

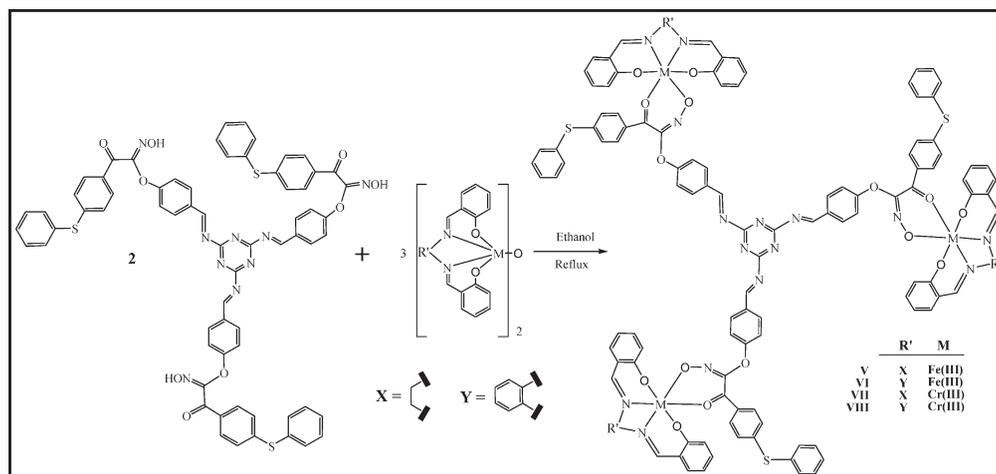
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2,4,6-tris(4-hydroxybenzimidino)-1,3,5-triazine [1,2] (**III**) have been synthesized by the reaction of 1 equiv melamine and three equiv 4-hydroxybenzaldehyde, and characterized by means of elemental analysis, <sup>1</sup>H-NMR (nuclear magnetic resonance spectroscopy), Fourier transform infrared (FTIR) spectroscopy, liquid chromatography-mass spectroscopy (LC-MS). **L** (**IV**) has been synthesized by the reaction of one equiv (**III**) and three equiv 4-(thiophenoxy)phenyloxymoyl chloride (**II**), and characterized by means of the same methods. Then, four novel trinuclear Fe(III) and Cr(III) complexes involving tetradentate Schiff bases *N,N'*-bis(salicylidene)ethylenediamine-(salenH<sub>2</sub>) or bis(salicylidene)-*o*-phenylenediamine-(salophen H<sub>2</sub>) with **L** (**IV**) have been synthesized and characterized by means of elemental analysis, FTIR spectroscopy, LC-MS, thermal analyses. The metal ratios of the prepared complexes have been determined using AAS. The aim of the present study is synthesis of novel tridirectional-trinuclear systems and to present their effects on magnetic behavior of [salenFe(III)], [salophenFe(III)], [salenCr(III)], and [salophenCr(III)] capped complexes. The complexes have also been characterized as low-spin distorted octahedral Fe(III) and Cr(III) bridged by keton-oxime group.

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## INTRODUCTION

1,3,5-Triazine derivatives are widely used as herbicides [3], drugs [4], or polymers [5], like melamine formaldehyde that has excellent thermal and electrical properties [6]. An important class of compounds having anticancer, antitumor, antiviral, and antifungal activity consists of substituted 1,3,5-triazine (*s*-triazine) derivatives. These macrocyclic compounds have been used in the treatment of depression and hence gained a considerable importance. These are valuable bases for estrogen receptor modulators [7] and also used as bridging agents to synthesize herbicides and in the production of drugs or polymers [8].

Macrocyclic molecules present a multitude of new properties [9] and open up vast vistas for applications in

many fields [10,11], such as supramolecular devices, luminescent labels, fluorescent probes in biological and medical applications, magnetic resonance imaging, and catalytic cleavage of RNA, and they are also important ligands [12] for recognizing inorganic and organic cations, anions, and neutral molecules.

The great interest in synthetic macrocycles and macrocycles and their corresponding metal complexes is related to the fact that they can mimic naturally occurring macromolecules in their structural features. The formation of tripodal complexes depends significantly on the dimension of the internal cavity, on the rigidity of the ligand, on the nature of its donor atoms, and on the complexing properties of the counterion. For tripodal compounds, like podands, higher flexibility of arms and

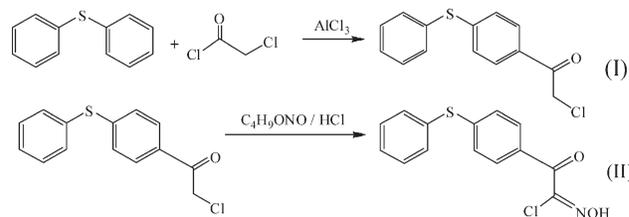
complexation ability grows with the ionic radius of various metal ions [13].

Interest in the metal coordination environment has prompted the study of oxime ligands due to their variable geometries and the tunability of their substituents. Oxime ligands are used as analytical reagents and serve as models for biological systems (e.g. vitamin B12 and dioxygen carriers) as well as catalysts in chemical processes [14].

The magnetochemical properties of the  $\mu$ -oxo-bridged complexes  $[\{\text{Fe}(\text{salen})\}_2\text{O}]$  [ $\text{salenH}_2 = N,N'$ -bis(salicylidene) ethylenediamine)] and  $[\{\text{Fe}(\text{salophen})\}_2\text{O}]$  [ $\text{salophenH}_2 = \text{bis}(\text{salicylidene})\text{-2-phenylenediamine}$ ] and their X-ray studies have widely been presented in the literature [15–22]. Koç and Ucan [23] have reported the synthesis and characterization of 1,3,5-tricarboxylato bridges with  $[\text{salenFe}(\text{III})]$  and  $[\text{salophenFe}(\text{III})]$ . Uysal and Uçan have reported the synthesis and characterization of tricarboxylato triazine and tricatechol triazine bridges with  $[\text{salenFe}(\text{III})]$ ,  $[\text{salophenFe}(\text{III})]$ ,  $[\text{salenCr}(\text{III})]$  and  $[\text{salophenCr}(\text{III})]$  [24,25]. Uysal and Koç have also reported the synthesis and characterization of dendrimeric carboxylato triazine bridges with  $[\text{salenFe}(\text{III})]$ ,  $[\text{salophenFe}(\text{III})]$ ,  $[\text{salenCr}(\text{III})]$ , and  $[\text{salophenCr}(\text{III})]$  [2]. Other complexes of composition  $[\{\text{Fe}(\text{salen})\}_2\text{L}]$  (where L = glutarate, adipate, pimelate, suberate, and dithiooxamidedianion) were prepared by Smekal et al. [26].

A Schiff base complex of chromium(III),  $[\text{Cr}(\text{salen})(\text{OH}_2)_2]^+$ , 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 [27,28]. Their applications have grown rapidly. Various metal-salen complexes in the homogeneous phase such as manganese(III), chromium(III) and nickel(II) salen have been used for the epoxidation of olefins [29–32].

The aim of this study is synthesis of novel tridirectional-trinuclear systems and to present their effects on magnetic behavior of  $[\text{salenFe}(\text{III})]$ ,  $[\text{salophenFe}(\text{III})]$ ,  $[\text{salenCr}(\text{III})]$ , and  $[\text{salophenCr}(\text{III})]$  capped complexes. We also report that synthesized tridirectional melamine Schiff bases present a new scaffold. The reaction of melamine ( $\text{C}_3\text{N}_6\text{H}_6$ ) with 3 equiv of 4-hydroxybenzaldehyde in benzene produces the desired tris-iminophenol in a single step under reflux, coded to be **III**. Then, the reaction of **III** with 3 equiv of 4-(thiophenoxy)phenyloxyhydroxymoyl chloride (**II**) [33] in benzene in a single step under reflux, coded to be **L (IV)**. Their structures were characterized by FTIR,  $^1\text{H-NMR}$ , LC-MS, TGA-DTA, and magnetic susceptibility. The metal ratios of the prepared complexes have been determined using AAS.



**Figure 1.** The synthesis routes for the preparation 4-(thiophenoxy)phenyloxy hydroxymoyl chloride.

## RESULTS AND DISCUSSION

The target ligands were synthesized in two-step from melamine. The conversion of melamine to the trisubstituted-melamine derivative was accomplished in 71% yield. The structural formula of **L (IV)** was verified by elemental analyses,  $^1\text{H-NMR}$ , FTIR and mass spectral data [2,25,33,34] (Figs. 1 and 2, Tables 1, 2). The ligand is soluble in common organic solvents. Synthetic strategy for preparing **L** uses a complex as a “ligand” that contains a potential donor group capable of coordinating to another ligand. Therefore, we choose  $[\text{Fe}(\text{salen})_2\text{O}]$ ,  $[\text{Fe}(\text{salophen})_2\text{O}]$ ,  $[\text{Cr}(\text{salen})_2\text{O}]$ , and  $[\text{Cr}(\text{salophen})_2\text{O}]$  as “ligand complex” [2,24,25,35]. These complexes are some of the first examples of melamine-based trinuclear complexes bridged to the iron/chromium centers by keton and oxime groups. All compounds are stable at room temperature in the solid state, and they are only soluble in organic solvents such as ethylacetate, DMSO, DMF, and insoluble in water. The results of the elemental analyses, given in Table 1, are in a good harmony with the structures suggested for the ligands and their complexes. The results show that all complexes are trinuclear.

When 4-(thiophenoxy)phenyloxyhydroxymoyl chloride (**II**) was added to tripodal Schiff base ligand (**III**), phenolic OH band at  $3338\text{ cm}^{-1}$  disappeared. The vibrations of the triazine C=N (a), azomethine C=N (b), oxime C=N (c), C=O and C—O—C of the free ligands have been observed at 1579, 1628, 1598, 1654, and  $1378\text{ cm}^{-1}$ , respectively, [32,35,36]. In the FTIR spectra of (**IV**), the band at  $3278\text{ cm}^{-1}$  and  $997\text{ cm}^{-1}$  can be assigned to the oxime- O—H and oxime N—O group vibrations, respectively. IR bands at  $1649\text{ cm}^{-1}$  for complex (**V**),  $1653\text{ cm}^{-1}$  for complex (**VI**),  $1652\text{ cm}^{-1}$  for complex (**VII**) and  $1649\text{ cm}^{-1}$  for complex (**VIII**) were assigned to C=N (c) stretching vibrations, 1013, 1015, 1009, and  $1008\text{ cm}^{-1}$  were assigned to N—O stretching vibrations and band at 1536, 1538, 1540, and  $1542\text{ cm}^{-1}$  were assigned to C=N (d) stretching vibrations for complexes (**V**), (**VI**), (**VII**), and (**VIII**), respectively, whereas C=N (d) stretching vibration bands were found at  $1560\text{--}1567\text{ cm}^{-1}$  for  $[\text{Fe}(\text{salen})_2\text{O}]$ ,  $[\text{Fe}(\text{salophen})_2\text{O}]$ ,  $[\text{Cr}(\text{salen})_2\text{O}]$ , and  $[\text{Cr}(\text{salophen})_2\text{O}]$

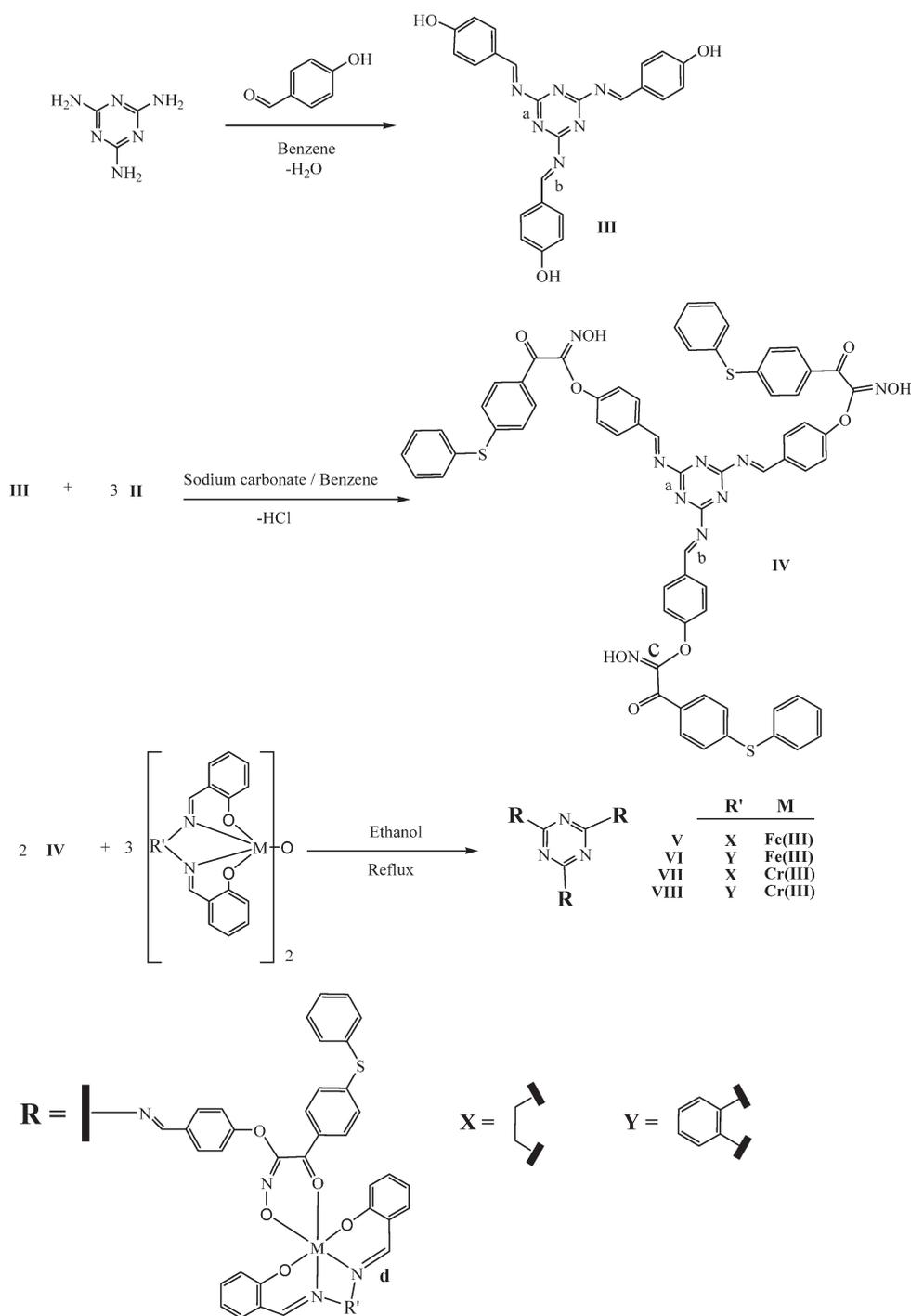


Figure 2. Synthetic routes for the preparation ligand IV and its metal complexes.

complexes [2,23,24,36–41]. In the the FTIR spectra of tripodal-trinuclear complexes, oxime OH band disappears and oxime N–O bands shift upward, suggesting chelation of oxygen atoms to the metal. Bands at 1711, 1709, 1705, and 1710  $\text{cm}^{-1}$  for complexes (V), (VI), (VII), and (VIII) were also assigned to C=O groups since coordination of [Fe(salen)]<sub>2</sub>O, [Fe(salophen)]<sub>2</sub>O, [Cr(salen)]<sub>2</sub>O,

and [Cr(salophen)]<sub>2</sub>O to keton-oxime groups. In the tripodal-trinuclear complexes, the bands in the 545–539 and 477–470  $\text{cm}^{-1}$  ranges can be attributed to the M–N and M–O stretching modes [42].

To identify the structures of the ligands, the <sup>1</sup>H-NMR spectra were recorded in DMSO-*d*<sub>6</sub>. In the <sup>1</sup>H-NMR spectra of (III), the presence of singlet at  $\delta = 6.08$  ppm

**Table 1**

Some physical properties, molecular weight (g/mol) data and elemental analyses, AAS analyses of the ligands and complexes.

Compounds	$\mu_B$ B.M. 296 K	M.p. °C	Yield (%)	Color M <sub>w</sub> [g/mol]	Found (calculated) % of				
					C	H	N	Fe	Cr
C <sub>24</sub> H <sub>18</sub> N <sub>6</sub> O <sub>6</sub> ( <b>III</b> )	–	142	72	White [438.45]	65.67 (65.75)	4.12 (4.14)	19.15 (19.17)	–	–
C <sub>66</sub> H <sub>45</sub> N <sub>9</sub> O <sub>9</sub> S <sub>3</sub> L ( <b>IV</b> )	–	234	62	Orange [1204.34]	65.82 (65.64)	3.77 (3.68)	10.47 (10.31)	–	–
C <sub>114</sub> H <sub>90</sub> N <sub>15</sub> O <sub>15</sub> S <sub>3</sub> Fe <sub>3</sub> L(FeSalen) <sub>3</sub> ( <b>V</b> )	1.72	183 <sup>a</sup>	66	Brown [2173.81]	61.45 (62.99)	3.94 (4.17)	8.73 (9.67)	7.13 (7.71)	–
C <sub>126</sub> H <sub>90</sub> N <sub>15</sub> O <sub>15</sub> S <sub>3</sub> Fe <sub>3</sub> L(FeSalophen) <sub>3</sub> ( <b>VI</b> )	1.75	191 <sup>a</sup>	68	Brown [2317.94]	63.57 (65.29)	3.11 (3.91)	8.23 (9.06)	6.89 (7.23)	–
C <sub>114</sub> H <sub>90</sub> N <sub>15</sub> O <sub>15</sub> S <sub>3</sub> Cr <sub>3</sub> L(CrSalen) <sub>3</sub> ( <b>VII</b> )	3.69	146 <sup>a</sup>	65	Green [2162.26]	61.68 (63.33)	3.33 (4.20)	8.54 (9.72)	–	6.79 (7.21)
C <sub>126</sub> H <sub>90</sub> N <sub>15</sub> O <sub>15</sub> S <sub>3</sub> Cr <sub>3</sub> L(CrSalophen) <sub>3</sub> ( <b>VIII</b> )	3.74	155 <sup>a</sup>	70	Green [2306.39]	64.71 (65.62)	3.28 (3.93)	8.34 (9.11)	–	5.81 (6.76)

<sup>a</sup>Decomposition.

for three phenolic OH and singlet at  $\delta = 9.77$  ppm for MeI–N=CH–Ph–OH showed that three directional linked to melamine had occurred [2]. Then, also <sup>1</sup>H-NMR spectra of confirmed the structures of the synthesized compound **L** (**IV**) had seen that the value of OH chemical shift disappeared [2]. The signal in <sup>1</sup>H-NMR spectrum of (**IV**) at  $\delta$  11.53 ppm correspond to the oxime –OH proton resonances. The peak in <sup>1</sup>H-NMR spectrum of **L** (**IV**) at 10.00 ppm (singlet) correspond to the triazine–CH=N– proton resonances.

The magnetic moments of the complexes given in Table 1 were measured at room temperature. On the basis of spectral evidence, the Fe(III) and Cr(III) complexes have trinuclear structures in which the Fe(III) and Cr(III) cations have a nearly octahedral environment. The magnetic behavior of Fe(III) and Cr(III) complexes is good harmony with proposed trinuclear

structures [43]. The magnetic moment value per metal atom of trinuclear complexes which were constructed from (**IV**) and one of these ligand complexes, [Fe(salen)]<sub>2</sub>O, [Fe(salophen)]<sub>2</sub>O, [Cr(salen)]<sub>2</sub>O, and [Cr(salophen)]<sub>2</sub>O, shows paramagnetic property with a magnetic susceptibility value per atom at 296 K: 1.72–1.75 B.M. [22] and 3.69–3.74 B.M., respectively. For Fe(III) complexes such as (salen or salophen)Fe(III), magnetic moments depend greatly upon the axial ligands. Many literatures have reported that Fe(III) cores exhibit high spin electronic structure ( $S = 5 \times 1/2$ ), if only one ligand donor oxygen atom coordinates to the Fe(III) cores of salen or salophen complexes [44,45]. We reported here that if keton-oxime groups coordinates to Fe(III) core of salen or salophen complexes through its both oxygen atoms, Fe(III) core exhibits low spin electronic structure ( $S = 1/2$ ). That is, Fe(III) has the electronic structure of

**Table 2**

Decomposition steps with the temperature range and weight loss for ligand and complexes.

Compound	Step no	Temp. range(°C)	Weight loss found (calcd.) (%)	Fragment <sup>a</sup>
C <sub>114</sub> H <sub>90</sub> N <sub>15</sub> O <sub>15</sub> S <sub>3</sub> Fe <sub>3</sub> L(FeSalen) <sub>3</sub> ( <b>V</b> )	<b>I</b>	183–286	10.63 (11.59)	CO, NO
	<b>II</b>	314–382	23.47 (25.71)	C <sub>6</sub> H <sub>6</sub> , SH <sub>2</sub>
	<b>III</b>	490–623	34.68 (37.01)	C <sub>6</sub> H <sub>6</sub> , CO <sub>2</sub> , H <sub>2</sub> O, N <sub>2</sub>
	<b>IV</b>	664–787	19.12 (21.96)	C <sub>6</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>2</sub> , N <sub>2</sub>
C <sub>126</sub> H <sub>90</sub> N <sub>15</sub> O <sub>15</sub> S <sub>3</sub> Fe <sub>3</sub> L(FeSalophen) <sub>3</sub> ( <b>VI</b> )	<b>I</b>	191–295	9.34 (10.91)	CO, NO
	<b>II</b>	323–397	22.83 (24.07)	C <sub>6</sub> H <sub>6</sub> , SH <sub>2</sub>
	<b>III</b>	506–648	37.41 (40.92)	C <sub>6</sub> H <sub>6</sub> , CO <sub>2</sub> , H <sub>2</sub> O, N <sub>2</sub>
	<b>IV</b>	679–792	17.96 (20.59)	C <sub>6</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>2</sub> , N <sub>2</sub>
C <sub>114</sub> H <sub>90</sub> N <sub>15</sub> O <sub>15</sub> S <sub>3</sub> Cr <sub>3</sub> L(CrSalen) <sub>3</sub> ( <b>VII</b> )	<b>I</b>	146–221	9.82 (11.66)	CO, NO
	<b>II</b>	286–356	22.91 (25.84)	C <sub>6</sub> H <sub>6</sub> , SH <sub>2</sub>
	<b>III</b>	424–563	35.41 (37.23)	C <sub>6</sub> H <sub>6</sub> , CO <sub>2</sub> , H <sub>2</sub> O, N <sub>2</sub>
	<b>IV</b>	671–790	18.32 (21.52)	C <sub>6</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>2</sub> , N <sub>2</sub>
C <sub>126</sub> H <sub>90</sub> N <sub>15</sub> O <sub>15</sub> S <sub>3</sub> Cr <sub>3</sub> L(CrSalophen) <sub>3</sub> ( <b>VIII</b> )	<b>I</b>	155–232	8.97 (10.93)	CO, NO
	<b>II</b>	291–368	23.11 (24.23)	C <sub>6</sub> H <sub>6</sub> , SH <sub>2</sub>
	<b>III</b>	435–576	38.93 (41.15)	C <sub>6</sub> H <sub>6</sub> , CO <sub>2</sub> , H <sub>2</sub> O, N <sub>2</sub>
	<b>IV</b>	669–784	18.03 (20.18)	C <sub>6</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>2</sub> , N <sub>2</sub>

<sup>a</sup>These are conjectural data.

$t_{2g}^5 e_g^0$  [23–25,39]. It is seen that the  $[\text{Fe}(\text{salen})]_2\text{O}$ ,  $[\text{Fe}(\text{salophen})]_2\text{O}$ ,  $[\text{Cr}(\text{salen})]_2\text{O}$ , and  $[\text{Cr}(\text{salophen})]_2\text{O}$  containing compounds are represented by the electronic structure of  $t_{2g}^5 e_g^0$  and  $t_{2g}^3 e_g^0$ . The magnetic data for the  $[\text{Fe}(\text{salen})]$ ,  $[\text{Fe}(\text{salophen})]$ ,  $[\text{Cr}(\text{salen})]$ , and  $[\text{Cr}(\text{salophen})]$  containing tripodal complexes show good harmony with the low-spin  $d^5$  and  $d^3$  metal ion in an octahedral structure. This consequence is supported by the results of the elemental analyses suggesting that these trinuclear complexes have also an octahedral structure [22,23,38–40,43,46].

All the complexes have also been thermally investigated in the range of 30–900°C and their plausible degradation schemes are presented in Table 2 [47,48]. Thermal decomposition of the anhydrous  $[\text{Fe}(\text{salen})]$ ,  $[\text{Fe}(\text{salophen})]$ ,  $[\text{Cr}(\text{salen})]$ , and  $[\text{Cr}(\text{salophen})]$  complexes left from the ligand (IV) have started in the range of the first step 146–295. And, the anhydrous  $[\text{Fe}/\text{Cr}(\text{salen}$  or  $\text{salophen})]$  complexes detached from the ligand IV. The thermal analyses (TG, DTA) of complexes V–VIII showed a weight loss theoretically calculated to be 10.59–11.66%, experimentally they were observed to be 8.97–10.63%, respectively. It can be attributed that keton-oxime groups decomposed in this step. At the second step was observed in the range 286–397°C. The thermal analyses (TG, DTA) of complexes V–VIII showed a weight loss theoretically calculated to be 24.07–25.84%, experimentally they were observed to be 22.83–23.47%, respectively. It can be attributed that salen or salophen groups decomposed in this step. The third step was observed in the range 424–648°C. The thermal analyses (TG, DTA) of complexes V–VIII showed a weight loss theoretically calculated to be 37.01–41.15%, experimentally they were observed to be 34.68–38.93%, respectively. It can be attributed that diphenyltyoeter groups decomposed in this step. And, the final decomposition step 664–794°C. The final decomposition products were metals and triazine ring. The observed weight losses for all ligands and complexes are in good harmony with the calculated values.

All ligand and complexes were investigated their LC-MS (ESI+) spectrum. The calculated molecular weights of all ligand and complexes have been given in (Table 1). Molecular peaks of the cations are observed with the same isotope distribution as the calculated ones, theoretically. That is, from the investigation of LC-MS spectra of the compounds, it has been seen that molecular weights of ligands and complexes are in good harmony with the intensity observed values in LC-MS spectra.

## CONCLUSIONS

In this study, novel tridirectional and melamine cored Schiff bases III were synthesized. Synthetic strategy for preparing tripodal-trinuclear uses a complex as a

“ligand” that contains a potential donor group capable of coordinating to the other ligand. We have chosen  $[\text{Fe}(\text{salen})]_2\text{O}$ ,  $[\text{Fe}(\text{salophen})]_2\text{O}$ ,  $[\text{Cr}(\text{salen})]_2\text{O}$ , and  $[\text{Cr}(\text{salophen})]_2\text{O}$  as “ligand complexes” as they can coordinate to the other ligand. These complexes are the examples of tripodal-trinuclear complexes bridged by ketoxime groups to the iron and chromium centers. Their structures were characterized by means of elemental analysis,  $^1\text{H-NMR}$ , FTIR spectroscopy, LC-MS, thermal analyses, and magnetic susceptibility measurements. The magnetic data for the tripodal-trinuclear complexes show good harmony with the  $d^5$  and  $d^3$  metal ion in an octahedral structure.

## EXPERIMENTAL

**General.** Melamine, 4-hydroxybenzaldehyde and all other reagents were purchased from Merck and used without further purification.  $[\text{Fe}(\text{salen})]_2\text{O}$ ,  $[\text{Fe}(\text{salophen})]_2\text{O}$ ,  $[\text{Cr}(\text{salen})]_2\text{O}$ , and  $[\text{Cr}(\text{salophen})]_2\text{O}$  were prepared according to previously published methods [22,44,46]. 4-(Chloroacetyl)diphenylthioether (I), 4-(thiophenoxy)phenyloxylohydroxymoyl chloride (II), 2,4,6-tris(4-hydroxybenzimidino)–1,3,5-triazine (III) were synthesized according to previous reported methods [2,33].  $^1\text{H-NMR}$  spectra were taken using a Varian-Mercury 200 NMR spectrometer. The chemical shifts for NMR spectra are ascribed in relation to the external TMS standard. IR spectra were recorded using a Perkin-Elmer 1600 FTIR spectrometer using KBr pellets. Elemental analyses were carried out using a Hewlett-Packard 185 analyzer. Metal contents in complexes were determined using Unicam 929 AAS spectrometer. Mass spectra of the compounds were obtained on Varian MAT 711 spectrometer. pH values were measured on a WTW pH, 537 pH meter. Magnetic susceptibilities of metal complexes were determined using a Sheerwood Scientific MX Gouy magnetic susceptibility apparatus carried out using the Gouy method with  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as calibrant. The effective magnetic moments,  $\mu_{\text{eff}}$ , per metal atom was calculated from the expression:  $\mu_{\text{eff}} = 2.84\sqrt{\chi_M T}$  B.M., where  $\chi_M$  is the molar susceptibility.

**The synthesis of L (IV).** To a suspension of 2,4,6-tris(4-hydroxybenzimidino)–1,3,5-triazine (2.19 g, 5 mmol) and sodium carbonate (10.00 g) in 100 mL of benzene, stirred at room temperature for 10 min, 3 equiv amount of 4-(thiophenoxy)phenyloxylohydroxymoyl chloride (4.38 g, 15 mmol) in 20 mL benzene was added. The mixture was refluxed for 120 h and then filtered. The precipitate washed with hot ethylacetate, and the solvent mixture was evaporated under vacuum. The benzene-ethylacetate solution of product was evaporated. The product was purified using Column Chromatography and using 1:4 ethylacetate/*n*-hexane mixture as eluent. FTIR( $\text{cm}^{-1}$ ) 3278 (OH), 2895 (CHar), 1579 (triazine C=N a), 1628 (CH=N b), 1598 (CH=N c), 1654 (C=O), 997 (N–O), and 1378 (C–O–C).  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ )  $\delta$  11.53 (s, broad, 3H),  $\delta$  10.00 (s, 3H), 8.16 (dd, 12H, Ar-H, *J* 8.4, 4.3 Hz), 7.52–7.46 (m, 21H), 7.29 (d, 6H, Ar-H, *J* 8.5 Hz). LC-MS data for IV *m/z*: 1204 [100%, IV]. Molecular peaks of the cations are observed with the same isotope distribution as the theoretical

ones. Some physical properties and yield for **IV** is given in Table 1.

**Preparation of L(FeSalen)<sub>3</sub> (V), L(FeSalophen)<sub>3</sub> (VI), L(CrSalen)<sub>3</sub> (VII) and L(CrSalophen)<sub>3</sub> (VIII) complexes.** A solution of **L (IV)** (2.41 g, 2.0 mmol) and [Fe(salen)]<sub>2</sub>O or [Cr(salen)]<sub>2</sub>O (3.0 mmol) or [Fe(salophen)]<sub>2</sub>O or [Cr(salophen)]<sub>2</sub>O (3.0 mmol) in 50 mL of ethanol were refluxed for 20 h. The mixture was allowed to room temperature. Then the mixture was filtered and dried in vacuum. LC-MS data, *m/z*: 2173 [100%, **V**], *m/z*: 2317 [100%, **VI**], *m/z*: 2162 [100%, **VII**], and *m/z*: 2306 [100%, **VIII**]. Molecular peaks of the cations are observed with the same isotope distribution as the theoretical ones. Some physical properties and yield for **V**, **VI**, **VII**, and **VIII** are given in Table 1. FTIR(cm<sup>-1</sup>) for complexes **V**: 2892 (CH<sub>ar</sub>), 1571 (triazine C=N a), 1633 (CH=N b), 1649 (C=N c), 1536 (C=N d), 1711 (C=O), 1013 (N—O), 1376 (C—O—C), 539 (M—N), 476 (M—O), for complexes **VI**: 2890 (CH<sub>ar</sub>), 1568 (triazine C=N a), 1629 (CH=N b), 1653 (C=N c), 1538 (C=N d), 1709 (C=O), 1015 (N—O), 1379 (C—O—C), 541 (M—N), 477 (M—O), for complexes **VII**: 2889 (CH<sub>ar</sub>), 1572 (triazine C=N a), 1631 (CH=N b), 1652 (C=N c), 1540 (C=N d), 1705 (C=O), 1009 (N—O), 1380 (C—O—C), 545 (M—N), 470 (M—O), for complexes **VIII**: 2888 (CH<sub>ar</sub>), 1570 (triazine C=N a), 1627 (CH=N b), 1649 (C=N c), 1542 (C=N d), 1710 (C=O), 1008 (N—O), 1382 (C—O—C), 541 (M—N), 476 (M—O).

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