Synthesis and Characterization of Dendrimeric Bridged Salen/Saloph Complexes and Investigation of Their Magnetic and Thermal Behaviors

by **Ziya Erdem Koç*** and **Şaban Uysal**

Selcuk University, Faculty of Science, Department of Chemistry, 42075-Konya, Turkey
(phone: +90-536-2263303; e-mail: zerdemkoc@gmail.com)

Eight new multinuclear Fe^{III} and Cr^{III} complexes involving the tetradentate *Schiff* bases *N*,*N*′-bis(salicylidene)ethylenediamine ($salenH_2$) or *N*,*N*′-bis(salicylidene)benzene-1,2-diamine ($salophH_2$) and the two new ligands 4,4′,4″,4‴,4⁗,4′′′′′-[1,3,5-triazine-2,4,6-triyltris(nitrilomethylidyne-4,1-phenyleneoxy-1,3,5-triazine-6,2,4-triyldiimino)]hexakis[benzoic acid] (**4**) or 5,5′,5″,5‴,5⁗,5′′′′′-[1,3,5-triazine-2,4,6-triyltris(nitrilomethylidyne-4,1-phenyleneoxy-1,3,5-triazine-6,2,4-triyldiimino)]hexakis[benzene-1,3-dicarboxylic acid] (**5**) were synthesized (*Schemes 1* and *2*) and characterized by means of ^{1}H-NMR and FT-IR spectroscopy, elemental analysis, LC/MS analysis, AAS (atomic-absorption spectrum) analysis, thermal analyses, and magnetic-susceptibility measurements. The complexes can also be characterized as low-spin distorted-octahedral Fe^{III} and Cr^{III} complexes bridged by carboxylato moieties.

Introduction. – An important class of compounds having anticancer, antitumor, antiviral, and antifungal activities consists of substituted *s*-triazine (=1,3,5-triazine) derivatives. These compounds have been used in the treatment of depression and hence gained considerable significance. They are valuable bases for estrogen-receptor modulators [1] and also used as bridging agents to synthesize herbicides and in the production of drugs or polymers [2].

We now report the synthesis and characterization of dendrimeric *Schiff* bases including six or twelve carboxylic acid groups as new templates. The reaction of melamine (=1,3,5-triazine-2,4,6-triamine) with 4-hydroxybenzaldehyde in benzene gave the desired tris(nitrilomethylidyne) and triphenolic moieties in a single step [3]. The phenolic OH groups [4][5] were then modified with trimeric cyanuric chloride (=2,4,6-trichloro-1,3,5-triazine) as a single-directional linker [6–10], followed by treatment with 4-aminobenzoic acid or 5-aminoisophthalic acid [11–20] to give the mentioned new dendrimeric *Schiff* bases which we call 'oxy-*Schiff* bases' (*cf.* [4][5]).

The magnetochemical properties of the *μ*-oxo-bridged complexes [$\{Fe(salen)\}_2O$] [($salenH_2$ = *N*,*N*′-bis(salicylidene)ethylenediamine) = 2,2′-[ethane-1,2-diylbis(nitrilomethylidyne)]bis[phenol]] and [$\{Fe(saloph)\}_2O$] [($salophH_2$ = *N*,*N*′-bis(salicylidene)benzene-1,2-diamine) = 2,2′-[1,2-phenylenebis(nitrilomethylidyne)]bis[phenol]] and their X-ray studies have widely been presented in the literature [21–24]. *Kessel* and *Hendrickson* [25] have studied *Schiff*-base complexes of Fe^{III} incorporating *p*-quinone bridges. The reaction of [$\{Fe(salen)\}_2O$] with carboxylic acids have been reported by *Wollmann* and *Hendrickson* [26]. They used trichloroacetic, trifluoroacetic, salicylic, and picric acids, and characterized the prepared complexes as dimers of the composition [Fe(salen)X]$_2$, where X is the monoanion of the appropriate acid. The complexes [{Fe(salen)}$_2$L] and [{Fe(saloph)}$_2$L] (where L = terephthalato(2 –), fumarato(2 –), oxalato(2 –), and succinato(2 –)) have also been prepared [21]. The crystal and molecular structure of [{Fe(salen)}$_2$ter] (H$_2$ter = terephthalic acid) have been reported [21]. Other complexes of composition [{Fe(salen)}$_2$L] (where L = glutarato(2 –), adipato(2 –), pimelato(2 –), suberato(2 –), and dithiooxamidato(2 –)) were prepared by *Smekal et al.* [27].

Therefore, in the present study, we aimed at the synthesis of other dendrimeric hexa- and dodecacarboxylato bridges and to present their presumed influence on the magnetic behavior of the prepared complexes. We were also interested in dendrimeric hexa- and dodecanuclear systems formed by means of carboxylato bridges because some interesting work dealing with this kind of bridge and associated data has been reported [28 – 32].

Result and Discussion. – The 4,4′,4″-[1,3,5-triazine-2,4,6-triyltris(nitrilomethylidyne)]tris[phenol] (**2**) was prepared in nearly quantitative yield from melamine (**1**) and 3 equiv. of 4-hydroxybenzaldehyde (*Scheme 1*, *Table 1*). Afterward, **2** was treated with cyanuric chloride at 0 – 5°, and the structural formula of the produced N^2,N^4,N^6-tris{{4-[(4,6-dichloro-1,3,5-triazin-2-yl)oxy]phenyl}methylene}-1,3,5-triazine-2,4,6-triamine (**3**) was verified by elemental analysis (*Table 1*), ^{1}H-NMR, FT-IR, and MS data. The reaction of **3** with 4-aminobenzoic acid or 5-aminoisophthalic acid (= 5-aminobenzene-1,3-dicarboxylic acid) at reflux temperature readily furnished the dendrimeric 'oxy-*Schiff* bases' **4** or **5**, respectively, containing six or twelves COOH groups.

The tripodal 'oxy-*Schiff* base' **2** was characterized by its elemental analysis, thermal analyses, ^{1}H-NMR, FT-IR, AAS (atomic-absorption spectrum), and MS data. To establish the structure of **2**, the ^{1}H-NMR spectra were recorded in (D$_6$)DMSO [33][34]. Thus the signals at δ(H) 9.77 (*s*) correspond to three N=CH groups and that at δ(H) 6.08 (*s*) to three OH groups. The data also showed that three directional linkages to the melamine moiety are present in **2**. In addition, when 3 equiv. of cyanuric chloride were added to **2**, the phenolic OH signal at δ 6.08 disappeared. Elemental analysis (*Table 1*), ^{1}H-NMR, FT-IR, and MS data of the product **3** from **2** and cyanuric chloride established that each OH group of **2** had reacted with cyanuric acid. This was confirmed by *Fujiwara*'s test [7]. Moreover, when 6 equiv. of 4-aminobenzoic acid or 5-aminoisophthalic acid were added to **3**, the NH$_2$ signals at δ(H) 5.90 of the former and at δ(H) 5.19 of the later shifted to δ(H) 4.55 or 4.75 (NH of **4** or **5**, resp.). The ^{1}H-NMR spectrum of **4** and **5** showed signals at δ(H) 13.92 – 13.96 and 10.03 – 10.05 corresponding to the carboxylic OH and 'oxy-*Schiff* base' N=CH resonances, respectively. Moreover, the ^{1}H-NMR spectrum of **5** was similar to that of **4**, thus establishing their structures. The new ligands **4** and **5** are soluble in common organic solvents.

The synthetic strategy for preparing dendrimeric hexa- or dodecanuclear complexes consists of the use of a complex as a 'ligand' containing a potential donor group (COO$^-$) capable of coordinating with another ligand. We chose [{Fe(salen) or (saloph)}$_2$O] and [{Cr(salen) or (saloph)}$_2$O] as 'ligand complex' **6** because it can coordinate with another ligand [35 – 37]. Thus, the dendrimeric hexa- or dodecanuclear complexes **7** – **14** with bridging carboxylato groups to the Fe and Cr centers were

Scheme 1. *Synthesis of the Dendrimeric ‘Oxy*-Schiff *Bases’* **4** *and* **5**

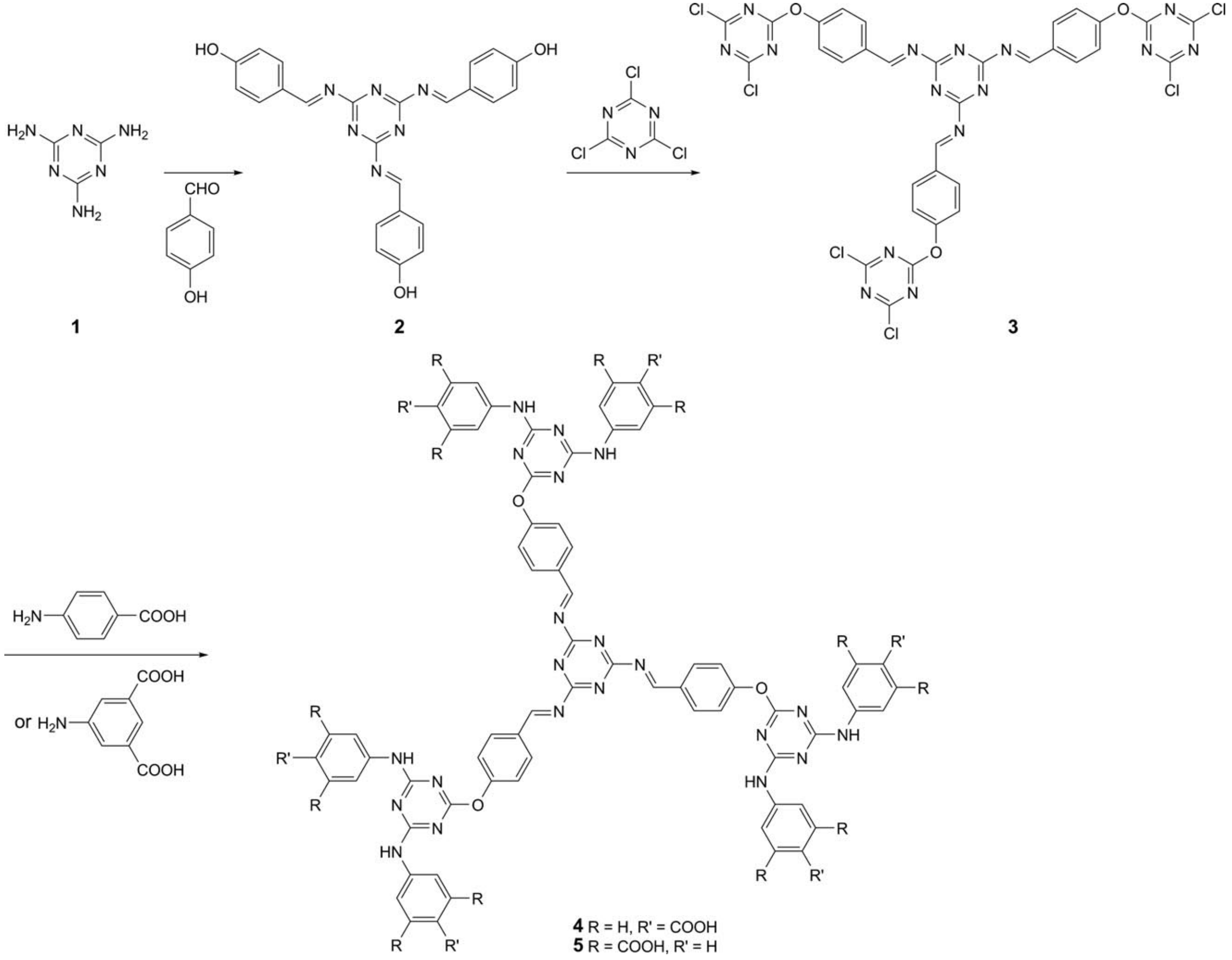
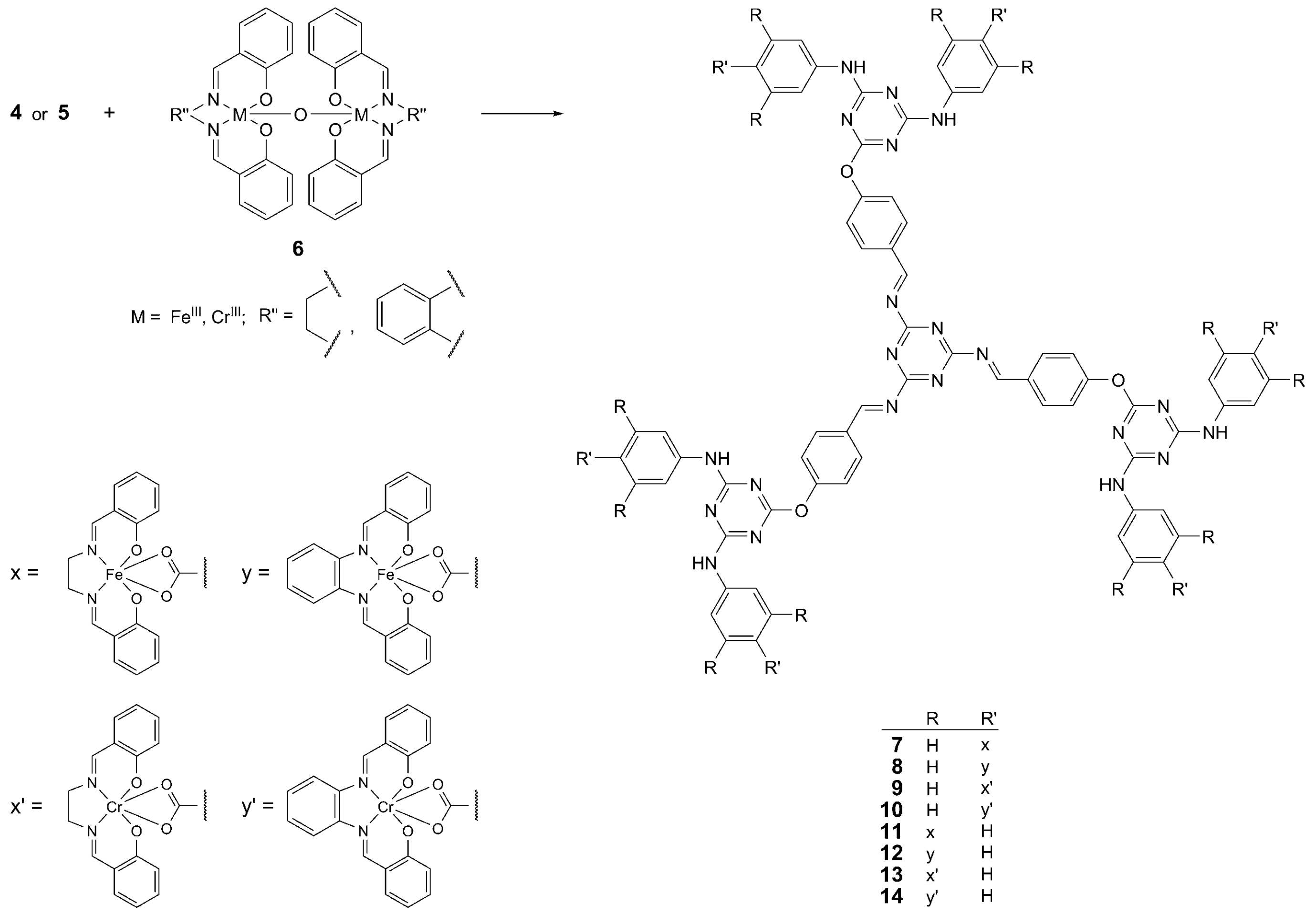


Table 1. *Some Physical Properties, Molecular Weight* ([g/mol]) *Data and Elemental Analyses, AAS Analyses of the Ligands and Complexes*

Compound	Molecular formula	μ_{eff} (296 K) [B.M.]	M.p. [°]	Yield [%]	Color	M_r	Anal. found (calc.) [%]				
							C	H	N	Fe	Cr
2	$C_{24}H_{18}N_6O_3$	–	142	72	pink	438.45	65.67 (65.75)	4.12 (4.14)	19.15 (19.17)	–	–
3	$C_{33}H_{15}Cl_6N_{15}O_3$	–	278	80	pale white	882.30	42.88 (42.92)	1.67 (1.71)	23.77 (23.81)	–	–
4	$C_{75}H_{51}N_{21}O_{15}$	–	285	68	dirty white	1486.37	60.59 (60.61)	3.42 (3.46)	19.75 (19.79)	–	–
5	$C_{81}H_{51}N_{21}O_{27}$	–	293	60	grey	1750.40	55.56 (55.58)	2.90 (2.94)	16.72 (16.80)	–	–
7	$C_{171}H_{141}Fe_6N_{33}O_{27}$	1.65	200[a]	68	brown	3425.32	59.92 (59.96)	4.11 (4.15)	13.43 (13.49)	9.72 (9.78)	–
8	$C_{195}H_{141}Fe_6N_{33}O_{27}$	1.70	205[a]	65	brown	3713.58	63.05 (63.07)	3.81 (3.83)	12.35 (12.45)	8.95 (9.02)	–
9	$C_{171}H_{141}Cr_6N_{33}O_{27}$	3.75	212[a]	55	orange	3402.21	60,25 (60.37)	4.15 (4.18)	13.54 (13.59)	–	9.12 (9.17)
10	$C_{195}H_{141}Cr_6N_{33}O_{27}$	3.90	225[a]	59	orange	3690.48	63.45 (63.47)	3.81 (3.85)	12.48 (12.52)	–	8.41 (8.45)
11	$C_{273}H_{231}Fe_{12}N_{45}O_{51}$	1.62	208[a]	68	dark brown	5628.32	58.22 (58.26)	4.09 (4.14)	11.22 (11.20)	11.87 (11.91)	–
12	$C_{321}H_{231}Fe_{12}N_{45}O_{51}$	1.68	210[a]	72	dark brown	6204.86	62.12 (62.14)	3.74 (3.75)	10.11 (10.16)	10.73 (10.80)	–
13	$C_{273}H_{231}Cr_{12}N_{45}O_{51}$	3.70	215[a]	62	green	5582.11	58.70 (58.74)	4.12 (4.14)	11.26 (11.29)	–	11.14 (11.18)
14	$C_{321}H_{231}Cr_{12}N_{45}O_{51}$	3.88	220[a]	67	dark green	6158.64	62.47 (62.60)	3.73 (3.78)	10.20 (10.23)	–	10.10 (10.13)

[a]) Decomposition.

Scheme 2. *Synthesis of the Hexa- and Dodecanuclear Complexes* **7**–**14**



	R	R'
7	H	x
8	H	y
9	H	x'
10	H	y'
11	x	H
12	y	H
13	x'	H
14	y'	H

obtained from **6** and the ligands **4** or **5** (*Scheme 2*). All compounds **7**–**14** are stable at room temperature in the solid state, and their elemental analyses (*Table 1*) were in agreement with the proposed structures. The results showed that **7**–**14** are hexa- or dodecanuclear complexes. They are only soluble in organic solvents such as DMSO and DMF, and insoluble in H_2O.

In the IR spectra of the free ligands **4** and **5**, the vibrations of the azomethine C=N, triazine C=N, and C–O–C of the free ligands **4** and **5** were observed at 1618–1605, 1574–1560, and 1375–1359 cm^{-1}, respectively [38][39]. In the complexes **7**–**14**, these bands were shifted to lower frequencies, which indicated that the N- and O-atoms of the dendrimeric 'oxy-*Schiff*-base' ligands **4** and **5** are coordinated with the 'ligand complexes' **6**. In the free ligands **4** and **5**, the bands at 3258–3234 or 3425–3427 cm^{-1} were assigned to the carboxylic OH or NH group vibrations, respectively [10][28]. In the complexes **7**–**14**, the OH bands of the COOH groups were missing, thus evidencing chelation of the O-atom to the metal [21][28][30][31][35–37]. These results were consistent with previous studies; especially in [21][28][31] is reported that the carboxylic OH bands disappeared as a result of chelation of the carboxylato O-atom to the metal. In the complexes **7**–**14**, the bands in the ranges of 544–532 and 478–468 cm^{-1} were attributed to the M–N and M–O stretching modes [30–33].

The magnetic moments of the complexes **7**–**14** given in *Table 1* were measured at room temperature. On the basis of spectral evidence, these dendrimeric low-spin Fe^{III} and Cr^{III} complexes have a hexanuclear or dodecanuclear structure in which the low-spin Fe^{III} and Cr^{III} cations have an approximately octahedral environment. The magnetic behavior of these low-spin Fe^{III} and Cr^{III} complexes is in accordance with the proposed hexanuclear or dodecanuclear structures; their magnetic moments established their paramagnetic property, the magnetic susceptibility value per atom being 1.65–1.70 B.M. and 3.75–3.90 B.M., respectively. It is seen that the [{Fe(salen) or (saloph)}$_2$O] and [{Cr(salen) or (saloph)}$_2$O] containing compounds **7**–**14** are represented by the electronic structure $t_{2g}{}^5eg^0$ and $t_{2g}{}^3eg^0$. The magnetic data for the dendrimeric Fe- and Cr-complexes were in accordance with the low-spin d^5 and d^3 metal ion in an octahedral structure, respectively. This conclusion is supported by the results of the elemental analyses suggesting that the dendrimeric complexes **7**–**14** have also an octahedral structure [21][28–32].

The ligands **4** and **5** and complexes **7**, **10**, **12**, and **13** were also thermally investigated, and their plausible degradation schemes are presented in *Table 2* [40][41]. It is well known that there is a strong relation between the temperature range for the dehydration process and the binding mode of the H_2O molecules of the respective metal complexes. The elimination of H_2O took place in a single-step process attributed to the release of the hydrating H_2O molecules of **7**$\cdot x$ H_2O, **10**$\cdot x$ H_2O, **12**$\cdot x$ H_2O, and **13**$\cdot x$ H_2O (in the range of 60–135°). Thermal decomposition of the anhydrous [{Fe(salen) or (saloph)}$_2$O] and [{Cr(salen) or (saloph)}$_2$O] complexes left from the ligands **4** and **5** started in the range of 290–390° and was completed in the range 565–650°. The final decomposition products were metal oxides and triazine ring. The observed weight losses for all ligands and complexes were consistent with the calculated values.

The LC/MS data of all compounds **2**–**5** and **7**–**14** given in the *Exper. Part* confirm their relative molecular mass M_r (*Table 1*).

Table 2. *Decomposition Steps with the Temperature Range and Weight Loss for Ligands* **4** *and* **5** *and Complexes* **7**, **10**, **12**, *and* **13**[a])

	Molecular formula	Temp. range [°]	Weight loss, found (calc.) [%]	Fragment
4	$C_{75}H_{51}N_{21}O_{15}$	65–125	18.12 (17.00)	CO_2, H_2
		300–375	37.71 (39.60)	N_2, H_2O
			21.33 (20.82)	N_2, C_2H_2
5	$C_{81}H_{51}N_{21}O_{27}$	60–120	31.62 (30.17)	CO_2, H_2
		220–315	31.42 (33.64)	N_2, H_2O
		317–390	18.41 (17.68)	N_2, C_2H_2
7	$C_{171}H_{141}Fe_6N_{33}O_{27}$	60–130	7.76 (7.50)	H_2O, CO_2
		200–310	15.03 (14.37)	N_2, C_2H_4
		335–450	55.42 (54.62)	CO_2, N_2, H_2, C_6H_6
10	$C_{195}H_{141}Cr_6N_{33}O_{27}$	60–125	7.31 (6.99)	CO_2, H_2O
		225–325	21.88 (21.16)	N_2, C_6H_6, C_2H_4
		335–455	51.78 (50.71)	CO_2, N_2, H_2, C_6H_6
12	$C_{321}H_{231}Fe_{12}N_{45}O_{51}$	60–122	10.18 (9.24)	CO_2, H_2O
		210–295	18.27 (17.65)	N_2, C_6H_6, C_2H_4
		315–410	61.45 (59.13)	CO_2, N_2, H_2, C_6H_6
13	$C_{273}H_{231}Cr_{12}N_{45}O_{51}$	60–135	8.92 (8.32)	H_2O, CO_2
		215–320	27.01 (25.17)	N_2, C_2H_4
		325–445	55.48 (53.56)	CO_2, N_2, H_2, C_6H_6

[a]) The final thermal decomposition products are metal oxides.

Conclusions. – In this study, the novel tri-directional *Schiff* bases **2**–**5**, derived from melamine and cyanuric chloride were synthesized. The synthetic strategy for the preparation of the hexa- and dodecanuclear complexes **7**–**14** involved a 'ligand complex' that contains a potential donor group (COO^-) capable of coordinating to another ligand. We chose [{Fe(salen or saloph)}$_2$O] and [{Cr(salen or Saloph)}$_2$O] as 'ligand complexes' because their central Fe- or Cr-atom can coordinate to the ligands **4** and **5** *via* the carboxylate anions derived from the latter. The structures of the complexes **7**–**14** were characterized by means of elemental analysis, ^{1}H-NMR and FT-IR spectroscopy, thermal analyses, LC/MS analysis, and magnetic susceptibility measurements. The magnetic data for these hexa- and dodecanuclear complexes were consistent with an octahedral environment of the d^5 and d^3 metal ion.

Experimental Part

1. *General.* All chemicals were purchased from *Aldrich*. Vacuum drying in a *Vacucell 22 MMM-Medcenter Einrichtungen GmbH*. Flash chromatography (FC): *CombiFlash*® chromatography. M.p.: *Büchi-SMP-20* melting point apparatus. IR Spectra: *Perkin-Elmer-1600* FT-IR spectrophotometer; KBr discs; $\tilde{\nu}$ in cm^{-1}. ^{1}H-NMR Spectra: *Bruker-200* spectrometer in (D_6)DMSO; δ in ppm rel. to Me_4Si as internal standard, J in Hz. MS: *Varian-MAT-711* spectrometer; in m/z (rel. %). LC/MS: in m/z. Elemental analyses: *Carlo-Erba-1106* elemental analyzer; metal contents in complexes were determined with a *Unicam-929* atomic absorption spectrometer.

Thermal analyses: *Shimadzu-DTA-50* and *TG-50-H* instruments; 10 mg samples under dry N_2; heating rates 10°/min, from 22–750°. Magnetic susceptibilities: *Sheerwood-Scientific-MX-Gouy* magnetic susceptibility apparatus; measurements by the *Gouy* method with Hg[Co(SCN)$_4$] as calibrant;

calculation of the effective magnetic moment μ_{eff} per metal atom from $\mu_{\mathrm{eff}} = 2.84\sqrt{\chi_{\mathrm{M}} T}$ B.M., where χ_{M} is the molar susceptibility.

2. '*Ligand Complexes*'. [{Fe(salen) or (saloph)}$_2$O] and [{Cr(salen) or (saloph)}$_2$O] were prepared by adding conc. NH_3 soln. to a stirred hot EtOH solns. of [Fe(salen) or (saloph)Cl] and [Cr(salen) or (saloph)Cl], resp., until it became alkaline [21][35–37].

3. *4,4′,4″-[1,3,5-Triazine-2,4,6-triyltris(nitrilomethylidyne)]tris[phenol]* (**2**). Melamine (**1**; 5 mmol, 0.63 g) was suspended in benzene (10 ml), and a suspension of 4-hydroxybenzaldehyde (1.83 g, 15 mmol) in benzene (25 ml) was added by stirring. The mixture was boiled under reflux for 5 h, and the pink powder formed was dried under vacuum [3]. The obtained mixture was purified by FC (*CombiFlash*®, AcOEt/hexane 1:4): **2** (*ca.* quant). FT-IR: 3338 (OH), 2842 (CH), 1615 (CH=N), 1565 (triazine C=N). ^{1}H-NMR ((D_6)DMSO): 9.77 (*s*, 3 H); 7.76, 7.73 (2*d*, *J* = 0.028, 6 H); 6.93–6.90 (*d*, *J* = 0.028, 6 H); 6.08 (*s*, 3 H). LC/MS: 438 ± 2.

4. N^2,N^4,N^6*-Tris{{4-[4,6-dichloro-1,3,5-triazin-2-yl)oxy]phenyl}methylene}-1,3,5-triazine-2,4,6-triamine* (**3**). A cyanuric chloride (2.76 g, 15 mmol) soln. in acetone (100 ml) was added dropwise to a soln. of **2** (2.19 g, 5 mmol) and NaOH (0.6 g, 15 mmol) in H_2O (50 ml) at 0–5°, while stirring. The mixture was stirred vigorously for 3 h at 0–5° and then for 2 h at 15–20°. At these stages, *Fujiwara*'s test [7] for dichlorotriazine was positive. The temp. was allowed to increase to 25° and maintained at 25–30°. The pale white solid was filtered and washed with cold H_2O, then with EtOH. The obtained mixture was purified by FC (*CombiFlash*®, AcOEt/hexane 1:4), and the recrystallized from acetone: **3** (3.09 g, 70%). FT-IR: 2847 (CH), 1618 (CH=N), 1574 (triazine C=N), 1366 (C–O–C), 845 (C–Cl). ^{1}H-NMR ((D_6)DMSO): 10.03 (*s*, 3 H); 8.05–8.01 (*d*, *J* = 0.42, 6 H); 7.56, 7.52 (2 *d*, *J* = 0.42, 6 H). LC/MS: 882 ± 2.

5. *4,4′,4″,4‴,4⁗,4‴″-[1,3,5-Triazine-2,4,6-triyltris(nitrilomethylidyne-4,1-phenyleneoxy-1,3,5-triazine-6,2,4-triyldiimino)]hexakis[benzoic Acid]* (**4**) *or 5,5′,5″,5‴,5⁗,5‴″-[1,3,5-Triazine-2,4,6-triyltris(nitrilomethylidyne-4,1-phenyleneoxy-1,3,5-triazine-6,2,4-triyldiimino)]hexakis[benzene-1,3-dicarboxylic Acid]* (**5**). A soln. of **3** (0.88 g, 1 mmol) in acetone (50 ml) was added dropwise to deionized (100 ml) H_2O cooled in an ice bath (0–5°), under vigorous stirring. 4-Aminobenzoic acid (0.82 g, 6 mmol) or 5-aminoisophthalic acid (1.09 g, 6 mmol), resp., and sat. Na_2CO_3 soln. (0.636 g, 6 mmol) in deionized H_2O were added. The mixture was stirred for 3 h while being cooled in the ice bath and then boiled under reflux for 10 h. The dirty white or grey powder formed was dried under vacuum and subjected to FC (*CombiFlash*®, AcOEt/hexane 1:4): **4** (1.00 g, 68%) or **5** (1.05 g, 60%).

Data of **4**: FT-IR: 3421 (NH), 3155 (OH), 2835 (CH), 1690 (C=O), 1605 (CH=N), 1560 (triazine C=N), 1405 (COO^-), 1359 (COC). ^{1}H-NMR ((D_6)DMSO): 13.92 (br. *s*, 6 H); 10.03 (*s*, 3 H); 7.88, 6.67 (*d*, 24 H); 7.43, 6.87 (*d*, 12 H); 4.55 (*d*, 6 H). LC/MS: 1486 ± 2.

Data of **5**: FT-IR: 3425 (NH), 3165 (OH), 2840 (CH), 1692 (C=O), 1615 (CH=N), 1573 (triazine C=N), 1408 (COO^-), 1372 (COC). ^{1}H-NMR ((D_6)DMSO): 13.96 (br. *s*, 12 H); 10.05 (*s*, 3 H); 8.25 (*s*, 6 H); 7.68 (*d*, 12 H); 6.82 (*d*, 6 H); 7.45 (*d*, 6 H); 4.75 (*d*, 6 H). LC/MS: 1750 ± 2.

6. *Hexakis{{2,2′-{ethane-1,2-diylbis[(nitrilo-κ*N*)methylidyne]}bis[phenolato-κ*O*]}(2–)}- and Hexakis{{2,2′-{1,2-phenylenebis[(nitrilo-κ*N*)methylidyne]}bis[phenolato-κ*O*]}(2–)}{*μ_6*-{4,4′,4″,4‴,4⁗,4‴″-[1,3,5-triazine-2,4,6-triyltris(nitrilomethylidyne-4,1-phenyleneoxy-1,3,5-triazine-6,2,4-triyldiimino)]hexakis[benzoato-*$\kappa O^{1}:\kappa O^{1'}:\kappa O^{1''}:\kappa O^{1'''}:\kappa O^{1''''}:\kappa O^{1'''''}$*)}}hexairon* (**7** and **8**, resp.) *or Hexakis{{2,2′-{ethane-1,2-diylbis[(nitrilo-κ*N*)methylidyne]}bis[phenolato-κ*O*]}(2–)}- and Hexakis{{1,2′-{2,2-phenylenebis-[(nitrilo-κ*N*)methylidyne]}bis[phenolato-κ*O*]}(2–)}{*μ_6*-{4,4′,4″,4‴,4⁗,4‴″-[1,3,5-triazine-2,4,6-triyltris-(nitrilomethylidyne-4,1-phenyleneoxy-1,3,5-triazine-6,2,4-triyldiimino)]hexakis[benzoato-*$\kappa O^{1}:\kappa O^{1'}:\kappa O^{1''}:\kappa O^{1'''}:\kappa O^{1''''}:\kappa O^{1'''''}$*)}}hexachromium* (**9** and **10**, resp.) [{Fe(salen) or (saloph)}$_2$O] (1.98 g, 3 mmol; or 2.27 g, 3 mmol) or [{Cr(salen) or (saloph)}$_2$O] (1.96 g, 3 mmol; or 2.25 g, 3 mmol) was suspended in hot EtOH (50 ml), and a soln. of **4** (1.49 g, 1 mmol) in EtOH was added under stirring. The mixture was boiled under reflux for 4 h, and the solid formed was dried under vacuum. The obtained mixtures were purified by FC (*CombiFlash*®, MeOH/hexane 1:4): **7** (2.33 g, 68%), **8** (2.41 g, 65%), **9** (1.87 g, 55%), or **10** (2.18 g, 59%).

Data of **7** *and* **9**: FT-IR: 3425 (NH), 2895 (CH_2), 2837 (CH), 1540–1617 (CH=N), 1580 (triazine C=N), 1385 (COO^-), 1369 (COC), 534 (M–N), 468 (M–O). LC/MS: 3425 ± 2 (**7**); 3402 ± 2 (**9**).

Data of **8** *and* **10**: FT-IR: 3423 (NH), 2847 (CH), 1545–1627 (CH=N), 1587 (triazine, C=N), 1382 (COO^-), 1372 (COC), 544 (M–N), 478 (M–O). LC/MS: 3713 ± 2 (**8**); 3690 ± 2 (**10**).

7. *Dodecakis{{2,2′-{ethane-1,2-diylbis[(nitrilo-κ*N*)methylidyne]}bis[phenolato-κ*O*]}(2 –)}- and Dodecakis{{2,2′{1,2-phenylenebis[(nitrilo-κ*N*)methylidyne]}bis[phenolato-κ*O*]}(2 –)}{μ_{12}-{5,5′,5″,5‴,5⁗,5′′′′′-[1,3,5-triazine-2,4,6-triyltris(nitrilomethylidyne-4,1-phenyleneoxy-1,3,5-triazine-6,2,4-triyldiimino)]hexakis[benzene-1,3-dicarboxylato(2 –)-κO^{1}:κO$^{1'}$:κO$^{1''}$:κO$^{1'''}$:κO$^{1''''}$:κO$^{1'''''}$:κO^{3}:κO$^{3'}$:κO$^{3''}$:κO$^{3'''}$:κO$^{3''''}$:κO$^{3'''''}$]}}dodecairon* (**11** and **12**, resp.) or *Dodecakis{{2,2′-{ethane-1,2-diylbis[(nitrilo-κ*N*)methylidyne]}bis[phenolato-κ*O*]}(2 –)}- and Dodecakis{{2,2′{1,2-phenylenebis[(nitrilo-κ*N*)methylidyne]}bis[phenolato-κ*O*]}(2 –)}{μ_{12}-{5,5′,5″,5‴,5⁗,5′′′′′-[1,3,5-triazine-2,4,6-triyltris(nitrilomethylidyne-4,1-phenyleneoxy-1,3,5-triazine-6,2,4-triyldiimino)]hexakis[benzene-1,3-dicarboxylato(2 –)-κO^{1}:κO$^{1'}$:κO$^{1''}$:κO$^{1'''}$:κO$^{1''''}$:κO$^{1'''''}$:κO^{3}:κO$^{3'}$:κO$^{3''}$:κO$^{3'''}$:κO$^{3''''}$:κO$^{3'''''}$]}}dodecachromium* (**13** and **14**, resp.). [{Fe(salen) or (saloph)}$_2$O] (3.96 g, 6 mmol; or 4.54 g, 6 mmol) or [{Cr(salen) or (saloph)}$_2$O] (3.92 g, 6 mmol; or 4.49 g, 6 mmol) was suspended in hot EtOH (100 ml), and a soln. of **5** (1.75 g, 1 mmol) in EtOH was added by stirring. The mixture was boiled under reflux for 4 h, and the solid formed was dried under vacuum. The obtained mixtures were purified by FC (*CombiFlash*®, MeOH/hexane 1:4): **11** (3.83 g, 68%), **12** (4.47 g, 72%), **13** (3.46 g, 62%), or **14** (4.13 g, 67%).

Data of **11** *and* **13**: FT-IR: 3427 (NH), 2892 (CH_2), 2838 (CH), 1542–1615 (CH=N), 1583 (triazine C=N), 1381 (COO^-), 1371 (COC), 532 (M–N), 470 (M–O). LC/MS: 5628 ± 2 (**11**); 5582 ± 2 (**13**).

Data of **12** *and* **14**: FT-IR: 3424 (NH), 2840 (CH), 15456–1617 (CH=N), 1588 (triazine C=N), 1384 (COO^-), 1375 (COC), 538 (M–N), 476 (M–O). LC/MS: 6204 ± 2 (**12**); 6158 ± 2 (**14**).

REFERENCES

[1] K. Srinivas, U. Srinivas, V. Jayathirtha Rao, K. Bhanuprakash, K. Hara Kishore, U. S. N. Murty, *Bioorg. Med. Chem. Lett.* **2005**, *15*, 1121.
[2] P. de Hoog, P. Gamez, W. L. Driessen, J. Reedijk, *Tetrahedron Lett.* **2002**, *43*, 6783.
[3] O. B. Akopova, L. S. Shabyshev, L. N. Kotovich, N. V. Pankratova, *Russ. J. Phys. Chem. A* **1996**, *70*, 3, 421.
[4] D. C. Tahmassebi, T. Sasaki, *J. Org. Chem.* **1994**, *59*, 679.
[5] D. C. Tahmassebi, T. Sasaki, *J. Org. Chem.* **1998**, *63*, 728.
[6] Q. Fang, L. Jiang, *Synth. Commun.* **2001**, *31*, 2631.
[7] Q. Fang, X. Ding, X. Wu, L. Jiang, *Polymer* **2001**, *42*, 7595.
[8] K. Srinivas, U. Srinivas, K. Bhanuprakash, K. Harakishore, U. S. N. Murty, V. Jayathirtha Rao, *Eur. J. Med. Chem.* **2006**, *41*, 1240.
[9] C. Kim, Y. Chang, J. S. Kim, *Macromolecules* **1996**, *29*, 6353.
[10] P. M. Patel, S. K. Patel, K. C. Patel, *Eur. Polym. J.* **2000**, 36, 861.
[11] P. Gamez, P. de Hoog, M. Lutz, A. L. Spek, J. Reedijk, *Inorg. Chim. Acta* **2003**, *351*, 319.
[12] J. Z. Jan, B. H. Huang, J.-J. Lin, *Polymer* **2003**, *44*, 1003.
[13] H.-M. Ma, Z.-H. Wang, M.-H. Su, *J. Chromatogr., A* **2002**, *955*, 125.
[14] S. F. Teng, K. Sproule, A. Husain, C. R. Lowe, *J. Chromatogr., B* **2001**, *740*, 1.
[15] T. Q. Hu, D. A. Osmond, J. A. Schmidt, *Polym. Degrad. Stab.* **2004**, *83*, 547.
[16] K. Takagi, T. Hattori, H. Kunisada, Y. Yuki, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4385.
[17] H. S. Patel, V. C. Patel, *Des. Monomers Polym.* **2000**, *3*, 191.
[18] H. S. Patel, V. C. Patel, *Eur. Polym. J.* **2001**, *37*, 2263.
[19] J. T. Thurston, J. R. Dudley, D. W. Kaiser, I. Hechenbleikner, F. C. Schaefer, D. Holm-Hansen, *J. Am. Chem. Soc.* **1951**, *73*, 2981.
[20] M. Y. Arica, G. Bayramoğlu, *Process Biochem.* **2005**, *40*, 1433.
[21] P. Kopel, Z. Sindelar, R. Klicka, *Transition Metal Chem.* **1998**, *23*, 139.
[22] F. M. Ashmawy, A. R. Ujaimi, C. A. McAuliffe, R. V. (Dick) Parish, R. G. Pritchard, *Inorg. Chim. Acta* **1991**, *187*, 155.
[23] A. Elmali, O. Atakol, I. Svoboda, H. Fuess, *Z. Kristallogr.* **1993**, *203*, 271.
[24] J. Kamenicek, Z. Travnicek, Z. Sindelar, J. Walla, *Pol. J. Chem.* **1996**, *70*, 854.
[25] S. L. Kessel, D. N. Hendrickson, *Inorg. Chem.* **1978**, *17*, 2630.
[26] R. G. Wollmann, D. N. Hendrickson, *Inorg. Chem.* **1978**, *17*, 926.

[27] J. Marek, Z. Smekal, Z. Travnicek, *Acta Univ. Palacki. Olomuc., Fac. Rer. Nat.* **1996**, *35*, 33.

[28] Z. E. Koç, H. İ. Uçan, *Transition Met. Chem.* **2007**, *32*, 597.

[29] Z. E. Koç, H. İ. Uçan, *J. Macromol. Sci. A.* **2008**, *45*, 1072.

[30] Ş. Uysal, A. Coşkun, Z. E. Koç, H. İ. Uçan, *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2008**, *45*, 727.

[31] Ş. Uysal, H. İ. Uçan, *J. Inclusion Phenom. Macrocyclic Chem.* **2009**, *65*, 299.

[32] Ş. Uysal, H. İ. Uçan, *J. Inclusion Phenom. Macrocyclic Chem.* **2009**, *65*, 403.

[33] F. Karipcin, H. İ. Uçan, İ. Karataş, *Transition Met. Chem.* **2002**, *27*, 813.

[34] S. M. E. Khalil, A. A. Emara, *J. Coord. Chem.* **2002**, *55*, 17.

[35] M. Gembicky, R. Boča, F. Renz, *Inorg. Chem. Commun.* **2000**, *3*, 662.

[36] G.-M. Yang, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan, G.-L. Wang, *Transition Met. Chem.* **1998**, *23*, 313.

[37] S.-G. Teoh, G.-Y. Yeap, C.-C. Loh, L.-W. Foong, S.-B. Teo, H.-K. Fun, *Polyhedron* **1997**, *16*, 2213.

[38] İ. Karataş, H. I. Uçan, *Synth. React. Inorg. Met.-Org. Chem.* **1998**, *28*, 383.

[39] H. I. Uçan, İ. Karataş, G. Irez, M. A. Deveci, B. Mercimek, *Synth. React. Inorg. Met.-Org. Chem.* **1998**, *28*, 331.

[40] N. M. El-Metwally, I. M. Gabr, A. A. El-Asmy, A. A. Abou-Hussen, *Transition Met. Chem.* **2006**, *31*, 71.

[41] W. Brzyska, A. Król, *Thermochim. Acta* **1993**, *223*, 241.

Received August 10, 2009