

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

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Eight new multinuclear Fe^{III} and Cr^{III} complexes involving the tetradentate *Schiff* bases *N,N'*-bis(salicylidene)ethylenediamine (salenH₂) or *N,N'*-bis(salicylidene)benzene-1,2-diamine (salophH₂) and the two new ligands 4,4',4'',4''',4''''-[1,3,5-triazine-2,4,6-triyltris(nitrilomethylidyne-4,1-phenyleneoxy-1,3,5-triazine-6,2,4-triyl-diimino)]hexakis[benzoic acid] (**4**) or 5,5',5'',5''',5''''-[1,3,5-triazine-2,4,6-triyltris(nitrilomethylidyne-4,1-phenyleneoxy-1,3,5-triazine-6,2,4-triyl-diimino)]hexakis[benzene-1,3-dicarboxylic acid] (**5**) were synthesized (*Schemes 1* and *2*) and characterized by means of ¹H-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 $[\{\text{Fe}(\text{salen})\}_2\text{O}]$ [$(\text{salenH}_2 = N,N'$ -bis(salicylidene)ethylenediamine) = 2,2'-[ethane-1,2-diylbis(nitrilomethylidyne)]bis[phenol]] and $[\{\text{Fe}(\text{saloph})\}_2\text{O}]$ [$(\text{salophH}_2 = N,N'$ -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 $[\{\text{Fe}(\text{salen})\}_2\text{O}]$ 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 $[\text{Fe}(\text{salen})\text{X}]_2$, where X is the monoanion of the appropriate acid. The complexes $[\{\text{Fe}(\text{salen})\}_2\text{L}]$ and $[\{\text{Fe}(\text{saloph})\}_2\text{L}]$ (where L = terephthalato(2-), fumarato(2-), oxalato(2-), and succinato(2-)) have also been prepared [21]. The crystal and molecular structure of $[\{\text{Fe}(\text{salen})\}_2\text{ter}]$ (H_2ter = terephthalic acid) have been reported [21]. Other complexes of composition $[\{\text{Fe}(\text{salen})\}_2\text{L}]$ (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(nitrilomethylidene)]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*), $^1\text{H-NMR}$, 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 twelve COOH groups.

The tripodal ‘oxy-Schiff base’ **2** was characterized by its elemental analysis, thermal analyses, $^1\text{H-NMR}$, FT-IR, AAS (atomic-absorption spectrum), and MS data. To establish the structure of **2**, the $^1\text{H-NMR}$ spectra were recorded in (D_6)DMSO [33][34]. Thus the signals at $\delta(\text{H})$ 9.77 (s) correspond to three N=CH groups and that at $\delta(\text{H})$ 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*), $^1\text{H-NMR}$, 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 $\delta(\text{H})$ 5.90 of the former and at $\delta(\text{H})$ 5.19 of the later shifted to $\delta(\text{H})$ 4.55 or 4.75 (NH of **4** or **5**, resp.). The $^1\text{H-NMR}$ spectrum of **4** and **5** showed signals at $\delta(\text{H})$ 13.92–13.96 and 10.03–10.05 corresponding to the carboxylic OH and ‘oxy-Schiff base’ N=CH resonances, respectively. Moreover, the $^1\text{H-NMR}$ 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 $[\{\text{Fe}(\text{salen})$ or $(\text{saloph})\}_2\text{O}]$ and $[\{\text{Cr}(\text{salen})$ or $(\text{saloph})\}_2\text{O}]$ 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

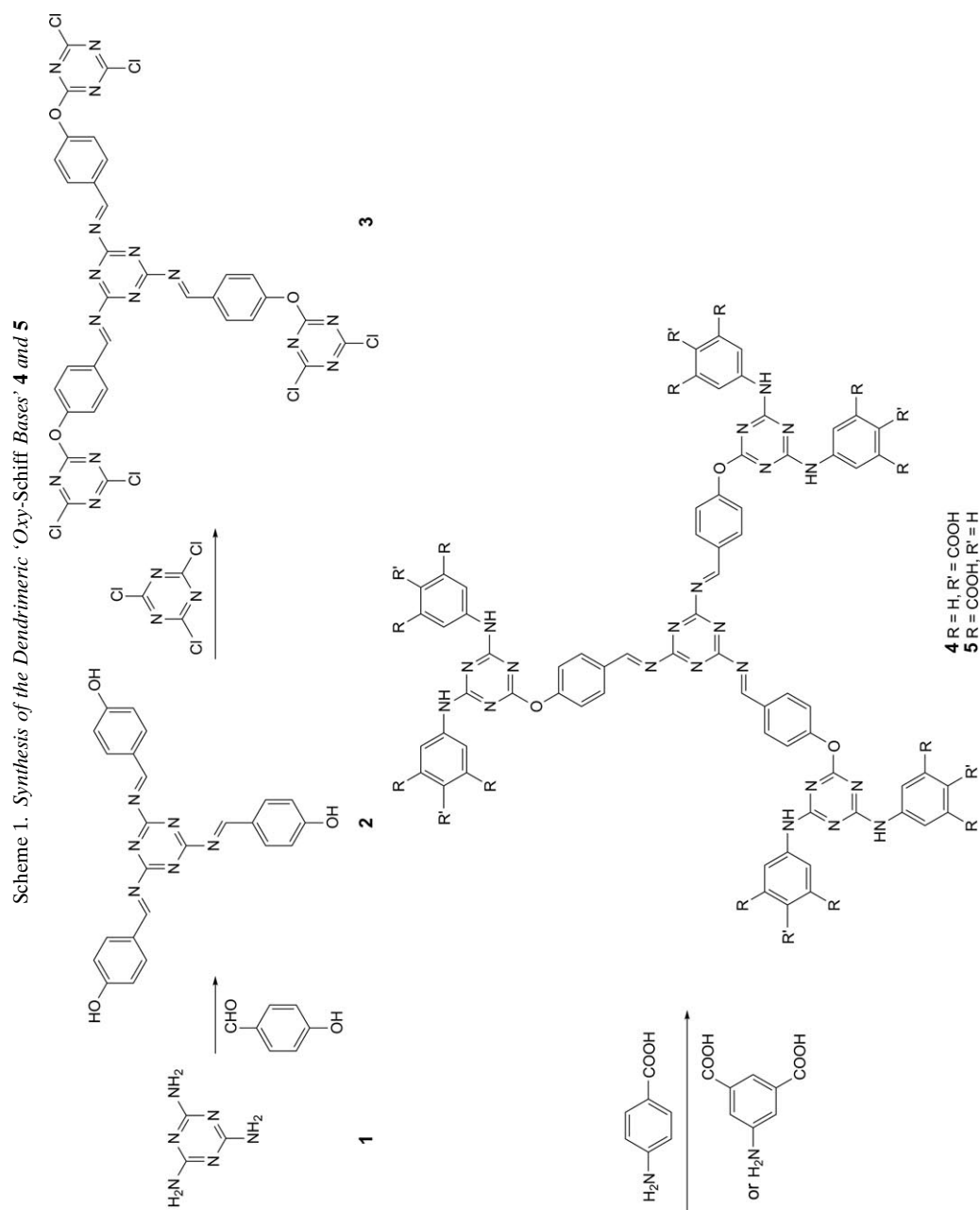
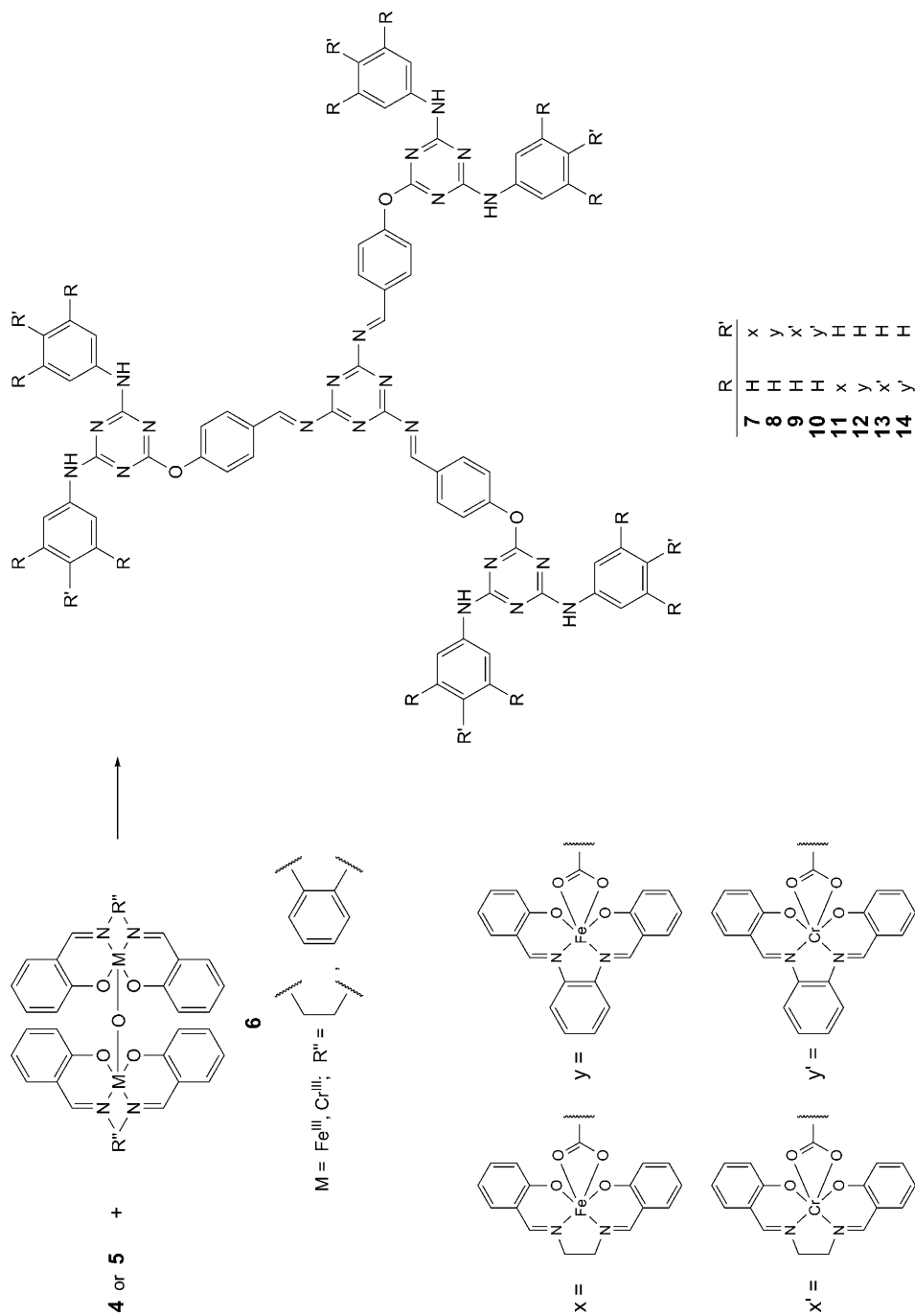


Table 1. Some Physical Properties, Molecular Weight ([g/mol]) Data and Elemental Analyses, AAS Analyses of the Ligands and Complexes

Com- pound	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	$C_{81}H_{51}N_{31}O_{27}$	–	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



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 H₂O.

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)}₂O] and [{Cr(salen) or (saloph)}₂O] containing compounds **7–14** are represented by the electronic structure t_{2g}⁵eg⁰ and t_{2g}³eg⁰. The magnetic data for the dendrimeric Fe- and Cr-complexes were in accordance with the low-spin d⁵ and d³ 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 H₂O molecules of the respective metal complexes. The elimination of H₂O took place in a single-step process attributed to the release of the hydrating H₂O molecules of **7**·x H₂O, **10**·x H₂O, **12**·x H₂O, and **13**·x H₂O (in the range of 60–135°). Thermal decomposition of the anhydrous [{Fe(salen) or (saloph)}₂O] and [{Cr(salen) or (saloph)}₂O] 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 ₂ O
			21.33 (20.82)	N ₂ , C ₂ H 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 ₂ O
		317–390	18.41 (17.68)	N ₂ , C ₂ H ₂
7	C ₁₇₁ H ₁₄₁ Fe ₆ N ₃₃ O ₂₇	60–130	7.76 (7.50)	H ₂ O, CO ₂
		200–310	15.03 (14.37)	N ₂ , C ₂ H ₄
		335–450	55.42 (54.62)	CO ₂ , N ₂ , H ₂ , C ₆ H ₆
10	C ₁₉₅ H ₁₄₁ Cr ₆ N ₃₃ O ₂₇	60–125	7.31 (6.99)	CO ₂ , H ₂ O
		225–325	21.88 (21.16)	N ₂ , C ₆ H ₆ , C ₂ H ₄
		335–455	51.78 (50.71)	CO ₂ , N ₂ , H ₂ , C ₆ H ₆
12	C ₃₂₁ H ₂₃₁ Fe ₁₂ N ₄₅ O ₅₁	60–122	10.18 (9.24)	CO ₂ , H ₂ O
		210–295	18.27 (17.65)	N ₂ , C ₆ H ₆ , C ₂ H ₄
		315–410	61.45 (59.13)	CO ₂ , N ₂ , H ₂ , C ₆ H ₆
13	C ₂₇₃ H ₂₃₁ Cr ₁₂ N ₄₅ O ₅₁	60–135	8.92 (8.32)	H ₂ O, CO ₂
		215–320	27.01 (25.17)	N ₂ , C ₂ H ₄
		325–445	55.48 (53.56)	CO ₂ , N ₂ , H ₂ , C ₆ H 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)]₂O] and [[Cr(salen or Saloph)]₂O] 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, ¹H-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 d⁵ and d³ 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}. ¹H-NMR Spectra: *Bruker-200* spectrometer in (D₆)DMSO; δ in ppm rel. to Me₄Si 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 N₂; 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 $\mu_{\text{eff}} = 2.84\sqrt{\chi_M T}$ B.M., where χ_M is the molar susceptibility.

2. 'Ligand Complexes'. $[\{\text{Fe}(\text{salen}) \text{ or } (\text{saloph})\}_2\text{O}]$ and $[\{\text{Cr}(\text{salen}) \text{ or } (\text{saloph})\}_2\text{O}]$ were prepared by adding conc. NH_3 soln. to a stirred hot EtOH solns. of $[\text{Fe}(\text{salen}) \text{ or } (\text{saloph})\text{Cl}]$ and $[\text{Cr}(\text{salen}) \text{ or } (\text{saloph})\text{Cl}]$, 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). ¹H-NMR ((D₆)DMSO): 9.77 (s, 3 H); 7.76, 7.73 (2d, $J = 0.028$, 6 H); 6.93–6.90 (d, $J = 0.028$, 6 H); 6.08 (s, 3 H). LC/MS: 438 ± 2.

4. *N²,N⁴,N⁶-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 H₂O (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 H₂O, 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). ¹H-NMR ((D₆)DMSO): 10.03 (s, 3 H); 8.05–8.01 (d, $J = 0.42$, 6 H); 7.56, 7.52 (2d, $J = 0.42$, 6 H). LC/MS: 882 ± 2.

5. *4,4',4'',4''',4''''-[1,3,5-Triazine-2,4,6-triyltris(nitrilomethylidyne-4,1-phenyleneoxy-1,3,5-triazine-6,2,4-triylidimino)]hexakis[benzoic Acid]* (**4**) or *5,5',5'',5''',5''''-[1,3,5-Triazine-2,4,6-triyltris(nitrilomethylidyne-4,1-phenyleneoxy-1,3,5-triazine-6,2,4-triylidimino)]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) H₂O 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. Na₂CO₃ soln. (0.636 g, 6 mmol) in deionized H₂O 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). ¹H-NMR ((D₆)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). ¹H-NMR ((D₆)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-κN)methylidyne]}bis[phenolato-κO]}(2-)- and Hexakis{[2,2'-{1,2-phenylenebis[(nitrilo-κN)methylidyne]}bis[phenolato-κO]}(2-)}{μ₆-[4,4',4'',4''',4''''-[1,3,5-triazine-2,4,6-triyltris(nitrilomethylidyne-4,1-phenyleneoxy-1,3,5-triazine-6,2,4-triylidimino)]hexakis[benzoato-κO¹:κO²:κO³:κO⁴:κO⁵:κO⁶]}hexairon* (**7** and **8**, resp.) or *Hexakis{[2,2'-{ethane-1,2-diylbis[(nitrilo-κN)methylidyne]}bis[phenolato-κO]}(2-)- and Hexakis{[1,2'-{2,2-phenylenebis[(nitrilo-κN)methylidyne]}bis[phenolato-κO]}(2-)}{μ₆-[4,4',4'',4''',4''''-[1,3,5-triazine-2,4,6-triyltris(nitrilomethylidyne-4,1-phenyleneoxy-1,3,5-triazine-6,2,4-triylidimino)]hexakis[benzoato-κO¹:κO²:κO³:κO⁴:κO⁵:κO⁶]}hexachromium* (**9** and **10**, resp.) $[\{\text{Fe}(\text{salen}) \text{ or } (\text{saloph})\}_2\text{O}]$ (1.98 g, 3 mmol; or 2.27 g, 3 mmol) or $[\{\text{Cr}(\text{salen}) \text{ or } (\text{saloph})\}_2\text{O}]$ (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 (CH₂), 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-κN)methylidyne]}bis[phenolato-κO]}(2-)- and Dodecakis{[2,2'-{1,2-phenylenebis[(nitrilo-κN)methylidyne]}bis[phenolato-κO]}(2-)}{[μ₁₂-{5,5',5'',5''',5''''-}1,3,5-triazine-2,4,6-triyltris(nitrilomethylidyne-4,1-phenyleneoxy-1,3,5-triazine-6,2,4-triylidimino)]hexakis[benzene-1,3-dicarboxylato(2-)-κO¹:κO^{1'}:κO^{1''}:κO^{1'''}:κO^{1''''}:κO^{1'''''}:κO³:κO^{3'}:κO^{3''}:κO^{3'''}:κO^{3''''}:κO^{3'''''}]}dodecairon (**11** and **12**, resp.) or Dodecakis{[2,2'-{ethane-1,2-diylbis[(nitrilo-κN)methylidyne]}bis[phenolato-κO]}(2-)- and Dodecakis{[2,2'-{1,2-phenylenebis[(nitrilo-κN)methylidyne]}bis[phenolato-κO]}(2-)}{[μ₁₂-{5,5',5'',5''',5''''-}1,3,5-triazine-2,4,6-triyltris(nitrilomethylidyne-4,1-phenyleneoxy-1,3,5-triazine-6,2,4-triylidimino)]hexakis[benzene-1,3-dicarboxylato(2-)-κO¹:κO^{1'}:κO^{1''}:κO^{1'''}:κO^{1''''}:κO^{1'''''}:κO³:κO^{3'}:κO^{3''}:κO^{3'''}:κO^{3''''}:κO^{3'''''}]}dodecachromium (**13** and **14**, resp.). [[Fe(salen) or (saloph)₂O] (3.96 g, 6 mmol; or 4.54 g, 6 mmol) or [[Cr(salen) or (saloph)₂O] (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 (CH₂), 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**).

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