



Investigation of Dipodal oxy-Schiff base and its salen and salophen Fe(III)/Cr(III)/Mn(III) Schiff bases (N₂O₂) capped complexes and their magnetic and thermal behaviors



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HIGHLIGHTS

- New dipodal s-triazine based Schiff base was synthesized.
- Six complexes involved Schiff bases with triazine have been synthesized.
- The ligand and complexes were characterized.
- The magnetic data for the complexes were showed the high-spin.

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ABSTRACT

Six new dinuclear Fe(III)/Cr(III)/Mn(III) complexes have been involved tetradentate (N₂O₂) Schiff bases (salenH₂) and (salophenH₂) with 2,4-bis(4-hydroxyphenylimino-4'-formylphenoxy)-6-methoxy-1,3,5-triazine have been synthesized. The complexes were characterized as high-spin ($S = 5/2$) distorted trigonal bipyramidal salen/salophenFe(III) bridged, distorted trigonal bipyramidal ($S = 3/2$) salen/salophenCr(III) and high-spin distorted trigonal bipyramidal ($S = 2$) salen/salophenMn(III) by OH⁻ groups. The structures of ligand and complexes were identified by using elemental analysis, thermal analysis, magnetic susceptibility, LC-MS, ICP-AES, ¹H NMR and FT-IR spectral data.

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Introduction

1,3,5-Triazine (or s-triazines) derivatives are known for a long period of time, and still continue the object of considerable interest, mainly due to their applications in different fields, include the production of pharmaceutical, textile, plastic, and rubber industries, and they have been used as pesticides, dyestuffs, optical bleaches, explosives, polymer photostabiliser and surface active agents. The chemistry of this group of compounds has been studied intensively and they are the subject of many reviews [1–8].

During the last decade, a remarkable development in the preparation of self-assembled architecture through metal ion coordination has been observed [9–12]. Number of derivatives containing s-triazine ring have been reported as heterocyclic compounds.

They are applicable mostly as reactive dyes and some of them are used as polymers, herbicides, drugs, and magnetic materials in recent years [13–18].

The main issues in modern synthetic organic chemistry are selectivity, mildness, improvement of efficiency, and the avoidance of toxic reagents and by-products. From this point of view, considerable attention has been devoted to the development of new 1,3,5-triazine derivatives as reagents in organic synthesis [7]. s-Triazine and Schiff base containing paramagnetic transition metal ions have been synthesized. The magnetochemical properties of the μ -oxo-bridged complexes [Fe(salen)]Cl (salenH₂ = N,N'-bis(salicylidene)ethylenediamine) and [Fe(salophen)]Cl (salophenH₂ = N,N'-bis(salicylidene)-o-phenylenediamine) have particularly been proven, and their properties are mentioned in numerous works [19–22]. Because there is well known that the class of transition-metal contains high-spin molecules has been enriched considerably over last twenty years [23–25]. The Fe(III), Cr(III) and Mn(III)

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complexes contain salen and salophen are high-spin ($S = 5/2$), ($S = 3/2$) and ($S = 2$), respectively [26].

All of the s-triazine derivatives that have wide practical applications are 2,4,6-mono, di- or tri-substituted, symmetrical and non-symmetrical compounds are bearing different substituents [7]. The most important reagent of obtained these compounds is cyanuric chloride (CC), owing to the reactivity of its chlorine atoms toward nucleophiles [7,27]. Due to the advantage of the temperature-dependent stepwise substitution of its three chlorine atoms by different nucleophiles [28], cyanuric chloride has been proved to be a very useful template for the synthesis of dendrimers, macrocycles, calixarene, supramolecular and combinatorial libraries [7,30–33].

The present study reports a method for achieving Dipodal-Dinuclear systems formed by reaction 2,4-Bis(4-hydroxyphenylimino-4'-formylphenoxy)-6-methoxy-1,3,5-triazine (**2**) and ligand complexes are containing N_2O_2 units. And, these complex materials have paramagnetic characters [34]. Herein, we reported the synthesis of a dialdehyde and its Schiff base as a new template. The reaction of cyanuric chloride with 1 equiv methanol and 2 equiv of p-hydroxybenzaldehyde gave the desired dialdehyde, **DIPOD** (Fig. 1), in a two step. The dialdehyde [35] was reacted with 4-aminophenol to afford the corresponding oxy-Schiff base. This oxy-Schiff base was reacted with Ligand Complexes [19] (**LC1–LC6**, Fig. 2) in methanol compose this aimed Dipodal-Dinuclear complexes.

Experimental

Materials

The chemicals were purchased from Aldrich and used as received. Compound **1** was prepared according to the literature procedures [35]. Melting points were measured by using an Optimelt Automated Melting Point System (Digital Image Processing Technology) SRS apparatus (Nyköping – Sweden). Elemental analyses

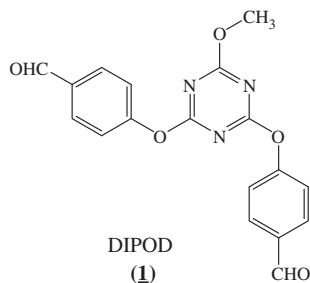


Fig. 1. 2,4-Bis(p-formylphenoxy)-6-methoxy-1,3,5-triazine (DIPOD, **1**).

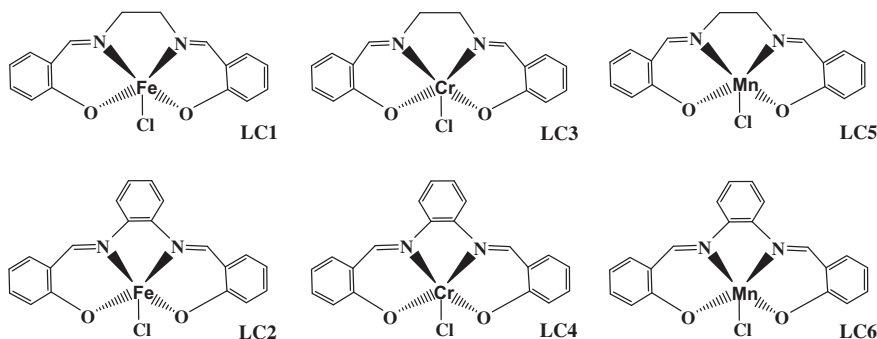


Fig. 2. The structure of ligand complexes.

(C, H, N) were performed by using a Leco, CHNS-932 model analyzer (Massachusetts, USA). 1H NMR spectra were recorded by the Varian, 400 M spectrometer at room temperature. Trimethylsilane (TMS) was used as internal standard (California, USA). FT-IR spectra were recorded using on a Perkin-Elmer Spectrum 100 with Universal ATR Polarization Accessory (Shelton, USA). Thermal analyses were performed on a Shimadzu DTA 50 and TG 50 H on 5 mg samples. The DTA and TG curves were obtained at the heating rate of $10\text{ }^\circ\text{C}/\text{min}$ from $22\text{--}900\text{ }^\circ\text{C}$ under dry N_2 (Kyoto, Japan). Mass spectra were recorded with a Varian MAT 711 spectrometer. The metal complexes were determined quantitatively with a Varian, Vista AX CCD Simultaneous Model ICP-AES spectrophotometer (Palo Alto, USA). Magnetic susceptibilities of the metal samples were measured at 296 K using a Sheerwood Scientific MX Gouy magnetic susceptibility apparatus (Gouy method) with $Hg[Co(SCN)_4]$ as a calibration by constant magnetic field. The effective magnetic moments, μ_{eff} , per metal atom were calculated from the expression, $\mu_{eff} = 2.84\sqrt{\chi_M T}$ B.M., where χ_M is the molar susceptibility (Cambridge, UK).

Preparation of ligand complexes

Ligand Complexes $[Fe(salen)]Cl$ **LC1**, $[Fe(salophen)]Cl$ **LC2**, $[Cr(salen)]Cl$ **LC3**, $[Cr(salophen)]Cl$ **LC4**, $[Mn(salen)]Cl$ **LC5**, $[Mn(salophen)]Cl$ **LC6** were synthesized according to the literature procedures [19,26,34].

Synthesis of 2,4-bis(4-hydroxyphenylimino-4'-formylphenoxy)-6-methoxy-1,3,5-triazine (**2**)

4-aminophenol (2 mmol, 0.22 g) in methanol (50 mL) in Dean-Stark trap and reflux condenser were added to the suspension of DIPOD³⁵ (0.35 g, 1 mmol) in ethanol (20 mL) with stirring drop wise. The mixture was then allowed to stir under reflux for 36 h. The mixture was cooled to room temperature and the precipitate solid light yellow powder product was filtered. The light yellow powder was filtered and washed with sodium bisulfate solution to remove the excess of aldehyde. The product was dried in a vacuum cabinet and stored in a desiccators' over $CaCl_2$. LC-MS (ESI⁺) $m/z = 533$ [100%, (2,4-bis(4-hydroxyphenylimino-4'-formylphenoxy)-6-methoxy-1,3,5-triazine (**2**)]. Molecular peaks of the compounds are observed with the same isotope distribution as the theoretical ones. FT-IR (cm^{-1}): 3373 (OH), 2948 (CH_3) 1623 ($CH=N$), 1581 ($C=N$ triazine), 1353 (COC). 1H NMR (400 MHz, $DMSO-d_6$): δ (ppm), 9.60 (s, 2H, OH), 8.56 (s, 2H, $CH_{olef.}$), 7.91 (d, 4H, $J = 8.4$ Hz, $CH_{arom.}$) 7.32 (d, 4H, $J = 8.4$ Hz, $CH_{arom.}$), 7.16 (d, 4H, $J = 8.8$ Hz, $CH_{arom.}$) 6.78 (d, 4H, $J = 8.8$ Hz, $CH_{arom.}$), 3.84 (s, 3H, CH_3).

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