  $\chi_{\rm M}$  is the molar susceptibility.

#### **Synthesis**

The target compounds **2a-b** were prepared via a threestep procedure which is shown in Figure 1. Compound **1** was synthesized by using phosphorus oxychloride and DMF according to a literature procedure.<sup>[31]</sup> For compound **1**, <sup>1</sup>H NMR (CDCl<sub>3</sub>  $\delta$ , ppm): 9.82 (s, 1H, CHO), 7.70 (d, 2H, J = 8.7 Hz, ArH), 7.36 (t, 4H, J = 7.7–8.2 Hz, ArH), 7.21–7.17 (m, 6H, ArH), 7.04 (d, 2H, J = 8.7 Hz, ArH).

## General Procedure for the Synthesis of Triphenylamine Derivatives Bearing Carboxylic Acid Groups (2a and 2b)

A solution of triphenylamine monoaldehyde (1) (1.0 mmol) in absolute EtOH (20 mL) was added 4-aminobenzoic acid or 5-aminoisophthalic acid (1.0 mmol) and refluxed for 24 h. Then, the reaction mixture was allowed to cool to room temperature, and filtered. The precipitate was washed with cool EtOH.

#### Compound 2a

<sup>1</sup>H NMR (CDCl<sub>3</sub>  $\delta$ , ppm): 8.33 (s, 1H, CHN), 8.13 (d, 2H, J = 8.6 Hz, ArH), 7.74 (d, 2H, J = 8.0 Hz, ArH), 7.28–7.33 (m, 4H, ArH), 7.22 (d, 2H, J = 8.0 Hz, ArH), 7.06–7.17 (m, 8H, ArH); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  122.3, 125.1, 125.8, 126.7, 128.1, 128.3, 129.5, 130.6, 131.5, 145.6, 148.3, 157.1, 159.9, 169.1.

#### Compound 2b

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.89 (t, 1H, J = 1.56 Hz, CHN), 8.48 (s, 1H, ArH), 8.04 (d, 2H, J = 1.56 Hz, ArH), 7.71 (d, 2H, J = 8.8 Hz, ArH), 7.25–7.30 (m, 4H, ArH), 7.03–7.14 (m, 8H, ArH); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  125.2, 125.7, 126.6, 128.1, 128.5, 129.2, 129.4, 130.6, 130.4, 145.2, 147.3, 153.1, 159.8, 168.3.

# Preparation of [Compound 2a-{Cr(III)(Salen/Salophen) (3a-b)}] and [Compound 2b- {Cr(III)(Salen/Salophen) (4a-b)}] Complexes

A solution of compound **2a** or **2b** (1 mmol) and  $[{Cr(Salen)}_2O](1.5 \text{ mmol}) \text{ or } [{Cr(Salophen)}_2O](1.5 \text{ mmol})$ 



FIG. 1. Synthesis of triphenylamine derivatives bearing carboxylic acid groups (2a) and (2b); (i) POCl<sub>3</sub>, DMF; (ii) 4-aminobenzoic acid, ethanol reflux for 24 h; (iii) 5-aminoisophthalic acid, ethanol reflux for 24 h.

 TABLE 1

 Elemental analysis, magnetic and physical properties of the compounds

Compound	Formula	Color	$\mu_{\rm eff}$ (B.M.)	m.p (°C)	Yield (%)	Found (Anal. Calcd.) (%)			
						С	Ν	Н	Cr
1	C <sub>19</sub> H <sub>15</sub> NO	Pale yellow	-	130	80	83.47	5.15	5.57	_
						(83.49)	(5.13)	(5.53)	_
2a	$C_{26}H_{20}N_{2}O_{2} \\$	Light yellow	-	203	78	78.34	7.22	5.12	—
						(79.50)	(7.14)	(5.14)	_
2b	$C_{27}H_{20}N_{2}O_{4} \\$	Light yellow	-	175	80	73.91	6.85	4.43	—
		-				(74.30)	(6.42)	(4.62)	_
3a	$C_{42}H_{34}N_4O_4Cr$	Light green	3.60	215	60	70.65	7.96	4.76	7.12
						(70.98)	(7.88)	(4.82)	(7.32)
3b	$C_{46}H_{34}N_4O_4Cr$	Green	3.72	220*	65	72.67	7.40	4.50	6.46
						(72.81)	(7.38)	(4.52)	(6.85)
<b>4</b> a	$C_{59}H_{48}N_6O_8Cr_2$	Dark green	3.65	350 <sup>a</sup>	65	65.96	7.92	4.40	9.28
						(66.04)	(7.83)	(4.51)	(9.69)
4b	$C_{67}H_{48}N_6O_8Cr_2$	Dark green	3.70	350 <sup>a</sup>	70	68.19 (68.83)	7.39 (7.19)	4.01 (4.14)	8.83 (8.89)

\*Decomposition.

in 40 mL of absolute ethanol was refluxed for 3 h. The mixture was allowed to cool to room temperature. Then the mixture was filtered and the residue was washed with ethanol and dried in vacuum. Elemental analysis and magnetic and physical properties of the synthesized complexes are given in Table 1.

# **RESULTS AND DISCUSSION**

#### Synthesis

In order to evaluate the complexation with  $[{Cr(Salen)}_2O]$ and  $[{Cr(Salophen)}_2O]$  of triphenylamine derivatives containing mono- and dicarboxylic acid groups as ligand (2a and **2b**), first we synthesized triphenylamin monoaldehyde (1) using phosphorus oxychloride and DMF according to literature procedure.<sup>[31]</sup> Then, compound **1** was reacted with 4-aminobenzoic acid and 5-aminoisophthalic acid in ethanol medium to obtain compound 2a and 2b, respectively (Figure 1). Then, the obtained compounds 2a and 2b were converted to complexes bridged by carboxylate anions to the chromium center with  $[{Cr(Salen)}_2O]$  and  $[{Cr(Salophen)}_2O]$  as ligand complex because it can coordinate to another ligand (Figure 2). Characterization of these compounds was made with <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR, and elemental analysis. Figures 3 and 4 show <sup>1</sup>H-NMR spectrums of **2a** and **2b**, respectively. The formation of 2a and 2b was confirmed by the disappearance of the aldehyde protons in triphenylamine monoaldehyde at 9.82 ppm and the appearance of imine protons (CH = N) at 8.33 and 8.89 ppm belong to 2a and 2b compounds, respectively (Figures 3 and 4). Also, the synthesis of 2a and 2b was supported by the appearance of carbon signals at 169.1 and 168.3 ppm belong to CH = N groups in <sup>13</sup>C-NMR. From the FT-IR results, the band of CH = O vibration of **1** observed at 1690 cm<sup>-1</sup> was disappeared and imine C = N bands for **2a** and **2b** were observed at 1668 and 1654 cm<sup>-1</sup>, respectively. The results of the elemental analyses, given in Table 1, are in a good agreement with the structures suggested for the ligands and their complexes. In addition, the synthesized Salen and Salophen capped complexes were characterized with thermal gravimetric analysis, magnetic susceptibility and FT-IR.

#### FT-IR Spectra

The characteristic FT-IR bands for compound 2a -2b and their Cr(III)-Salen/Salophen complexes (3a, 3b, 4a and 4b) were given Table 2. The FT-IR spectra of the complexes have different absorption peaks, compared with that of the ligands. As seen in Table 2, the vibrations of the carboxylic acid C = O and imine C = N of **2a** and **2b** have been observed at 1683, 1668 cm<sup>-1</sup> for **2a** and 1684, 1654 cm<sup>-1</sup> for **2b**, respectively. In the complexes, these bands are, however, shifted to lower or higher frequencies indicating that the nitrogen and oxygen atoms of compound 2a and 2b are coordinated to the ligand complexes [12]. The C = O band in complexes 3a and **3b** shifted from 1683 to 1688 and 1689 cm<sup>-1</sup>, the C = N band shifted from 1668 to 1645 and 1658 cm<sup>-1</sup>, respectively. Also, the C = O band in complexes **4a** and **4b** shifted from 1684 to 1616 and 1604 cm<sup>-1</sup>, the C = N band shifted from 1654 to 1601 and 1581  $\text{cm}^{-1}$ , respectively. In the FT-IR analysis of the complexes (3a, 3b, 4a, and 4b), the bands in the 556–533 and



FIG. 2. Synthetic routes for complexation between compound 2a-2b and Cr (III) (color figure available online).



FIG. 3. <sup>1</sup>H NMR spectrum of compound **2a** (color figure available online).



FIG. 4. <sup>1</sup>H NMR spectrum of compound **2b** (color figure available online).

 $465-478 \text{ cm}^{-1}$  range can be attributed to the M–N and M–O stretching modes.<sup>[32]</sup>

#### **Thermal Properties**

The thermal analysis of ligands and their complexes were recorded in argon atmosphere from 40 to 900°C. The correlations between the different decomposition steps of the compounds with the corresponding weight losses are discussed in terms of the proposed formula of the compounds. The thermal behaviors of the obtained complexes are summarized in Table 3. An exemplary TG curve of complex **3b** is depicted in Figure 5. The results show good agreement with the formula suggested from the analytical data (Table 1).

The ligand **2a** is thermally decomposed in only two successive decomposition steps. The mass loss of within the temperature range  $250-425^{\circ}$ C may be attributed to the loss of the CO<sub>2</sub> and triphenylamine groups. At the second decomposition step, C<sub>6</sub>H<sub>6</sub>N groups lefts from the main structure at 425–650°C. The TG results of **3a** and **3b** complexes show two decomposition steps within the temperature range of 40–900°C. For the

**3a** complex, at 200–475°C, ligand and CO<sub>2</sub> leave the complex structure. Moreover, the loss of  $C_6H_6$  was observed within 475–650°C. For the **3b** complex, the first step (40–350°C) is due to the loss of moisture and CO<sub>2</sub>. At the second decomposition step, the ligand and  $C_6H_6$  groups leave from structure at 350–800°C.

As seen in Table 3, ligand **2b** shows three decomposition steps within the 175–700°C temperature range. The decomposition within the 175–325°C, 325–460°C, and 460–700°C temperature ranges is due to the loss of CO<sub>2</sub>, triphenylamine, and C<sub>6</sub>H<sub>6</sub>N from main structure, respectively. The ligand **2a**'s Cr(III)-Salen/Salophen complexes (**4a**, **4b**) have different decomposition steps. While the complex **4a** thermally decomposed only three decomposition step, the complex **4b** decomposed four decomposition steps. The first decomposition step for **4a** (40–140°C) is due to the loss of moisture. At 175–325°C, the CO<sub>2</sub> left from the residue structure. Also, the loss of ligand and C<sub>6</sub>H<sub>6</sub> groups in **4a** was observed within 325–800°C. The decomposition of the complex **4b** proceeds with four main degradation steps. The first decomposition within the temperature

Characteristic FT-IR bands (cm <sup>-1</sup> ) of ligand and complexes					
Compounds	C = N	C = O	C-N	C-C <sub>ar</sub>	C-H <sub>aliph</sub>
2a	1668 s	1683 s	1163 s	1585 s	2865 w
3a	1645 m	1688 s	1155 s	1578 s	2829 w
3b	1658 m	1689 s	1164 s	1584 s	3059 w
2b	1654 s	1684 s	1157 s	1579 s	2978 m
4a	1601 s	1616 m	1050 m	1541 m	2969 w
4b	1581 s	1604 m	1048 m	1548 m	3063 m

 TABLE 2

 Characteristic FT-IR bands (cm<sup>-1</sup>) of ligand and complexe

Compounds	TG range (°C)	Weight loss found (Anal. Calcd.) (%)	Fragments
2a	250–425°C	67 50(68 38)	$CO_2$ triphenylenamine group
24	425–650°C	28 65(29 86)	loss of C <sub>4</sub> H <sub>4</sub> N
3a	200–475°C	54.50(55.49)	loss of ligand, CO <sub>2</sub>
	475-650°C	22.10(21.97)	loss of $C_6H_6$
		× ,	Metal oxide and $R(CN)_2$ residue
3b	40–350°C	7.21(5.80)	moisture, $CO_2$
	350-800°C	65.31(66.49)	loss of ligand and $C_6H_6$
			Metal oxide and $R(CN)_2$ residue
2b	175-325°C	19.77(20.18)	$CO_2$
	325–460°C	55.78(56.19)	triphenylenamine group
	460–700°C	22.13(24.08)	Loss of $C_6H_6N$ group
4a	40-140°C	3.28	moisture
	175–325°C	9.07(8.20)	$CO_2$
	325–800°C	59.45(61.50)	loss of ligand and $C_6H_6$ groups
			Metal oxide and R(CN) <sub>2</sub> residue
4b	40–120°C	2.23	Moisture
	200–350°C	8.12(7.52)	$CO_2$
	325–650°C	27.29(29.76)	loss of ligand
	650–900°C	25.71(26.68)	loss of $C_6H_6$ groups
			Metal oxide and $R(CN)_2$ residue

TABLE 3 TG results of the ligands and complexes



FIG. 5. TG and dTG curve of complex **3b** (color figure available online).



FIG. 6. Absorption spectra of the ligands and complexes  $(1 \times 10^{-5} \text{ mol } L^{-1} \text{ in DMSO})$ . (a) **2a**, **3a**, and **3b**; (b) **2b**, **4a**, and **4b**.

range 40–120°C could be attributed to the loss of moisture. The second step occurs within the temperature range 200–350°C, which is reasonably accounted for loss of CO<sub>2</sub> groups. The third and fourth decomposition within the temperature ranges of  $325-650^{\circ}$ C and  $650-900^{\circ}$ C corresponds to the liberation of ligand and C<sub>6</sub>H<sub>6</sub> groups, respectively.

The total weigh losses were theoretically calculated and compared with experimentally. The estimated mass losses for all complexes were presented in Table 3 and observed to good agreement with the formulae suggested from the analytical data.

# **Magnetic Moments Studies**

As is known, magnetic susceptibility measurements provide information regarding the geometric structure of the complexes. Magnetic susceptibility was determined using a magnetic susceptibility balance. The magnetic moment data of the solidstate complexes at room temperature are reported in Table 1. The magnetic susceptibility measurements show that the 3a-3b and 4a-4b complexes have paramagnetic property with a magnetic susceptibility value per atom: 3.60, 3.72 B.M. and 3.65, 3.70 B.M., respectively. These values for Cr(III) Salen/Salophen complexes (3a-4b) are consistent with expected spin-only magnetic moment of an S = 3/2 (3.87 BM). It is seen that the [{Cr(Salen)}<sub>2</sub>O] and [{Cr(Salophen)}<sub>2</sub>O] containing compounds are represented by the electronic structure of  $t_{2g}^{3}e_{g}^{0}$ . The magnetic data for the [{Cr(Salen)}<sub>2</sub>O] and [{Cr(Salophen)}<sub>2</sub>O] complexes demonstrate well agreement with the  $d^3$  metal ion in an octahedral structure. This consequence is supported by the results of the elemental analyses suggesting that these complexes have also an octahedral structure.[12 28]

#### The UV-Vis Spectra

The UV-Vis absorption spectra of ligands (**2a-2b**) and complexes (**3a**, **3b**, **4a**, and **4b**) in DMSO are shown in Figure 6 and their absorption peaks are summarized in Table 4. Figure 6 shows the UV-absorption spectra of **2a** and their complexes (**3a-3b**). The ligand (**2a**) has two absorption bands at around 294 and 375 nm, which originated from  $\pi - \pi^*$  transition of triphenylamine unit and intraligand  $\pi - \pi^*$  transition of the conjugated backbone (**2a**).<sup>[33]</sup> In the absorption spectra of the complexes **3a** and **3b**, the maximum absorptions of the complexes **3a** and **3b** are 360 and 354 nm, which can be assigned to intramolecular

TABLE 4Absorption peaks of the ligands and complexes

Compounds	Absorption peaks (nm)			
2a	294	376		
2b	292	364		
3a	289	360		
3b	290	354		
4a	277	372		
4b	289	358		

 $\pi - \pi^*$  transition of the conjugated backbone (Salen and Salophen). The  $\lambda_{\text{max}}$  of **3a** and **3b** was hypsochromically shifted by about 15 nm and 21 nm, respectively when compared with **2a**. Spectra of **2b** and its complexes (**4a-4b**) given in Figure 6 showed a maximum absorption peak at 364, 372, and 358 nm, respectively. The characteristic absorption peaks of tripheny-lamine unit in complex **4a** and **4b** are unapparent by reason of the enhancing  $\pi$ -conjugated structure.

# **CONCLUSIONS**

In conclusion, two novel Cr(III) Salen/Salophen complexes containing a triphenylamine unit have been efficiently synthesized. These complexes are the examples of mono- and dinuclear complexes bridged by carboxyl to the chromium centers. The UV-vis absorption spectra of these complexes in DMSO were investigated. Also, their structures were characterized by means of elemental analysis, <sup>1</sup>H NMR, FT-IR spectroscopy, thermal analyses, and magnetic susceptibility measurements. The prepared complexes exhibit good thermal stability with a decomposition temperature range from 200 to 900°C. Moreover, the magnetic data for the mono- and dinuclear complexes show good agreement with the d<sup>3</sup> metal ion in an octahedral structure.

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