

## Synthetic Communications

An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: 0039-7911 (Print) 1532-2432 (Online) Journal homepage: <http://www.tandfonline.com/loi/lcyc20>

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To cite this article: Şaban Uysal , Ziya Erdem Koç , Şeyma Çelikkbilek & H. İsmet Uçan (2012) Synthesis of Star-Shaped Macromolecular Schiff Base Complexes Having Melamine Cores and Their Magnetic and Thermal Behaviors, Synthetic Communications, 42:7, 1033-1044, DOI: 10.1080/00397911.2010.535635

To link to this article: <http://dx.doi.org/10.1080/00397911.2010.535635>



Accepted author version posted online: 06 Sep 2011.  
Published online: 06 Sep 2011.



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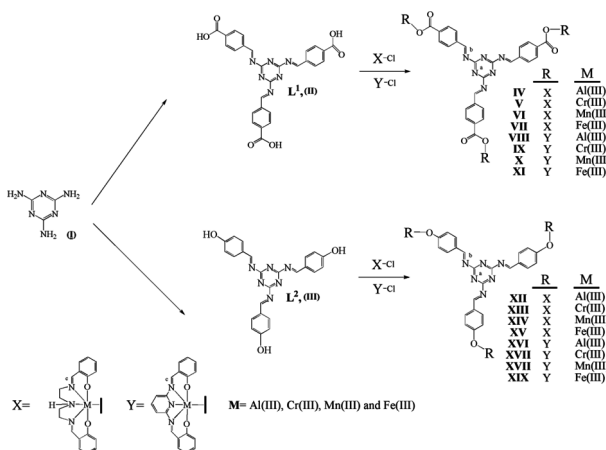
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## SYNTHESIS OF STAR-SHAPED MACROMOLECULAR SCHIFF BASE COMPLEXES HAVING MELAMINE CORES AND THEIR MAGNETIC AND THERMAL BEHAVIORS

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### GRAPHICAL ABSTRACT



**Abstract** We aim to study magnetic and thermal behaviors of some melamine cored macromolecular Schiff base complexes. In this context, tripodal ligands were synthesized by reacting melamine with 4-carboxybenzaldehyde or 4-hydroxybenzaldehyde. Then, 16 new trinuclear Fe(III), Cr(III), Mn(III), and Al(III) complexes were synthesized by reacting the ligands [tris-(4-carboxybenzimidino)-1,3,5-triazine] or tris-(4-hydroxybenzimidino)-1,3,5-triazine] with pentadentate Schiff bases *N,N'*-bis(1-hydroxy-2-benzylidene)-1,7-diamino-4-azaheptane or *N,N'*-bis(salicylidene)pyridine-2,6-diamine. Later, ligands and complexes were characterized by means of elemental analysis, infrared spectroscopy, <sup>1</sup>H NMR, liquid chromatography–mass spectrometry, thermal analyses, and magnetic susceptibility measurements. Finally, metal ratios of the prepared complexes were determined by using atomic adsorption spectrometry. The complexes were also characterized as distorted octahedral high-spin *d*<sup>3</sup> (*S* = 3 × 1/2) Cr(III), high-spin *d*<sup>5</sup> (*S* = 5 × 1/2) Fe(III),

Received September 16, 2010.

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*low-spin  $d^4$  ( $S=2 \times 1/2$ ) Mn(III), and diamagnetic Al(III) bridged by  $-OH$  group of  $COO^-$  or  $OH$  group of phenol.*

**Keywords** Melamine; metal complexes; saldeta; salpy; Schiff bases; s-triazine

## INTRODUCTION

Substituted s-triazine derivatives have biological activities such as anticancer,<sup>[1]</sup> antiviral,<sup>[2]</sup> estrogen receptor modulatory,<sup>[3]</sup> and antimalarial<sup>[4–10]</sup> activities. Considering this information, the design and synthesis of effective and potent antimicrobials are of immense significance for medicinal chemists.<sup>[11,12]</sup> Much effort has been devoted to the synthesis of s-triazine (melamine) derivatives by different groups in the recent years.<sup>[13–18]</sup>

Melamine resins have been used in many applications including the manufacture of plastic dishes under the trade name Melmac. 1,3,5-Triazine derivatives are widely used, such as melamine–formaldehyde, which has excellent thermal and electrical properties.<sup>[19,20]</sup>

The class of transition-metal-containing high-spin molecules has been enriched considerably over the past 20 years.<sup>[21–23]</sup> In parallel to the topology of iron(III), considerable attention has been given to the metal cyanides having octahedral vertices with extra metal complexes  $[M(\overset{\delta}{L})]$  surrounded by a suitable pentadentate blocking ligand.<sup>[24–26]</sup>  ${}^5LH_2 = \text{saldeta} = N,N'$ -bis(1-hydroxy-2-benzylidene)-1,7-diamino-4-azaheptane and  ${}^5L_{py}H_2 = \text{salpy} = N,N'$ -bis(salicylidene)pyridine-2,6-diamine represent two of the candidates to function as pentadentate blocking ligands. Fe(III) and Cr(III) complexes of saldeta have been well characterized.<sup>[26,27]</sup> The Fe(III) complex  $[Fe^{III}(\overset{\delta}{L})Cl]$  is high-spin. The pyridine complex  $[Fe^{III}(\overset{\delta}{L}_{py})Cl]$  exhibits the thermally induced spin crossover: the low-spin to high-spin transition.

Our previous work has included complexes with low-spin metal centers because both oxygen atoms of ligands coordinated to metal centers of the ligand complexes. Unlike our previous work, this study investigates whether magnetic moment values of the metal centers have high spin or low spin when only one oxygen atom of these ligands is coordinated to the metal center of ligand complexes.

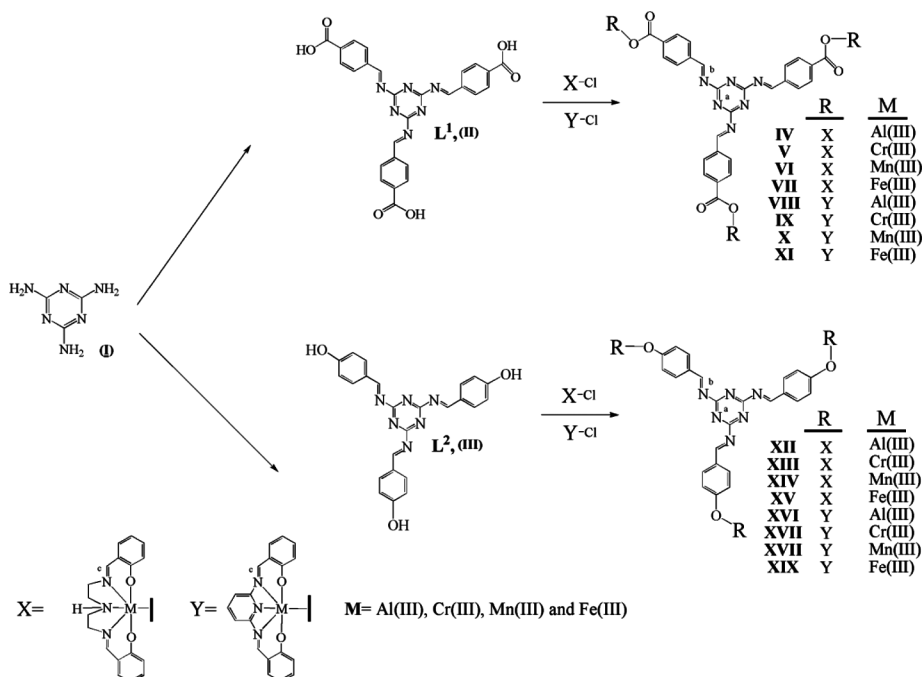
We report here that Schiff bases including tricarboxylate and triphenolate groups were synthesized to be new templates. The reaction of melamine ( $C_3N_6H_6$ ) with 3 equiv of 4-carboxybenzaldehyde or 4-hydroxybenzaldehyde in benzene constituted the desired triazomethine groups in a single step.<sup>[14,17]</sup> Therefore, in the present study, we aimed to synthesize other star-shaped macromolecular Schiff base complexes having melamine core bridges and to present their influences on the magnetic behavior of the prepared complexes. We also focused on trinuclear systems formed by the carboxylato or phenolato bridges, and associated data are in the literature.<sup>[13,14,17,28–32]</sup> Because they have high paramagnetic character, we plan to use some of these complexes as molecular magnets in the near future.

## RESULTS AND DISCUSSION

The target ligands were synthesized in one step from melamine.<sup>[14,17]</sup> The conversion of melamine to the trisubstituted-melamine derivative was accomplished

in 72–92% yield. The structural formula of the 2,4,6-tris(4-carboxybenzimidino)-1,3,5-triazine **L<sup>1</sup>** (**II**) and 2,4,6-tris(4-hydroxybenzimidino)-1,3,5-triazine **L<sup>2</sup>** (**III**) were verified by elemental analyses, <sup>1</sup>H NMR, Fourier transform infrared (FT-IR), and mass spectral data<sup>[14,17]</sup> (Fig. 1, Tables 1 and 2). The ligands are soluble in common organic solvents. Synthetic strategies for preparing trinuclear-iminocarboxylate and trinuclear-iminophenolate use a complex as a “ligand” that contains a potential donor group capable of coordinating to another ligand. Therefore, we chose [SaldetaAl/Cr/Mn/Fe]Cl or [SalpyAl/Cr/Mn/Fe]Cl as ligand complexes.<sup>[33]</sup> These complexes are some of the first examples of melamine-based trinuclear complexes bridged to the Al(III)/Cr(III)/Mn(III)/Fe(III) centers by carboxylate or phenolate anions. All compounds are stable at room temperature in the solid state, and they are only soluble in organic solvents such as ethylacetate, dimethylsulfoxide (DMSO) and dimethylformamide (DMF), but are 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.

To identify the structure of **II**, the <sup>1</sup>H NMR spectra were recorded in DMSO-d<sub>6</sub>. <sup>1</sup>H NMR spectra also confirmed the structure of the synthesized compound. The signals in the <sup>1</sup>H NMR spectrum of 2,4,6-tris(4-carboxybenzimidino)-1,3,5-triazine (**L<sup>1</sup>**) at δ 9.99 ppm correspond to three –N=CH– groups.<sup>[17]</sup> Similarly, to identify the structure of **III**, the <sup>1</sup>H NMR spectra were recorded in DMSO-d<sub>6</sub>. <sup>1</sup>H NMR spectra also confirmed the structure of the synthesized compound. The signals



**Figure 1.** Synthetic route of ligands and complexes. Bonds labelled as a, b, and c are listed in Table 2.

**Table 1.** Physical properties, molecular weight (g/mol), elemental analyses, and AAS analyses of the ligands and complexes

Compound	$\mu_B$	Mp (°C)	Yield (%)	$M_W$ (g/mol)	Found and (calculated) (%)				
					C	N	H	M	
<b>C<sub>27</sub>H<sub>18</sub>N<sub>6</sub>O<sub>6</sub></b> <b>L<sup>1</sup></b>	<b>II</b>	—	345 <sup>a</sup>	92	522.00	<b>61.98</b> (62.07)	<b>16.01</b> (16.09)	<b>3.40</b> (3.45)	
<b>C<sub>24</sub>H<sub>18</sub>N<sub>6</sub>O<sub>3</sub></b> <b>L<sup>2</sup></b>	<b>III</b>	—	142	72	438.45	<b>65.67</b> (65.75)	<b>19.15</b> (19.17)	<b>4.12</b> (4.14)	
<b>C<sub>81</sub>H<sub>72</sub>N<sub>15</sub>O<sub>12</sub>Al<sub>3</sub></b> [(AlSaldeta) <sub>3</sub> L <sup>1</sup> ]	<b>IV</b>	Dia	266 <sup>a</sup>	68	1472.28	<b>65.86</b> (66.02)	<b>13.88</b> (14.26)	<b>4.82</b> (4.89)	<b>5.42</b> (5.50)
<b>C<sub>81</sub>H<sub>72</sub>N<sub>15</sub>O<sub>12</sub>Cr<sub>3</sub></b> [(CrSaldeta) <sub>3</sub> L <sup>1</sup> ]	<b>V</b>	3.73	280 <sup>a</sup>	65	1498.00	<b>64.57</b> (64.89)	<b>13.86</b> (14.02)	<b>4.75</b> (4.81)	<b>10.08</b> (10.41)
<b>C<sub>81</sub>H<sub>72</sub>N<sub>15</sub>O<sub>12</sub>Mn<sub>3</sub></b> [(MnSaldeta) <sub>3</sub> L <sup>1</sup> ]	<b>VI</b>	2.94	265 <sup>a</sup>	75	1500.94	<b>64.35</b> (64.76)	<b>13.77</b> (13.99)	<b>4.72</b> (4.80)	<b>10.67</b> (10.99)
<b>C<sub>81</sub>H<sub>72</sub>N<sub>15</sub>O<sub>12</sub>Fe<sub>3</sub></b> [(FeSaldeta) <sub>3</sub> L <sup>1</sup> ]	<b>VII</b>	5.21	287 <sup>a</sup>	86	1501.85	<b>64.41</b> (64.72)	<b>13.75</b> (13.98)	<b>4.70</b> (4.79)	<b>10.87</b> (11.19)
<b>C<sub>84</sub>H<sub>54</sub>N<sub>15</sub>O<sub>12</sub>Al<sub>3</sub></b> [(AlSalpyr) <sub>3</sub> L <sup>1</sup> ]	<b>VIII</b>	Dia	292 <sup>a</sup>	66	1490.28	<b>67.56</b> (67.64)	<b>14.01</b> (14.09)	<b>3.59</b> (3.62)	<b>5.41</b> (5.44)
<b>C<sub>84</sub>H<sub>54</sub>N<sub>15</sub>O<sub>12</sub>Cr<sub>3</sub></b> [(CrSalpyr) <sub>3</sub> L <sup>1</sup> ]	<b>IX</b>	3.78	288 <sup>a</sup>	60	1516.00	<b>66.15</b> (66.49)	<b>13.68</b> (13.85)	<b>3.50</b> (3.56)	<b>10.00</b> (10.29)
<b>C<sub>84</sub>H<sub>54</sub>N<sub>15</sub>O<sub>12</sub>Mn<sub>3</sub></b> [(MnSalpyr) <sub>3</sub> L <sup>1</sup> ]	<b>X</b>	2.97	283 <sup>a</sup>	70	1518.94	<b>66.11</b> (66.36)	<b>13.62</b> (13.83)	<b>3.50</b> (3.56)	<b>10.61</b> (10.86)
<b>C<sub>84</sub>H<sub>54</sub>N<sub>15</sub>O<sub>12</sub>Fe<sub>3</sub></b> [(FeSalpyr) <sub>3</sub> L <sup>1</sup> ]	<b>XI</b>	5.25	285 <sup>a</sup>	85	1519.85	<b>66.13</b> (66.32)	<b>13.63</b> (13.82)	<b>3.51</b> (3.55)	<b>10.85</b> (11.05)
<b>C<sub>78</sub>H<sub>72</sub>N<sub>15</sub>O<sub>9</sub>Al<sub>3</sub></b> [(AlSaldeta) <sub>3</sub> L <sup>2</sup> ]	<b>XII</b>	Dia	215 <sup>a</sup>	70	1388.28	<b>66.91</b> (67.42)	<b>15.02</b> (15.13)	<b>5.11</b> (5.19)	<b>5.80</b> (5.83)
<b>C<sub>78</sub>H<sub>72</sub>N<sub>15</sub>O<sub>9</sub>Cr<sub>3</sub></b> [(CrSaldeta) <sub>3</sub> L <sup>2</sup> ]	<b>XIII</b>	3.75	234 <sup>a</sup>	68	1414.00	<b>61.60</b> (61.65)	<b>13.77</b> (13.83)	<b>4.65</b> (4.78)	<b>10.16</b> (10.27)
<b>C<sub>78</sub>H<sub>72</sub>N<sub>15</sub>O<sub>9</sub>Mn<sub>3</sub></b> [(MnSaldeta) <sub>3</sub> L <sup>2</sup> ]	<b>XIV</b>	2.98	260 <sup>a</sup>	77	1416.94	<b>65.88</b> (66.06)	<b>14.75</b> (14.82)	<b>5.03</b> (5.08)	<b>11.43</b> (11.64)
<b>C<sub>78</sub>H<sub>72</sub>N<sub>15</sub>O<sub>9</sub>Fe<sub>3</sub></b> [(FeSaldeta) <sub>3</sub> L <sup>2</sup> ]	<b>XV</b>	5.22	263 <sup>a</sup>	84	1417.85	<b>61.13</b> (61.19)	<b>13.66</b> (13.72)	<b>4.68</b> (4.74)	<b>10.82</b> (10.94)
<b>C<sub>81</sub>H<sub>54</sub>N<sub>15</sub>O<sub>9</sub>Al<sub>3</sub></b> [(AlSalpyr) <sub>3</sub> L <sup>2</sup> ]	<b>XVI</b>	Dia	140 <sup>a</sup>	70	1406.28	<b>68.45</b> (69.12)	<b>14.64</b> (14.93)	<b>3.75</b> (3.84)	<b>5.68</b> (5.76)
<b>C<sub>81</sub>H<sub>54</sub>N<sub>15</sub>O<sub>9</sub>Cr<sub>3</sub></b> [(CrSalpyr) <sub>3</sub> L <sup>2</sup> ]	<b>XVII</b>	3.76	145 <sup>a</sup>	64	1432.00	<b>63.17</b> (63.28)	<b>13.54</b> (13.67)	<b>3.48</b> (3.54)	<b>10.09</b> (10.15)
<b>C<sub>81</sub>H<sub>54</sub>N<sub>15</sub>O<sub>9</sub>Mn<sub>3</sub></b> [(MnSalpyr) <sub>3</sub> L <sup>2</sup> ]	<b>XVIII</b>	2.96	168 <sup>a</sup>	75	1434.94	<b>67.43</b> (67.74)	<b>14.27</b> (14.63)	<b>3.55</b> (3.76)	<b>11.21</b> (11.49)
<b>C<sub>81</sub>H<sub>54</sub>N<sub>15</sub>O<sub>9</sub>Fe<sub>3</sub></b> [(FeSalpyr) <sub>3</sub> L <sup>2</sup> ]	<b>XIX</b>	5.24	150 <sup>a</sup>	82	1435.85	<b>62.67</b> (62.81)	<b>13.46</b> (13.56)	<b>3.44</b> (3.51)	<b>10.73</b> (10.82)

<sup>a</sup>Decomposition, M = Al, Cr, Mn, Fe.

in the <sup>1</sup>H NMR spectrum of 2,4,6-tris(4-hydroxybenzimidino)-1,3,5-triazine (**L2**) at  $\delta$  9.77 ppm correspond to three  $-\text{N}=\text{CH}-$  groups and at  $\delta$  6.08 ppm correspond to three  $-\text{OH}$  groups.<sup>[14]</sup>

FT-IR spectra of **II** show two strong bands for C=N (**a**) and C=N (**b**) at 1594 and 1659  $\text{cm}^{-1}$  in accordance with the study reported recently.<sup>[13–17]</sup> A strong broad band at 1690  $\text{cm}^{-1}$  indicates the presence of carboxylic acid carbonyl C=O stretching vibration.<sup>[13,17,34,35]</sup> The band at 1448  $\text{cm}^{-1}$  is for phenyl group (Table 2). FT-IR spectra of **III** show two strong bands for C=N (**a**) and C=N (**b**) at 1565 and

**Table 2.** The characteristic FTIR bands (cm<sup>-1</sup>) for ligands and complexes

Compounds	C=N	C=O	C-H <sub>ar</sub>	C-H <sub>al</sub>	COO-	C-O <sub>ph</sub>	N-H	O-H
<b>II</b>	1594	1690	3155	2863	1405	—	—	3012
<b>C<sub>27</sub>H<sub>18</sub>N<sub>6</sub>O<sub>6</sub></b> <b>L<sup>1</sup></b>	1659							
<b>III</b>	1565 <sup>a</sup>	—	3163	2842	—	1296	—	3338
<b>L<sup>2</sup></b>	1615 <sup>b</sup>							
<b>IV</b>	1591 <sup>a</sup>	1692	3192	2918	1386	1295	3258	—
<b>C<sub>81</sub>H<sub>72</sub>N<sub>15</sub>O<sub>12</sub>Al<sub>3</sub></b> <b>[(AlSaldeta)<sub>3</sub>L<sup>1</sup>]</b>	1621 <sup>b</sup> 1540 <sup>c</sup>			2818				
<b>V</b>	1591 <sup>a</sup>	1691	3197	2925	1383	1294	3258	—
<b>C<sub>81</sub>H<sub>72</sub>N<sub>15</sub>O<sub>12</sub>Cr<sub>3</sub></b> <b>[(CrSaldeta)<sub>3</sub>L<sup>1</sup>]</b>	1620 <sup>b</sup> 1545 <sup>c</sup>			2815				
<b>VI</b>	1591 <sup>a</sup>	1692	3195	2927	1385	1295	3268	—
<b>C<sub>81</sub>H<sub>72</sub>N<sub>15</sub>O<sub>12</sub>Mn<sub>3</sub></b> <b>[(MnSaldeta)<sub>3</sub>L<sup>1</sup>]</b>	1622 <sup>b</sup> 1541 <sup>c</sup>			2819				
<b>VII</b>	1591 <sup>a</sup>	1692	3193	2920	1383	1296	3258	—
<b>C<sub>81</sub>H<sub>72</sub>N<sub>15</sub>O<sub>12</sub>Fe<sub>3</sub></b> <b>[(FeSaldeta)<sub>3</sub>L<sup>1</sup>]</b>	1619 <sup>b</sup> 1542 <sup>c</sup>			2813				
<b>VIII</b>	1591 <sup>a</sup>	1690	3198	2938	1390	1295	—	—
<b>C<sub>84</sub>H<sub>54</sub>N<sub>15</sub>O<sub>12</sub>Al<sub>3</sub></b> <b>[(AlSalpy)<sub>3</sub>L<sup>1</sup>]</b>	1608 <sup>b</sup> 1536 <sup>c</sup> –1552 <sup>py</sup>			2829				
<b>IX</b>	1591 <sup>a</sup>	1691	3192	2932	1389	1294	—	—
<b>C<sub>84</sub>H<sub>54</sub>N<sub>15</sub>O<sub>12</sub>Cr<sub>3</sub></b> <b>[(CrSalpy)<sub>3</sub>L<sup>1</sup>]</b>	1610 <sup>b</sup> 1537 <sup>c</sup> –1555 <sup>py</sup>			2822				
<b>X</b>	1591 <sup>a</sup>	1690	3194	2940	1388	1296	—	—
<b>C<sub>84</sub>H<sub>54</sub>N<sub>15</sub>O<sub>12</sub>Mn<sub>3</sub></b> <b>[(MnSalpy)<sub>3</sub>L<sup>1</sup>]</b>	1612 <sup>b</sup> 1537 <sup>c</sup> –1554 <sup>py</sup>			2829				
<b>XI</b>	1591 <sup>a</sup>	1690	3196	2935	1386	1294	—	—
<b>C<sub>84</sub>H<sub>54</sub>N<sub>15</sub>O<sub>12</sub>Fe<sub>3</sub></b> <b>[(FeSalpy)<sub>3</sub>L<sup>1</sup>]</b>	1606 <sup>b</sup> 1536 <sup>c</sup> –1553 <sup>py</sup>			2827				
<b>XII</b>	1585 <sup>a</sup>	—	3195	2938	—	1294	3258	—
<b>C<sub>78</sub>H<sub>72</sub>N<sub>15</sub>O<sub>9</sub>Al<sub>3</sub></b> <b>[(AlSaldeta)<sub>3</sub>L<sup>2</sup>]</b>	1629 <sup>b</sup> 1540 <sup>c</sup>			2815				
<b>XIII</b>	1586 <sup>a</sup>	—	3178	2929	—	1295	3258	—
<b>C<sub>78</sub>H<sub>72</sub>N<sub>15</sub>O<sub>9</sub>Cr<sub>3</sub></b> <b>[(CrSaldeta)<sub>3</sub>L<sup>2</sup>]</b>	1624 <sup>b</sup> 1541 <sup>c</sup>			2818				
<b>XIV</b>	1588 <sup>a</sup>	—	3186	2927	—	1295	3258	—
<b>C<sub>78</sub>H<sub>72</sub>N<sub>15</sub>O<sub>9</sub>Mn<sub>3</sub></b> <b>[(MnSaldeta)<sub>3</sub>L<sup>2</sup>]</b>	1628 <sup>b</sup> 1540 <sup>c</sup>			2813				
<b>XV</b>	1584 <sup>a</sup>	—	3185	2925	—	1296	3258	—
<b>C<sub>78</sub>H<sub>72</sub>N<sub>15</sub>O<sub>9</sub>Fe<sub>3</sub></b> <b>[(FeSaldeta)<sub>3</sub>L<sup>2</sup>]</b>	1625 <sup>b</sup> 1541 <sup>c</sup>			2812				
<b>XVI</b>	1585 <sup>a</sup>	—	3055	2930	—	1294	—	—
<b>C<sub>81</sub>H<sub>54</sub>N<sub>15</sub>O<sub>9</sub>Al<sub>3</sub></b> <b>[(AlSalpyr)<sub>3</sub>L<sup>2</sup>]</b>	1605 <sup>b</sup> 1535 <sup>c</sup> –1554 <sup>py</sup>			2825				
<b>XVII</b>	1587 <sup>a</sup>	—	3055	2926	—	1296	—	—
<b>C<sub>81</sub>H<sub>54</sub>N<sub>15</sub>O<sub>9</sub>Cr<sub>3</sub></b> <b>[(CrSalpyr)<sub>3</sub>L<sup>2</sup>]</b>	1608 <sup>b</sup> 1536 <sup>c</sup> –1556 <sup>py</sup>			2832				
<b>XVIII</b>	1583 <sup>a</sup>	—	3055	2924	—	1295	—	—
<b>C<sub>81</sub>H<sub>54</sub>N<sub>15</sub>O<sub>9</sub>Mn<sub>3</sub></b> <b>[(MnSalpyr)<sub>3</sub>L<sup>2</sup>]</b>	1605 <sup>b</sup> 1535 <sup>c</sup> –1555 <sup>py</sup>			2826				

(Continued)

Table 2. Continued

Compounds	C=N	C=O	C-H <sub>ar</sub>	C-H <sub>al</sub>	COO-	C-O <sub>ph</sub>	N-H	O-H
<b>XIX</b>	1583 <sup>a</sup>	—	3055	2928	—	1294	—	—
<b>C<sub>81</sub>H<sub>54</sub>N<sub>15</sub>O<sub>9</sub>Fe<sub>3</sub></b> [(FeSalpyr) <sub>3</sub> L <sup>2</sup> ]	1604 <sup>b</sup>	—	—	2821	—	—	—	—
	1537 <sup>c</sup> –1555 <sup>py</sup>	—	—	—	—	—	—	—

<sup>a</sup>, <sup>b</sup>, and <sup>c</sup> shown in this table were shown in Figure 1.

1615 cm<sup>-1</sup> in accordance with the study reported recently.<sup>[13–17]</sup> A broad band at 3338 cm<sup>-1</sup> and a band at 1296 cm<sup>-1</sup> indicate the presence of phenolic-OH and phenolic-CO groups, respectively.<sup>[13,17,34,35]</sup> The band at 1446 cm<sup>-1</sup> is for phenyl group (Table 2).

FT-IR spectra of all trinuclear star-shaped complexes show for C=N (**a**) bands at 1583–1591 cm<sup>-1</sup>, for C=N (**b**) bands at 1604–1629 cm<sup>-1</sup>, for C=N (**c**) bands at 1535–1545 cm<sup>-1</sup>, and for C=N (py) bands at 1552–1556 cm<sup>-1</sup>. That the broad carboxylic –OH band observed for **II** at 3012 cm<sup>-1</sup>, the broad phenolic-OH band for **III** at 3338 cm<sup>-1</sup>, and M-Cl bands observed for [SaldetaAl/Cr/Mn/Fe]Cl or [SalpyAl/Cr/Mn/Fe]Cl completely disappeared in complexes **IV–XIX** proved that carboxylic-OH or phenolic-OH groups coordinate to metal centers of ligand complexes. Moreover, the bands at 1690 cm<sup>-1</sup> for carboxylic C=O were observed at the same point for these complexes. However, the bands at 1405 cm<sup>-1</sup> for the

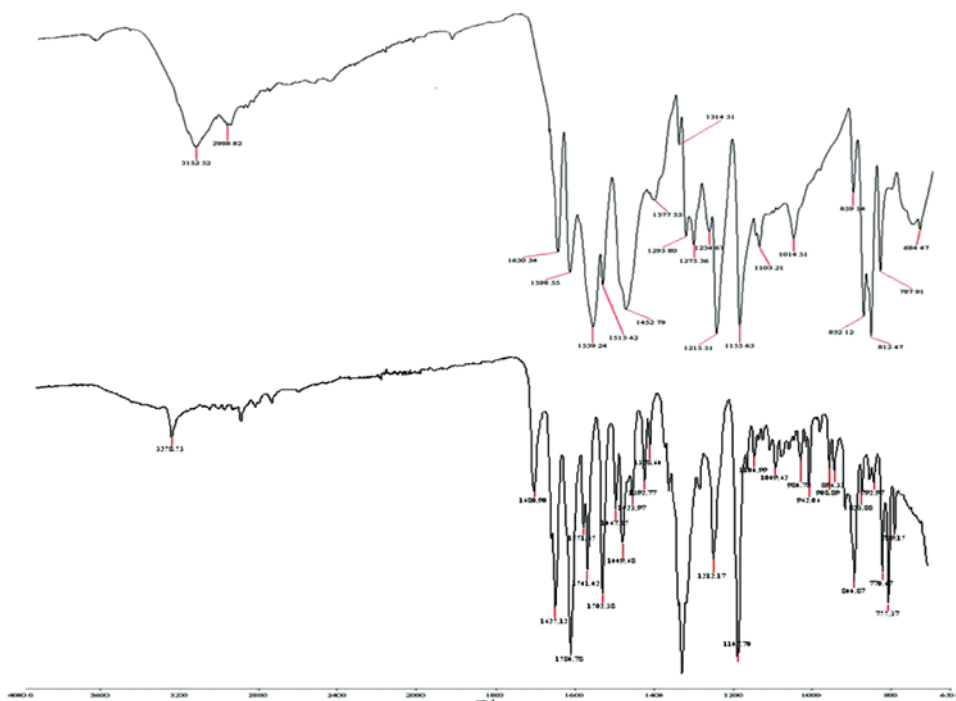


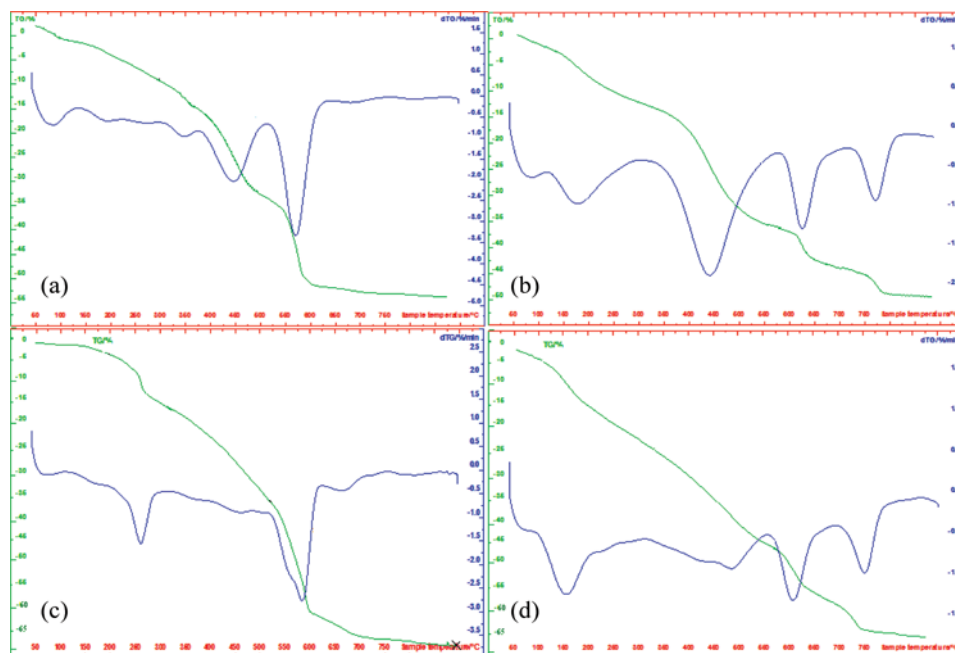
Figure 2. FT-IR spectra of L<sup>2</sup> (top) and [(FeSaldeta)<sub>3</sub>L<sup>2</sup>] (bottom). (Figure is provided in color online.)

**Table 3.** Decomposition steps with the temperature range and weight loss for complexes

Compound	Step	Temp. range (°C)	Weight loss (%)	
			Found	(calcd.)
VII	1	130–300	8.46	(8.79)
$C_{81}H_{72}N_{15}O_{12}Fe_3$ [(FeSaldeta) $_3L^1$ ]	2	300–500	23.53	(20.59)
	3	500–900	20.59	(22.39)
XI	1	125–315	10.61	(8.68)
$C_{84}H_{54}N_{15}O_{12}Fe_3$ [(FeSalpy) $_3L^1$ ]	2	315–570	23.52	(20.32)
	3	570–725	8.07	(8.29)
	4	725–900	5.29	(5.53)
XV	1	150–450	22.40	(25.41)
$C_{78}H_{72}N_{15}O_9Fe_3$ [(FeSaldeta) $_3L^2$ ]	2	450–900	48.25	(52.15)
XIX	1	100–450	23.34	(25.08)
$C_{81}H_{54}N_{15}O_9Fe_3$ [(FeSalpyr) $_3L^2$ ]	2	450–900	47.21	(52.78)

carboxylic  $COO^-$  group were seen at  $1383\text{--}1389\text{ cm}^{-1}$ . A downward shift  $\approx 20\text{ cm}^{-1}$  also showed that only one oxygen atom of  $COO^-$  group linked to metal center. The bands (N-H) seen at  $3258\text{ cm}^{-1}$  for complexes **IV–VII** and **XII–XV** and the bands  $C=N$  (py) seen at  $1552\text{--}1556\text{ cm}^{-1}$  for complexes **VIII–XI** and **XVI–XIX** also showed that ligand complexes capped to  $COO^-$  groups of the ligand (Table 2, Fig. 2).

Samples (**VII**, **XI**, **XV**, and **XIX**) chosen in all the complexes were thermally investigated. It is well known that there is a strong relationship between temperature

**Figure 3.** TGA diagram of VII (a), XI (b), XV (c), and XIX (d). (Figure is provided in color online.)



range for the dehydration process and the binding mode of the water molecules to the respective metal complexes.<sup>[36]</sup> The elimination of water was processed in a single-step process attributed to the release of the hydrated water molecules (in the range of 50–130 °C).<sup>[13,15,17,28,29,36,37]</sup> Thermal decomposition of the three armed complexes **VII** and **XI** started at 125–315 °C, and the anhydrous [SaldetaFe]Cl or [SalpyFe]Cl complexes detached from the ligand **III**, CO<sub>2</sub> gas left the medium. The COO<sup>-</sup> groups left the main frame in this step. The second decomposition step was observed in the range 300–570 °C. Thermal decompositions of the uncapped ligands were revealed in this step. The final decomposition step was completed in the range 500–900 °C, and ligand complexes decomposed in these steps. The final decomposition products were metaloxides and the triazine ring. The observed weight losses for both complexes were in good harmony with the calculated values (Table 3, Fig. 3a and 3b). Thermal decomposition of the three armed complexes **XV** and **XIX** started at 100–450 °C, and the anhydrous [SaldetaFe]Cl or [SalpyFe]Cl complexes detached from the ligand **III**. Thermal decompositions of the uncapped ligand occurred in this step. The second decomposition step was observed in the range 450–900 °C. At this decomposition step, ligand complexes decomposed. The final decomposition products were metaloxides and triazine ring. The observed weight losses for both complexes were in good harmony with the calculated values (Table 3, Fig. 3c and 3d).

The magnetic moments of the complexes given in Table 1 were measured at room temperature. On the basis of spectral evidence, the Al(III), Cr(III), Mn(III), and Fe(III) complexes had trinuclear structures in which the Al(III), Cr(III), Mn(III), and Fe(III) cations had an approximately octahedral environment. The magnetic behaviors of Al(III), Cr(III), Mn(III), and Fe(III) complexes were in favor of the proposed trinuclear structures. The magnetic moment values per metal atom of trinuclear complexes, which were constructed from [SaldetaAl/Cr/Mn/Fe] or [SalpyAl/Cr/Mn/Fe] and **L<sup>1</sup> (II)** or **L<sup>2</sup> (III)**, show paramagnetic properties with magnetic susceptibility values per atom of 3.73, 3.78, 3.75, and 3.76 B.M. for **V**, **IX**, **XIII**, and **XVII**, respectively; 2.94, 2.97, 2.98, and 2.96 B.M. for **VI**, **X**, **XIV**, and **XVIII**, respectively; and 5.21, 5.25, 5.22, and 5.24 B.M. for **VII**, **XI**, **XV**, and **XIX**, respectively. The [SaldetaCr/Mn/Fe]- or [SalpyCr/Mn/Fe]-containing compounds were represented by the electronic structures  $t_{2g}^3 e_g^0$ ,  $t_{2g}^4 e_g^0$ , and  $t_{2g}^3 e_g^2$ . The magnetic data for the [SaldetaCr/Mn/Fe] or [SalpyCr/Mn/Fe] triarmed complexes showed an accordance with the high-spin  $d^3$  ( $S = 3 \times 1/2$ ) Cr(III), low-spin  $d^4$  ( $S = 2 \times 1/2$ ) Mn(III), and high-spin  $d^5$  ( $S = 5 \times 1/2$ ) Fe(III) ions in an octahedral structure. [SaldetaAl] or [SalpyAl] triarmed complexes showed diamagnetic effects. This was supported by the results of the elemental analyses, suggesting that these trinuclear complexes had also octahedral structures.<sup>[21,26,33,38,39]</sup>

Liquid chromatography–mass spectrometry (LC-MS) (ESI<sup>+</sup>) spectra of the selected samples in the all complexes of both ligands were investigated. The calculated molecular weights of all ligand and complexes are shown in Table 1. Molecular peaks of the cations were observed with the same isotope distribution as the calculated ones, theoretically. Namely, from the investigation of LC-MS spectra of the compounds, it was observed that molecular weights of ligands and complexes supported the observed intensity values in LC-MS spectra.

## CONCLUSION

In this study, two tridirectional and melamine cored Schiff bases, 2,4,6-tris(4-carboxybenzimidino)-1,3,5-triazine and 2,4,6-tris(4-hydroxybenzimidino)-1,3,5-triazine, were synthesized.<sup>[14,17]</sup> This synthetic strategy for preparing tripodal-trinuclear bases uses a complex as a “ligand,” which contains a potential donor group capable of coordinating to the other ligands. We have chosen [SaldetaAl/Cr/Mn/Fe]Cl or [SalpyAl/Cr/Mn/Fe]Cl as “ligand complexes” because they can coordinate to the other ligands. These complexes are one of the first examples of star-shaped tripodal-trinuclear complexes bridged by an –OH group of –COOH or by an –OH group of phenol group to the Al(III)/Cr(III)/Mn(III)/Fe(III) centers. Their structures were characterized by means of elemental analyses, <sup>1</sup>H NMR, FT-IR spectroscopy, LC-MS, thermal analyses and magnetic susceptibility measurements. The magnetic data for the star-shaped tripodal-trinuclear complexes show good harmony with the high-spin  $d^3$  ( $S = 3 \times 1/2$ ) Cr(III), low-spin  $d^4$  ( $S = 2 \times 1/2$ ) Mn(III), and high-spin  $d^5$  ( $S = 5 \times 1/2$ ) Fe(III) ion in distorted octahedral structure. [SaldetaAl or SalpyAl] triarmed complexes showed diamagnetic effects.

## EXPERIMENTAL

### Materials and Methods

Melamine, 4-carboxybenzaldehyde, 4-hydroxybenzaldehyde, and all other reagents were purchased from Merck and used without further purification. 2,4,6-Tris(4-carboxybenzimidino)-1,3,5-triazine<sup>[17]</sup> and 2,4,6-tris(4-hydroxybenzimidino)-1,3,5-triazine<sup>[14]</sup> were synthesized in our previous study. All characterization data for the ligands were recorded in Refs. 14 and 17. <sup>1</sup>H and <sup>13</sup>C NMR spectra were taken using a Varian 400-MHz NMR spectrometer at room temperature. Tetramethylsilane (TMS) was used as external standard. IR spectra were recorded using a Perkin-Elmer Spectrum 100 Series FT-IR spectrophotometer. 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 a Varian MAT 711 spectrometer. pH values were measured through a WTW pH, 537 pH meter. The purification of the products obtained at the end of the reaction was carried out using column chromatography. Magnetic susceptibilities of metal complexes were determined using a Sheerwood Scientific MX Gouy magnetic susceptibility apparatus using the Gouy method with Hg[Co(SCN)<sub>4</sub>] as calibrant. The effective magnetic moments,  $\mu_{eff}$ , per metal atom were calculated from the expression  $\mu_{eff} = 2.84\sqrt{\chi_M T}$  B.M., where  $\chi_M$  is the molar susceptibility.

### Preparation of Ligand Complexes

[(N,N'-Bis(1-hydroxy-2-benzyliden)-1,7-diamino-4-azaheptane)Al/Cr/Mn/Fe] or [(N,N'-bis(salicylidene)pyridine-2,6-diamine)Al/Cr/Mn/Fe] were prepared according to previously published methods.<sup>[26]</sup> The pentadentate ligands  $H_2L^1 =$  Saldeta = N,N'-bis(1-hydroxy-2-benzyliden)-1,7-diamino-4-azaheptane or  $H_2L^2 =$  Salpyr = N,N'-bis(salicylidene) pyridine-2,6-diamine have been prepared by a Schiff

base condensation between diethylenetriamine or 2,6-diaminopyridine and corresponding salicylaldehyde at a ratio of 1:2. A mixture of the salicylaldehyde (0.2 mol) and diethylenetriamine (0.1 mol) or 2,6-diamino-pyridine (0.1 mol) in methanol (100 mL) was boiled for 10 min, and the solutions were subjected to crowding. The oily materials were obtained and used without any purification. A solution of anhydrous  $\text{AlCl}_3$  (10 mmol),  $\text{CrCl}_3$  (10 mmol),  $\text{MnCl}_3$  (10 mmol), or  $\text{FeCl}_3$  (10 mmol) in methanol (40 mL) was added to a solution of Saldeta or Salpyr (10 mmol) in methanol (40 mL). The mixtures were stirred at 50 °C for 10 min. Triethylamine (20 mmol) was added. The resulting solution was stirred at 50 °C for 1 h, and after cooling the crystals precipitated. These were collected, washed with methanol and diethylether, and dried in a vacuum.

### Preparation of the Target Complexes

A solution of  $\text{L}^1$  or  $\text{L}^2$  (1.0 mmol) and [SaldetaAl/Cr/Mn/Fe]Cl or [SalpyrAl/Cr/Mn/Fe]Cl (3.0 mmol) in 20 mL of absolute methanol was refluxed for 3 h. The mixture was allowed to cool to room temperature. Then the mixture was filtered and dried in a vacuum. LC-MS ( $\text{ESI}^+$ )  $m/z$ : 1472 [100%, **IV**]; LC-MS ( $\text{ESI}^+$ )  $m/z$ : 1498 [100%, **V**]; LC-MS ( $\text{ESI}^+$ )  $m/z$ : 1500 [100%, **VI**]; LC-MS ( $\text{ESI}^+$ )  $m/z$ : 1502 [100%, **VII**]; LC-MS ( $\text{ESI}^+$ )  $m/z$ : 1490 [100%, **VIII**]; LC-MS ( $\text{ESI}^+$ )  $m/z$ : 1516 [100%, **IX**]; LC-MS ( $\text{ESI}^+$ )  $m/z$ : 1519 [100%, **X**]; LC-MS ( $\text{ESI}^+$ )  $m/z$ : 1520 [100%, **XI**]; LC-MS ( $\text{ESI}^+$ )  $m/z$ : 1388 [100%, **XII**], LC-MS ( $\text{ESI}^+$ )  $m/z$ : 1414 [100%, **XIII**]; LC-MS ( $\text{ESI}^+$ )  $m/z$ : 1416 [100%, **XIV**]; LC-MS ( $\text{ESI}^+$ )  $m/z$ : 1417 [100%, **XV**]; LC-MS ( $\text{ESI}^+$ )  $m/z$ : 1406 [100%, **XVI**]; LC-MS ( $\text{ESI}^+$ )  $m/z$ : 1432 [100%, **XVII**]; LC-MS ( $\text{ESI}^+$ )  $m/z$ : 1435 [100%, **XVIII**], and LC-MS ( $\text{ESI}^+$ )  $m/z$ : 1435 [100%, **XIX**]. Molecular peaks of the cations are observed with the same isotope distribution as the calculated ones, theoretically. Some physical properties, calculated molecular weight, and yield for **IV–XIX** are given in Table 1.

### REFERENCES

1. Menicagli, R.; Samaritani, S.; Signore, G.; Vaglini, F.; Via, L. D. In vitro cytotoxic activities of 2-alkyl-4,6-diheteroalkyl-1,3,5-triazines: New molecules in anticancer research. *J. Med. Chem.* **2004**, *47*, 4649–4652.
2. Pandey, V. K.; Tusi, S.; Tusi, Z.; Joshi, M.; Bajpai, S. Synthesis and biological activity of substituted 2,4,6-s-triazines. *Acta Pharm.* **2004**, *54*, 1–12.
3. Henke, B. R.; Conslor, T. G.; Go, N.; Hale, R. L.; Hohman, D. R.; Jones, S. A.; Lu, A. T.; Moore, L. B.; Moore, J. T.; Orband-Miller, L. A.; Robinett, R. G.; Shearin, J.; Spearing, P. K.; Stewart, E. L.; Turnbull, P. S.; Weaver, S. L.; Williams, S. P.; Wisely, G. B.; Lambert, M. H. A new series of estrogen receptor modulators that display selectivity for estrogen receptor  $\beta$ . *J. Med. Chem.* **2002**, *45*, 5492–5505.
4. Jensen, N. P.; Ager, A. L.; Bliss, R. A.; Canfield, C. J.; Kotecka, B. M.; Rieckmann, K. H.; Terpinski, J.; Jacobus, D. P. Phenoxypoxybiguanides, prodrugs of dhfr-inhibiting diaminotriazine antimalarials. *J. Med. Chem.* **2001**, *44*, 3925–3931.
5. Agarwal, A.; Srivastava, K.; Puri, S. K.; Chauhan, P. M. S. Antimalarial activity and synthesis of new trisubstituted pyrimidines. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 531–533.
6. Srinivas, K.; Srinivas, U.; Harakishore, K.; Jayathirha Rao, V.; Bhanuprakash, K.; Murthy, U. S. N. Synthesis and antibacterial activity of 2,4,6-tri substituted s-triazines. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 1121–1123.

7. McKay, G. A.; Reddy, R.; Arhin, F.; Belley, A.; Lehoux, D.; Moeck, G.; Sarmiento, I.; Parr, T. R.; Gros, P.; Pelletier, J. A. R. Far Triaminotriazine DNA helicase inhibitors with antibacterial activity. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 1286–1290.
8. Ghaib, A.; Menager, S.; Verite, P.; Lafont, O. Synthesis of variously 9,9-dialkylated octahydropyrimido [3,4-a]-s-triazines with potential antifungal activity. *II Farmaco.* **2002**, *57*(2), 109–116.
9. Lubbers, T.; Angehrn, P.; Gmunder, H.; Herzig, S.; Kulhanek, J. Design, synthesis, and structure–activity relationship studies of ATP analogues as DNA gyrase inhibitors. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 821–826.
10. Lebreton, S.; Newcombe, N.; Bradley, M. Antibacterial single-bead screening. *Tetrahedron* **2003**, *59*, 10213–10222.
11. Hoog, D. P.; Gamez, P.; Dressen, W. L.; Reedijk, J. New polydentate and polynucleating N-donor ligands from amines and 2,4,6-trichloro-1,3,5-triazine. *Tetrahedron Lett.* **2002**, *43*, 6783–6786.
12. Koç, Z. E.; Bingol, H.; Saf, A. O.; Torlak, E.; Coskun, A. Synthesis of novel tripodal-benzimidazole from 2,4,6-tris(p-formylphenoxy)-1,3,5-triazine: Structural, electrochemical and antimicrobial studies: Polyimides containing s-triazine ring. *J. Hazard. Mater.* **2010**, *183*, 251–255.
13. Koç, Z. E.; Uçan, H. I. Complexes of iron(III) salen and saloph schiff bases with bridging 2,4,6-tris(2,5-dicarboxyphenylimino-4-formylphenoxy)-1,3,5-triazine and 2,4,6-tris(4-carboxyphenylimino-4'-formyl phenoxy)-1,3,5-triazine. *Transit. Metal Chem.* **2007**, *32*, 597–602.
14. Uysal, Ş.; Koç, Z. E. Synthesis and characterization of dendrimeric melamine cored [salen/salophFe(III)] and [salen/salophCr(III)] capped complexes and their magnetic behaviors. *J. Hazard. Mater.* **2010**, *175*, 532–539.
15. Koç, Z. E.; Uçan, H. I. Complexes of iron(III) and chrom(III) salen and saloph Schiff bases with bridging 2,4,6-tris(4-nitrophenylimino-4'-formylphenoxy)-1,3,5-triazine. *J. Macromol. Sci. A* **2008**, *45*(12), 1072–1077.
16. Uysal, Ş.; Uçan, H. I. The synthesis and characterization of 2,4,6-tris(3,4-dihydroxy benzimino)-1,3,5-triazine and its [salen/salophenFe(III)] and [salen/salophenCr(III)] capped complexes. *J. Inc. Phenom. Macrocycl. Chem.* **2009**, *65*, 403–409.
17. Uysal, Ş.; Uçan, H. I. The synthesis and characterization of melamine based Schiff bases and its trinuclear [salen/salophenFe(III)] and [salen/salophenCr(III)] capped complexes. *J. Inc. Phenom. Macrocycl. Chem.* **2009**, *65*, 299–304.
18. Tidido, J. M.; Gamez, P. The s-triazine ring, a remarkable unit to generate supramolecular interactions. *Inorg. Chim. Acta* **2007**, *360*, 381–404.
19. Patel, H. S.; Patel, V. C. Polyimides containing an s-triazine ring. *Eur. Polym. J.* **2001**, *37*, 2263–2271.
20. Hoog, P.; Gamez, P.; Luken, M.; Roubeau, O.; Krebs, B.; Reedijk, J. Hexanuclear copper(II) complex of a novel poly(pyridine) ligand exhibiting unique long-distance ferromagnetic interactions through a nitrate-O,O' bridge. *Inorg. Chim Acta* **2004**, *357*, 213–218.
21. Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.
22. Bencini, A.; Benelli, C.; Caneschi, A.; Dei, A.; Gatteschi, D. Crystal and molecular structure and magnetic properties of a trinuclear complex containing exchange-coupled GdCu<sub>2</sub> species. *Inorg. Chem.* **1986**, *25*, 572–575.
23. Caneschi, A.; Gatteschi, D.; Sessoli, R. Alternating current susceptibility, high field magnetization, and millimeter band EPR evidence for a ground S=10 state in [Mn<sub>12</sub>O<sub>12</sub>(CH<sub>3</sub>COO)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>]·2CH<sub>3</sub>COOH·4H<sub>2</sub>O. *J. Am. Chem. Soc.* **1991**, *113*, 5873–584.
24. Cano, J.; Ruiz, E.; Alvarez, S.; Verdager, M. Spin density distribution in transition metal complexes: Some thoughts and hints. *Comments Inorg. Chem.* **1998**, *20*, 27–56.

25. Sculler, A. Ph. D. Thesis, University of P. and M. Curie, Paris, 1999.
26. Gembicky, M.; Boca, R.; Renz, F. A heptanuclear Fe(II)–Fe(III)<sub>6</sub> system with twelve unpaired electrons. *Inorg. Chem. Commun.* **2000**, *3*, 662–665.
27. Boca, R.; Elias, H.; Haase, W.; Huber, M.; Klement, R.; Muller, L.; Paulus, H.; Svoboda, I.; Valko, M. Spectroscopic and magnetic properties and structure of a five-coordinate, O<sub>2</sub>-binding cobalt(II) Schiff base complex and of the copper(II) analogue. *Inorg. Chim. Acta* **1998**, *278*, 127–135.
28. Uysal, Ş.; Coşkun, A.; Koç, Z. E.; Uçan, H. I. Synthesis and characterization of a new dioxime and its heterotrinnuclear BF<sub>2</sub>+ capped complexes. *J. Macromol. Sci. A* **2008**, *45*, 727–732.
29. Uysal, Ş. Synthesis and characterization of a new dioxime: Thermal and magnetic behavior of its heterotrinnuclear BF<sub>2</sub><sup>+</sup>-capped complexes. *J. Coord. Chem.* **2010**, *63*(13), 2370–2378.
30. Uysal, Ş.; Uçan, H. I. The synthesis and characterization of single substitute melamine cored Schiff bases and their [Fe(III) and Cr(III)] complexes. *J. Inc. Phenom. Macrocycl. Chem.* **2010**, *68*, 165–173.
31. Uysal, Ş.; Uçan, H. I. The synthesis and characterization of melamine based and [Fe/CrSalen] or [Fe/CrSalophen] capped polymer Schiff base complexes. *J. Inorg. Organomet Polym.* **2010**, *20*(4), 720–726.
32. Koç, Z. E.; Uysal, Ş. Synthesis and characterization of dendrimeric bridged salen/saloph complexes and investigation of their magnetic and thermal behaviors. *Helv. Chim. Acta* **2010**, *93*(5), 910–919.
33. Yang, G. M.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P.; Wang, G. L. Novel oxalate-bridged trinuclear Fe<sup>III</sup>-M<sup>II</sup>-Fe<sup>III</sup> (M=Cu and VO) complexes: Synthesis and magnetism. *Transition Met. Chem.* **1998**, *23*, 313–315.
34. Karatas, I.; Uçan, H. I. The synthesis of biphenylglyoxime and bis(phenylglyoxime) and their complexes with Cu(II), Ni(II) and Co(II). *Synth. React. Inorg. Met.-Org. Chem.* **1998**, *28*, 383–391.
35. Uçan, H. I.; Karatas, I.; Irez, G.; Deveci, M. A.; Mercimek, B. The synthesis of four new schiff bases and some of their transition metal complexes. *Synth. React. Inorg. Met.-Org. Chem. (Kyoto)*. **1998**, *28*, 331–338.
36. El-Metwally, N. M.; Gabr, I. M.; El-Asmy, A. A. Spectral, magnetic, electrical and thermal studies on malonyl bis(thiosemicarbazide) complexes. *Transition Met. Chem.* **2006**, *31*, 71–78.
37. Brzyska, W.; Krol, A. Properties and thermal decomposition in air atmosphere of Co(II), Ni(II), Cu(II), and Zn(II) benzene-1,2-dioxyacetates. *Thermochim. Acta* **1993**, *223*, 241–249.
38. Kopel, P.; Sindelar, Z.; Klicka, R. Complexes of iron(III) salen and saloph Schiff bases with bridging dicarboxylic and tricarboxylic acids. *Transit. Metal. Chem.* **1998**, *23*, 139–142.
39. Dotson, D. L. Ph.D. dissertation, Virginia Polytechnic Institute and State University, 1996.