Complexes of Iron(III) and Chromium(III) Salen and Salophen Schiff Bases with Bridging 1,3,5-Triazine Derived Multidirectional Ligands

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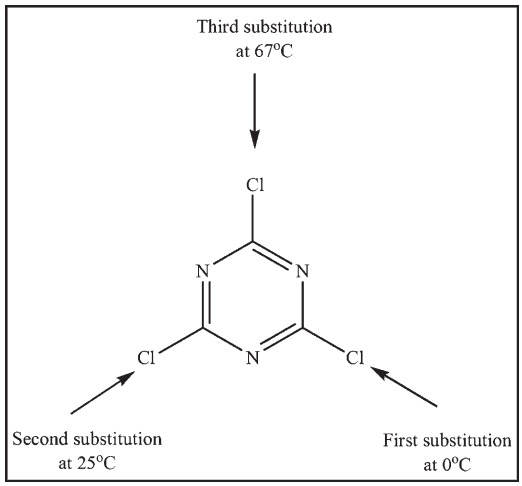

A new synthetic route for preparing multidirectional ligands was developed by using 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) as core. The reaction included the selective substitutions of 4-aminobenzoic acid onto three chlorides of the triazine ring via a stepwise manner at 1:1, 1:2, or 1:3 equiv. and 0, 25, 130°C, respectively. An efficient synthesis of a novel class of ''multidirectional ligands'' has been developed based on high-yielding chloride substitutions of 2,4,6-trichloro-1,3,5-triazine by amines. Sixteen new mono-, di-, tri-, and tetra-nuclear Fe(III) and Cr(III) complexes involving tetradenta Schiff bases *N,N′*-bis(salicylidene)ethylenediamine-(salenH_2) or bis(salicylidene)-*o*-phenylenediamine-(salophenH_2) with two new 1,3,5-triazine derived multidirectional ligands were synthesized and characterized by means of elemental analysis, ^{1}H NMR, FT-IR spectroscopy, LC-MS analysis, AAS, thermal analysis, and magnetic susceptibility measurements. The complexes were also characterized as low-spin distorted octahedral Fe(III) and Cr(III) bridged by carboxylic acids. It was understood that the [{Fe(salen)/(salophen)}$_2$O] and [{Cr(salen)/(salophen)}$_2$O] containing compounds could be represented by the electronic structure of $t_{2g}^5 e_g^0$ and $t_{2g}^3 e_g^0$.

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INTRODUCTION

The design and synthesis of supramolecular polynuclear metal complexes have been an area of rapid growth for the past 20 years. During the last decade, a remarkable development in the preparation of self-assembled architecture through metal ion coordination has been observed. The motivation behind much of the studies related with polynuclear metal complexes has been provided by the prospect of producing a wide range of purpose-built materials with predetermined structures and potential applications in separation, gas storage, molecular recognition, and catalysis [1]. The preparation of polymetallic complexes can be achieved using rationally designed polydentate ligands [2]. On the other hand, it has been demonstrated that the 1,3,5-triazine ring is a suitable structural element to be incorporated into thermotropic liquid crystals. Thus, aromatic esters involving a 1,3,5-triazine moiety have been found to exhibit calamitic mesophases [3].

Sophisticated s-triazine derivatives can be easily prepared from the cheap and readily available cyanuric chloride ($C_3N_3Cl_3$), 2,4,6-trichloro-1,3,5-triazine **(1)** [4,5]. Cyanuric chloride is definitely an excellent starting compound for the straightforward preparation of highly structured multitopic molecules. Indeed, each chloride atom of 2,4,6-trichloro-1,3,5-triazine can be substituted by any nucleophilic reactant (Fig. 1) [2]. The first substitution is exothermic. Therefore, the temperature of the reaction mixture has to be maintained to

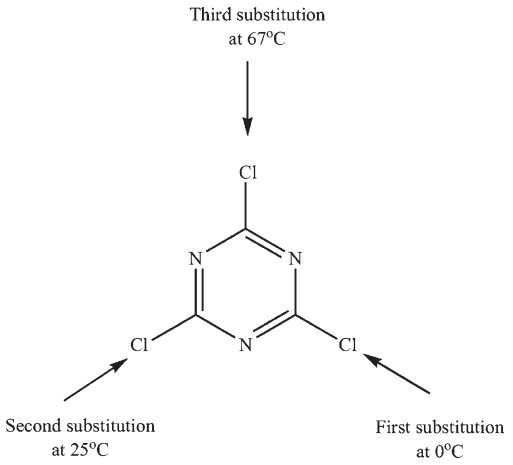


Figure 1. Preparation of polyfunctional s-triazine derivatives taking advantage of the differential reactivity of 2,4,6-trichloro-1,3,5-triazines.

0°C. The substitution of the second chloride can be performed at room temperature. Finally, the third position is functionalized under refiux of the solvent. As a result, a careful control of the temperature during the substitution reactions will allow the synthesis of 2,4,6-trisubstituted-triazines by sequential and very selective addition of amines, alcohols, thiols, or Grignard reagents (Fig. 1). The yield of each substitution often exceeds 95%, and the symmetric trisubstituted derivatives can even be obtained in a one pot synthesis. Various solvents can be used such as tetrahydrofuran, 1,2-dimethoxy ethane, acetonitrile, and diethyl ether [5].

The magnetochemical properties of the μ-oxo-bridged complexes [{Fe(salen)}$_2$O] [(salenH_2 = *N*,*N*′-bis(salicylidene) ethylenediamine)] and [{Fe(salophen)}$_2$O] [(salophenH_2 = bis(salicylidene)-2-phenylenediamine)] and their X-ray studies have widely been presented in the literature [6]. I have also reported the synthesis and characterization of 1,3,5-tricarboxylato, dendrimeric-carboxylato, single substitute carboxylato, single substitute catechol, and 1,3,5-tricatechol triazine bridges with [salenFe(III)], [salophenFe(III)], [salenCr(III)], and [salophenCr(III)] [7–13].

This article describes the preparation of rationally designed bidentate, tetradendate, and multidentade ligands. The relatively simple synthetic pathway to these multidirectional ligands is based on nucleophilic addition of 4-aminobenzoic acid to 2,4,6-trichloro-1,3,5-triazine. This method is the first demonstration used for the synthesis of 1,3,5-triazine-derived ''multidirectional ligands'' and its Schiff bases complexes of iron(III) or chromium(III) due to the direct bond between —COOH group [7–26]. Therefore, I have reported here that 1,3,5-triazine-derived ''multidirectional ligands'' and its Schiff bases complexes of iron(III) or chromium(III) have been synthesized to be a new template. The reaction of 2,4,6-trichloro-1,3,5-triazine with 1:1, 1:2, or 1:3 equiv and 0°C, 25°C, or 130°C of 4-aminobenzoic acid gave the desired ''multidirectional ligands,'' respectively [12–26]. The aim of this work was to make other bridges and try to as certain their influence on the magnetic behavior of the prepared complexes. As a future plan of this study, novel s-triazine Schiff base derivatives and some of their new multinuclear systems will be formed by the 1,3,5-tricarboxylato bridge.

EXPERIMENTAL

All chemicals were purchased from Aldrich. The linking agent, 2,4,6-trichloro-1,3,5-triazine (abbreviated as cyanuric chloride, mp 145–146°C), was obtained from Aldrich. Cyanuric chloride was purified by recrystallizations from pure petroleum ether (60–90°C) [24].

Elemental analyses were performed with Carlo Erba 1106 elemental analyzer. The IR spectra were recorded using KBr discs (4000–440 cm^{-1}) with Perkin Elmer 1600 series FT-IR spectrophotometer. Metal contents in complexes were determined using Unicam 929 AAS spectrometer. Mass spectra of the compounds were obtained registered on with Varian MAT 711 spectrometer. The ^{1}H NMR spectra in d_6-DMSO was obtained using a Bruker 200 MHz spectrometer. MMM-Medcenter and Einrichtungen GmbH Vacucell 22 were used as Vacuum Cabinets. Melting points were measured using a Buchi SMP-20 melting point apparatus. Arex Velp Sci. used as Heating Magnetic stirrer which is equipped with a contact Vetex thermostat connection for direct control of the temperature of the stirred liquid. The thermal analysis was performed with Shimadzu DTA 50 and TG 50 H models using 10 mg samples. The DTA and TG curves were obtained recorded at the heating rate of 10°C min^{-1}. In all cases, the temperature range between 22 and 750°C was used under dry nitrogen atmosphere. Magnetic Susceptibilities of metal samples were determined using a Sheerwood Scientific MX Gouy magnetic susceptibility apparatus and magnetic measurements were carried out using the Gouy method with Hg[Co(SCN)$_4$] as calibrant. The effective magnetic moments, μ_{eff}, per metal atom was calculated from the expression: $\mu_{eff} = 2.84\sqrt{\chi_M}\,TB.M.$, where χ_M is the molar susceptibility.

Preparation of ligand complexes. [{Fe(salen)/(salophen)}$_2$O] and [{Cr(salen)/(salophen)}$_2$O] were prepared by adding concentrated ammonia solution to stirred hot EtOH solutions of [Fe(salen)/(salophen)Cl] and [Cr(salen)/(salophen)Cl], respectively, until alkaline [6,27–29].

Synthesis of 2,4-dichloro-6-(4-carboxyanilino)-1,3,5-triazine (2). Previously, this compound was synthesized due to procedure mentioned in the study of Ragno et al. Typical procedures for the amination of cyanuric chloride **(1)** have been described by using 4-aminobenzoic acid as an example [30]. A solution of 4-aminobenzoic acid (1.37 g, 10 mmol) in acetone (50 mL) and deionized water (50 mL) was added dropwise to a cyanuric chloride **(1)** suspension made by pouring slurry cyanuric chloride **(1)** (1.84 g, 10 mmol) in acetone (50 mL) into 0–5°C deionised water (50 mL), with stirring, in an ice bath [31]. $NaHCO_3$ (2.10 g, 25 mmol) in water (50 mL) was added to maintain the pH between 6.0 and 7.0 during the reaction.

After 3 h, when no cyanuric chloride **(1)** could be detected by TLC (Thin Layer Chromatography) (solvent system: hexane–ethyl acetate, 1:4, v/v). At these stages, the Fujiwara Test [24] for dichlorotriazine was positive. The acetone was removed by vacuum, and the residue was suspended in water (100 mL). The precipitate was removed by filtration and the water phase extracted three times by dichloromethane. The product was then precipitated out of solution by acidifying the water phase to pH 4.0 with (5*M*) hydrochloric acid. A white powder solid product was collected by filtration and was washed with cold water (3 × 100 mL) and acetone [31]. ^{1}H NMR (d_6-DMSO) δ 12.80 (br, 1H, OH), 11.37 (s, 1H, NH), 7.70–7.67 (d, 2H), 7.95–7.78 (d, 2H).

Synthesis of 2-chloro-4,6-(4-carboxyanilino)-1,3,5-triazine (3). To stirred cyanuric chloride **(1)** (1.84 g, 10 mmol), dissolved in acetone (50 mL), was added dropwise a solution of 4-aminobenzoic acid (1.37 g, 10 mmol) in acetone (50 mL) and deionized water (50 mL) and $NaHCO_3$ (2.10 g, 25 mmol) in water (50 mL) saturated by N_2 at 0–5°C. The reaction mixture was stirred vigorously for 3 h at 0–5°C and for 2 h at 15–20°C. When no cyanuric chloride could be detected by TLC (solvent system: hexane–ethyl acetate, 1:4, v/v). At these stages, the Fujiwara test [24] for dichlorotriazine was positive. The temperature was allowed to increase to 25°C and maintained for 2 h at 25–30°C. When the test was negative, a solution of 4-aminobenzoic acid (1.37 g, 10 mmol) and $NaHCO_3$ (2.10 g, 25 mmol) in water (100 mL) saturated by N_2 was added dropwise to the mixture for 1 h. After the reaction mixture was stirred for 2 h at 35–40°C, the temperature was decreased to 0–5°C. The acetone was removed in vacuum, and the residue was suspended in water (100 mL). The precipitate was removed by filtration, and the water phase extracted three times with dichloromethane. Then, the product was precipitated out of solution by acidifying the water phase to pH 4.0 with (5*M*) hydrochloric acid. A dark grey powder solid product was collected by filtration and was washed with cold water (3 × 100 mL) to remove the sodium bicarbonate [31]. The crude product, 2-chloro-4,6-(4-carboxyanilino)-1,3,5-triazine **(3)** was purified by chromatography (solvent system: hexane–ethyl acetate, 1:4, hexane v/v) to afford a dark grey powder solid product dried in a vacuum cabinets (50°C) and stored in a desiccator over $CaCl_2$ that decomposes at 348°C in a yield of 65%; LC-MS data for **3** m/z: 386 ± 2, FT-IR(cm^{-1}) 3379 (NH), 3358 (OH), 2809 (CH), 1702 (C=O), 1564 (C=N triazine). ^{1}H NMR (d_6-DMSO) δ 12.87 (br, 2H, OH), 11.53 (s, 2H, NH), 7.23–7.19 (d, 4H, j = 0.92 Hz), 8.44–8.40 (d, 4H, j = 0.91 Hz).

Synthesis of 2,4,6-(4-carboxyanilino)-1,3,5-triazine (4). Cyanuric chloride **(1)** (1.84 g, 10 mmol) were dissolved in acetone (75 mL). $NaHCO_3$ (6.30 g, 75 mmol) in water (100 mL) saturated by N_2 was added and three necked round bottomed flask was cooled 0°C. 4-aminobenzoic acid (4.11 g, 30 mmol) was added portionwise. After the completion of the addition, the suspension mixture was warmed to room temperature and then heated under reflux for 48 h. The acetone was removed by vacuo and the residue was suspended in water (100 mL). The precipitate was removed by filtration and the water phase extracted three times with dichloromethane. The product was then precipitated out of solution by acidifying the water phase to pH 4 with (5*M*) hydrochloric acid. Brown powder solid product was collected by filtration and was washed with cold water (3 × 100 mL) to remove the sodium bicarbonate [32,33]. ^{1}H NMR (d_6-DMSO) δ 12.93 (br, 3H, OH), 11.94 (s, 3H, NH), 7.73–7.71 (d, 6H), 8.83–8.80 (d, 6H).

Synthesis of *N,N′*-{bis[4,6-(4-carboxyanilino)]-1,3,5-triazine}-ethylenediamine (5). To a stirred solution of (**3**) (2.31 g, 6 mmol) and *N*-ethyldiisopropylamine (DIPEA) (0.78 g, 6 mmol) in acetone (50 mL), ethylendiamine (0.20 mL, 3 mmol) was added and $NaHCO_3$ (0.42 g, 5 mmol) in water (100 mL) saturated by N_2 was added dropwise to the mixture for 1 h. This mixture was heated to 80°C for 48 h. The acetone was removed by vacuo, and the residue was suspended in water (100 mL). The precipitate was removed by filtration and the water phase extracted three times with dichloromethane. The product was then precipitated out of solution by acidifying the water phase to pH 4.0 with (5*M*) hydrochloric acid. The precipitate was filtered under reduced pressure, washed with acetone (3 × 20 mL) [2]. LC-MS data for **5** m/z: 758 ± 2, FT-IR(cm^{-1}) 3315–3295 (NH), 3291 (OH), 2864 (CH), 2860 (CH_2), 1710 (C=O), 1560 (C=N triazine). ^{1}H NMR (d_6-DMSO) δ 13.05 (br, 4H, OH), 9.93 (s, 4H, NH), 7.49 (s, 2H, NH), 7.84–7.78 (d, 4H, j = 0.91 Hz), 8.23–8.17 (d, 4H, j = 0.92 Hz), 3.52 (s, 4H, CH_2).

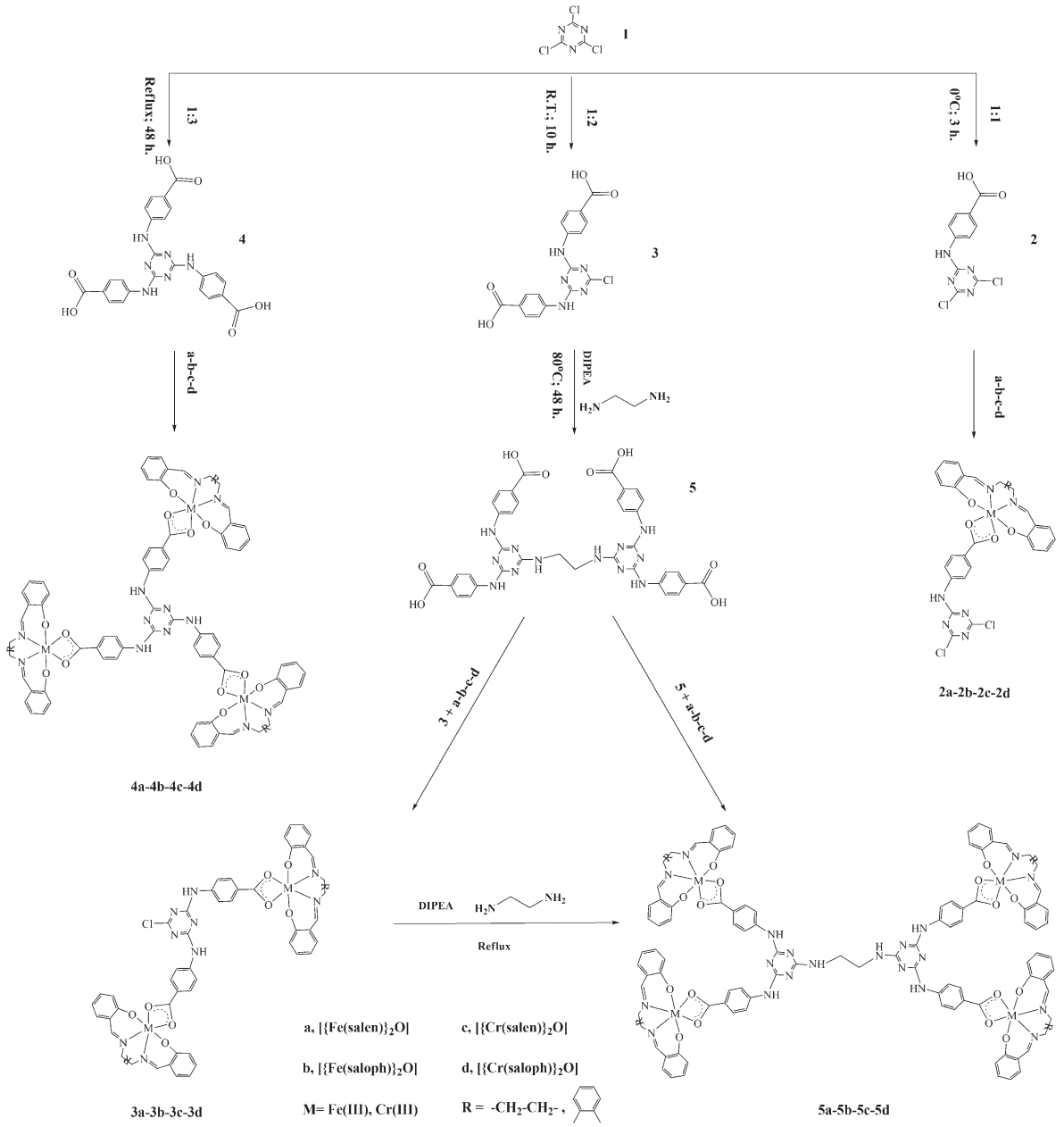
Synthesis of [H_2Lsalen/salophen]Fe(III) or [H_2Lsalen/salophen]Cr(III) complexes. [{Fe(salen)/(salophen)}$_2$O] (0.33, 0.66, 0.99, 1.32 g/0.5, 1, 1.5, 2 mmol – 0.38, 0.76, 1.14, 1.5 g/0.5, 1, 1.5, 2 mmol) or [{Cr(salen)/(salophen)}$_2$O] (0.33, 0.65, 0.98, 1.3 g / 0.5, 1, 1.5, 2 mmol – 0.36, 0.75, 1.13, 1.5 g / 0.5, 1, 1.5, 2 mmol) were suspended in hot EtOH (50 mL) and a solution of **(2)**, **(3)**, **(4)**, **(5)** (0.29, 0.39, 0.49, 0.76 g, 1 mmol) in EtOH was added by stirring, respectively. The reaction mixture was boiled under reflux for 4h, and the solid formed was dried under vacuum cabinets (50°C). **(2, 3/a, b, c, d)** FT-IR (cm^{-1}) 3427 (NH), 2895 (CH), 1550 (C=N triazine), 1385 (COO^-), 840 (C—Cl), 538 (M-N), 468 (M-O). **(4/a, b, c, d)** FT-IR (cm^{-1}) 3430 (NH), 2880 (CH), 1556 (C=N triazine), 1383 (COO^-), 619 (M-N), 495 (M-O). **(5/a, b, c, d)** FT-IR (cm^{-1}) 3433 (NH), 2873 (CH_2), 1553 (C=N triazine), 1398 (COO^-), 597 (M-N), 482 (M-O).

Different method for the synthesis of complexes (5a, 5b, 5c, 5d). To a stirred solution of (**3a, 3b, 3c, 3d**) (1.03, 1.13, 1.02, 1.12 g, 1 mmol) and *N*-ethyldiisopropylamine (DIPEA) (0.26 g, 2 mmol) in acetone (50 mL), ethylendiamine (0.14 mL, 2 mmol) was added dropwise to the mixture. This mixture was reflux for 48 h.

RESULTS AND DISCUSSION

''Multidirectional ligands'' bearing 1,3,5-triazine-derivative were prepared by the reaction of cyanuric chloride **(1)** with 4-aminobenzoic acid (Scheme 1). The first and second step have consisted of preparing 2,4-dichloro-6-(4-carboxyanilino)-1,3,5-triazine **(2)**, 2-chloro-4,6-(4-carboxyanilino)-1,3,5-triazine **(3),** 2,4,6-(4-carboxyanilino)-1,3,5-triazine **(4),** and *N,N′*-{bis[4,6-(4-carboxyanilino)]-1,3,5-triazine}ethylenediamine **(5)** by substitution of only chloride atoms of cyanuric chloride, which has been characterized by their elemental analysis, LC-MS analysis, thermal analysis, ^{1}H NMR, FT-IR, AAS, and magnetic susceptibility measurements where replacement of the chloro by

Scheme 1. Reactions of cyanuric chloride with 4-aminobenzoic acid.



the amine group causes lowering of the energy of the NH_2 stretch in the FT-IR spectrum, and a shift to higher field of the NH proton signal in the ^1H NMR spectrum. All the ligands are soluble in common organic solvents.

The optimization of reaction temperatures and the selectivity of amine substitution on the three chlorides of cyanuric chloride were studied by using 4-aminobenzoic acid as the starting amine. This 4-aminobenzoic acid has only a single $-NH_2$ functionality for substitution on the triazine ring. To validate the selectivity mode for the substitutions of three chlorides, the reactions were carried out with different reaction temperatures and molar ratios of triazine to amine at 1:1, 1:2, 1:3 equiv. Two 2-chloro-4,6-(4-carboxyanilino)-1,3,5-triazine (**3**) units were then bridged using ethylenediamine as linker where each amino group substituted the third chloride atom (Scheme 1).

The results indicate that the reaction temperature is important parameter in controlling the amine substitution. Under the reaction temperature of 0–5°C, the first chloride in the triazine ring was selectively substituted by first equiv of amine to produce a sole product. The substitution of second equiv. amines on the second chloride occurred at 25°C. Only at high temperature such as 130°C does the third chloride in the triazine ring was

Table 1

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

Compound	$\mu_{eff\ (296\ K)}$ B.M.	M.p. (°)	Yield (%)	Color M_W (g/mol)	Anal. Found Calc. (%) C	H	N	Fe	Cr
$C_{17}H_{12}ClN_5O_4$ **(3)**	–	348[a]	80	Dark grey (387.77)	**52.88**	**3.07**	**18.17**	–	–
					52.93	3.14	18.15		
$C_{36}H_{30}N_{12}O_8$ **(5)**	–	263[a]	83	White (758.23)	**56.95**	**3.92**	**22.18**	–	–
					56.99	3.99	22.15		
$C_{26}H_{19}Cl_2N_6O_4Fe$ **(2a)**	1.63	293[a]	60	Dark brown (606.22)	**51.46**	**3.10**	**13.82**	9.17	–
					51.51	3.16	13.86	9.21	
$C_{30}H_{19}Cl_2N_6O_4Fe$ **(2b)**	1.65	282[a]	68	Dark brown (654.26)	**54.98**	**3.01**	**12.78**	**8.62**	–
					55.07	2.93	12.85	8.54	
$C_{26}H_{19}Cl_2N_6O_4Cr$ **(2c)**	3.62	285[a]	65	Orange (602.37)	**51.78**	**3.12**	**13.90**	–	**8.58**
					51.84	3.18	13.95		8.63
$C_{30}H_{19}Cl_2N_6O_4Cr$ **(2d)**	3.61	288[a]	55	Orange (650.41)	**55.35**	**3.88**	**12.94**	–	**8.03**
					55.40	2.94	12.92		7.99
$C_{49}H_{38}ClN_9O_8Fe_2$ **(3a)**	1.67	295[a]	59	Dark brown (1028.02)	**57.19**	**3.67**	**12.28**	**10.87**	–
					57.25	3.73	12.26	10.86	
$C_{57}H_{38}ClN_9O_8Fe_2$ **(3b)**	1.62	298[a]	68	Dark brown (1124.11)	**60.85**	**3.37**	**11.22**	**9.97**	–
					60.90	3.41	11.21	9.94	
$C_{49}H_{38}ClN_9O_8Cr_2$ **(3c)**	3.68	290[a]	72	Dark brown (1020.33)	**57.62**	**3.77**	**12.36**	–	**10.13**
					57.68	3.75	12.35		10.19
$C_{57}H_{38}ClN_9O_8Cr_2$ **(3d)**	3.70	291[a]	62	Green (1116.41)	**61.26**	**3.45**	**11.26**	–	**9.30**
					61.32	3.43	11.29		9.31
$C_{72}H_{57}N_{12}O_{12}Fe_3$ **(4a)**	1.78	320[a]	67	Dark green (1449.83)	**59.58**	**3.93**	**10.54**	**10.50**	–
					59.65	3.96	11.59	11.56	
$C_{84}H_{57}N_{12}O_{12}Fe_3$ **(4b)**	1.80	325[a]	59	Dark green (1593.96)	**63.25**	**3.57**	**12.48**	**10.47**	–
					63.30	3.60	10.54	10.51	
$C_{72}H_{57}N_{12}O_{12}Cr_3$ **(4c)**	3.72	318[a]	68	Green (1438.28)	**60.08**	**4.03**	**11.82**	–	**10.67**
					60.13	3.99	10.85		11.69
$C_{84}H_{57}N_{12}O_{12}Cr_3$ **(4d)**	3.75	315[a]	72	Green (1582.41)	**63.70**	**3.58**	**10.66**	–	**9.82**
					63.76	3.63	10.62		9.86
$C_{100}H_{82}N_{20}O_{16}Fe_4$ **(5a)**	1.80	322[a]	60	Brown (2043.24)	**58.72**	**4.01**	**13.69**	**10.87**	–
					58.78	4.05	13.71	10.93	
$C_{116}H_{82}N_{20}O_{16}Fe_4$ **(5b)**	1.83	328[a]	58	Brown (2235.40)	**62.35**	**3.68**	**12.48**	**9.92**	–
					62.33	3.70	12.53	9.99	
$C_{100}H_{82}N_{20}O_{16}Cr_4$ ***(5c)***	3.77	316[a]	51	Green (2027.83)	**59.18**	**4.02**	**11.75**	–	**10.21**
					59.23	4.08	13.81		10.26
$C_{116}H_{82}N_{20}O_{16}Cr_4$ **(5d)**	3.79	319[a]	55	Green (2220.00)	**62.70**	**3.68**	**12.58**	–	**9.31**
					62.76	3.72	12.62		9.37

[a] Decomposition.

reactive for the third equiv. of amine. The reactions, using deviated temperatures from the optimized temperatures, for example, the reaction of 1:3 molar ratio of triazine/amine at 25°C instead of 130°C gave rise to a mixture, di-substituted and unreacted starting material amine, without a trace of tri-substituted product. This implies the third chloride was not reacted at 25°C [2].

Finally, ''multidirectional ligands'' **(2–5)** are described (Scheme 1). The temperature-controlled reaction of cyanuric chloride **(1)** with 4-aminobenzoic acid exclusively led to the formation of compound **(2–5)**. This chemo selectivity of the substitutions is due to the difference of nucleophilicity between an amine and a carboxylate —OH. Sodium bicarbonate was used in that case to avoid deprotonation of the carboxylate —OH group which would have resulted in mixed *N*- and/or *O*-substitution products [2,21,34].

Synthetic strategy for preparing mono-, di-, tri-, and tetra-nuclear is to use a complex as a ''ligand'' that contains a potential donor group capable of coordinating to another ligand. We have chosen [{Fe(salen/salophen)}$_2$O] and [{Cr(salen/Salophen)}$_2$O] as ''ligand complexes,'' because they can coordinate to another ligand [6,27–29]. These complexes are some of the first examples multidirectional complexes bridged by carboxylate anions to the iron and chromium centers (Scheme 1). The results of the elemental analysis, 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 multidirectional (Scheme 1). All complexes are stable at room temperature, and in only organic solvent such as DMSO, DMF and are insoluble in water.

Table 2

Decomposition steps with the temperature range and weight loss for ligands **3** and **5** and **2(a-b)**, **3(b-c)**, **4(c-d),** and **5c** complexes.

Molecular formula	Temp. range (°)	Weight loss, found (calc.) (%)	Fragment
$C_{17}H_{12}ClN_5O_4$ **(3)**	105–120	63.24 (63.43)	CO_2, C_6H_6, H_2, N_2, Cl_2
	220–390	18.87 (18.96)	
$C_{36}H_{30}N_{12}O_8$ **(5)**	94–114	07.52 (07.66)	CO_2, C_6H_6, H_2, N_2, C_2H_2
	123–145	63.72 (63.85)	
	232–387	07.80 (07.91)	
$C_{26}H_{19}Cl_2N_6O_4Fe$ **(2a)**	130–200	43.73 (43.82)	N_2, C_2H_4, CO_2, H_2, C_6H_6, Cl_2
	200–315	22.23 (22.40)	
	330–450	11.58 (11.69)	
$C_{30}H_{19}Cl_2N_6O_4Fe$ **(2b)**	127–215	47.85 (47.93)	N_2, CO_2, H_2, C_6H_6, Cl_2
	215–320	20.68 (20.76)	
	325–445	10.77 (10.83)	
$C_{57}H_{38}ClN_9O_8Fe_2$ **(3b)**	130–223	55.77 (55.82)	N_2, CO_2, H_2, C_6H_6, Cl_2
	227–285	22.12 (24.17)	
	315–410	03.11 (03.15)	
$C_{49}H_{38}ClN_9O_8Cr_2$ **(3c)**	125–235	51.87 (51.91)	N_2, C_2H_4, CO_2, H_2, C_6H_6, Cl_2
	245–318	26.69 (26.74)	
	325–440	03.44 (03.49)	
$C_{72}H_{57}N_{12}O_{12}Cr_3$ **(4c)**	110–218	54.10 (54.16)	N_2, CO_2, C_2H_4, CO, NH_3,H_2, C_6H_6
	223–320	23.83 (25.20)	
	325–445	03.05 (03.12)	
$C_{84}H_{57}N_{12}O_{12}Cr_3$ **(4d)**	120–222	59.30 (59.46)	N_2, CO_2, CO, NH_3,H_2, C_6H_6
	234–295	21.27 (22.91)	
	305–430	02.45 (2.84)	
$C_{100}H_{82}N_{20}O_{16}Cr_4$ **(5c)**	137–248	02.75 (02.85)	N_2, C_2H_4, CO_2, H_2, C_6H_6, C_2H_2
	265–305	51.18 (51.23)	
	316–450	25.24 (26.79)	

The final thermal decomposition products are metal oxides.

To identify the structures of the **(2–5)**, the ^{1}H NMR spectra were recorded in DMSO-d_6. ^{1}H NMR spectra were also in good correlation with the structures of the synthesized compounds. The ^{1}H NMR spectrum signals of ligands **(2–5)** at δ 12.80–12.87–12.93–13.05 and 11.37–11.53–11.94–9.93 ppm correspond to the carboxylate —OH and —NH proton resonances, respectively [30–34].

The vibrations of the N—H, C=N, and C=O of the free ligands **(2–5)** are observed at 3315–3379, 1560–1564, and 1702–1710 cm^{-1} range, respectively [7]. In the complexes, that these bands are, however, shifted to lower frequencies, has indicated that the nitrogen and oxygen atoms of the ''multidirectional ligands'' are coordinated to the ligand complexes. In the ligands, the bands at 3291–3358 cm^{-1} can be assigned to the carboxylate —OH group vibrations, respectively. In the multidirectional complexes, that these bands disappear has demonstrated chelation of oxygen to the metal. These may also overlap with vibrations near 1385–1398 cm^{-1} can be assigned to COO^-. In the tripodal-trinuclear complexes, the bands in the 538–619 and 468–495 cm^{-1} ranges can be attributed to the M-N and M-O stretching modes [7,8].

The magnetic behavior of Fe(III) and Cr(III) complexes is good harmony with proposed octahedral structures. The magnetic moment per mono-, di-, tri-, and tetranuclear complexes which were constructed from [{Fe(salen)/(salophen)}$_2$O] and [{Cr(salen)/(salophen)}$_2$O] either of **(2–5)** shows paramagnetic property with a magnetic susceptibility value per atom: 1.83–1.62 B.M. and 3.79–3.61 B.M., respectively. It is seen that the [{Fe(salen)/(salophen)}$_2$O] and [{Cr(salen)/(salophen)}$_2$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 [{Fe(salen)/(salophen)}$_2$O] and [{Cr(salen)/(salophen)}$_2$O] capped complexes show good harmony with the d^5 and d^3 metal ion in an octahedral structure. This consequence is supported by the results of the elemental analysis suggesting that these complexes have also an octahedral structure [7–13,27–30].

Thermal stabilities of compounds have also thermally been investigated, and their plausible degradation [35] schemes are presented in Table 2. Thermal decomposition of the anhydrous compounds starts in the range of 94–495°C and completes in the range 550–650°C. The observed weight losses for all compounds are in good agreement with the calculated values.

CONCLUSIONS

In this study, multidirectional cyanuric chloride based ''**(2)**, **(3)**, **(4)** and **(5)**'' were synthesized. Synthetic strategy

for preparing mono-, di-, tri-, and tetra-nuclear was used a complex as a ''ligand'' that contains a potential donor group capable of coordinating to the other ligand. [{Fe(salen/salophen)}$_2$O] and [{Cr(salen/Salophen)}$_2$O] were chosen as ''ligand complexes'' because the ligand complexes can be coordinated with other ligand. These complexes are the examples of mono-, di-, tri-, and tetra- nuclear complexes bridged by carboxylate anions to the iron and chromium centers. Their structures were characterized by means of FT-IR spectroscopy, elemental analysis, AAS, thermal analysis, and magnetic susceptibility measurements. The magnetic data for the mono-, di-, tri-, and tetra- nuclear complexes show well agreement with the d^5 and d^3 metal ion in an octahedral structure.

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