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Synthesis and Characterization of a N, N'- Bissalicylidene- 1, 2-Phenylenediamine (I)(Salophene) Galodinium

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Abstract: N, N'- bissalicylidene- 1, 2-phenylenediamine (I) (salophene) abbreviated as SPDAS was synthesized and characterized. N, N'- bissalicylidene- 1, 2-phenylenediamine (I) (salophene) galodiniumprepared by reaction of nitrate salt of $Gd(NO_3)_3.6H_2O$ with SPDAS. In this research, some of the inorganic complexes of galodinium with N- donor ligands were synthesized.These compounds were characterized by FT-IR and UV/Visible techniques. The electronic and vibrational spectra of SPDASand N, N'- bissalicylidene- 1, 2-phenylenediamine (I) (salophene) galodiniumhave been measured and studied. Analytical methods have been applied to the investigation of the structure of the compounds SPDASand N, N'- bissalicylidene- 1, 2-phenylenediamine (I) (salophene) galodinium.

Key words: Synthesis · Characterization, Spdas · N, N'- BisSalicylidene- 1 · 2-Phenylenediamine (I) (Salophene) Galodinium · Ft-Ir · Uv/Visible Techniques

INTRODUCTION

Gadolinium is a chemical element with the symbol Gd and atomic number64. It is a silvery-white, malleable and ductilerare-earth metal. It is named for gadolinite, one of the minerals in which it was found, in turn named for chemistJohan Gadolin. Gadolinium as a metal or salt has exceptionally high absorption ofneutrons and therefore is used for shielding in neutron radiography and in nuclear reactors. The Gd(III) ion occurring in water-soluble salts is quite toxic to mammals. However, chelated Gd (III) compounds are far less toxic because they carry Gd (III) through the kidneys and out of the body before the free ion can be released into tissue. Because of its paramagnetic properties, solutions of chelated organic gadolinium complexes are used as intravenously administered gadolinium-based MRI contrast agentsin medical magnetic resonance imaging. However, in a small minority of patients with renal failure, at least four such agents have been associated with development of the rare nodular inflammatory disease nephrogenic systemic fibrosis. This is thought to be due to gadolinium ion itself, since Gd(III) carrier molecules associated with the disease differ. It crystallizes in hexagonal, close-packed α- form at room temperature, but, when heated to temperatures above 1235°C, it transforms into its â- form, which has a body-centered cubic structure.Gadolinium has no known native biological role, but its compounds are used as research tools in biomedicine. It is used in various ion channel electrophysiology experiments to block sodium leak channels and stretch activated ion channels. A Schiffbase, named after Hugo Schiff, is a compound with a functional group that contains a carbon-nitrogendouble bond with the nitrogen atom connected to an aryloralkyl group, not hydrogen. Schiff bases in a broad sense have the general formula $R^1R^2C=NR^3$, where R is an organicside chain. In this definition, Schiff base is synonymous with azomethine. Some restrict the term to the secondaryaldimines (azomethines where the carbon is connected to a hydrogen atom), thus with the general formula RCH=NR'.The chain on the nitrogen makes the Schiff base a stableimine [1-8]. A Schiff base derived from ananiline, where R^3 is a phenyl or a substituted phenyl, can be called an anil.Schiff bases can be synthesized from

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an aromaticamine and a carbonylcompound by nucleophilic additionforming a hemiaminal, followed by a dehydration to generate an imine. There is a Schiff base intermediate in the fructose 1,6-bisphosphate aldolase catalyzed reaction during glycolysisand in the metabolism of amino acids.For the above reasons and in the course of our investigations on Gadoliniumcompounds of transition metals [9-13] and in continuation of our studies on the use of N, N'- bissalicylidene- 1, 2-phenylenediamine (I) (salophene)and after the synthesis of the N, N'- bissalicylidene- 1, 2-phenylenediamine (I) (salophene) and N, N'- bissalicylidene- 1, 2-phenylenediamine (I) (salophene) galodiniumwe were prompted to react N, N'- bissalicylidene- 1, 2-phenylenediamine (I) (salophene) and $Gd(NO_3)_3.6H_2O$. We have managed to prepare two new compounds of galodiniumthat are the analog of the above transition metal compounds. N, N'- bissalicylidene- 1, 2-phenylenediamine (I) (salophene) and N, N'- bissalicylidene- 1, 2-phenylenediamine (I) (salophene) galodiniumhave not been synthesized and reported so far. In this paper a direct, simple and one-step method has been used to synthesize these compounds.

Experimental

Material and Instruments: Acetonitrile (Fluka, P.A.) was distilled several times from phosphorus pentaoxide before use, thereby reducing its water content to <4 ppm. N, N'- bissalicylidene- 1, 2-phenylenediamine (I) (salophene)was bought from Merck. $Gd(NO_3)_3.6H_2O$(Merck, p.a.) was used without further purification. Solvents were purified by standard methods. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. The UV/Visible measurements were made on an Uvicon model 922 spectrometer. Galodinium was estimated iodometrically. The percent compositions of elements were obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

Synthesis Ofn, N'-Bissalicylidene- 1,2-phenylenediamine (I) (Salophene), SPDAS: For synthesis of the SPDASto a magnetically stirred of 1, 2-phenylenediamine (1.26g, 1mmol) in ethanol(25ml) was added to salicylaldehyd (2.318g, 2mmol) at room temperature. The compound was refluxed for 3 hours to ensure the completion and precipitation of the formed complex. The precipitated solid complex was filtered and washed several times with hexane and ether to remove any traces of the unreacted starting materials. Anal. Calcd of SPDAS; C; 76.01, H; 5.06, N; 8.86; found: C; 76.10, H. 5.11, N; 8.93. Mp: 163-165°C. FT-IR (KBr, cm^{-1}): 3444.70 (ν OH of phenol), 1614.36 (ν C=N of immine), 1479.50 (ν C=C of Ar ring), 1275.70 (ν C-O of phenol), UV/Vis:266(1416.67) [ε, M^{-1} cm^{-1}], 316.68(1291.67) [ε, M^{-1} cm^{-1}], 385(83.3) [ε, M^{-1} cm^{-1}].

Synthesis of N, N'-Bissalicylidene- 1,2-phenylenediamine (I) (Salophene) Galodinium: For synthesis of the N, N'- bissalicylidene- 1, 2-phenylenediamine (I) (salophene) galodiniumto a magnetically stirred of SPDAS(0.047g) in acetonitrile (20ml) was added to $Gd(NO_3)_3.6H_2O$ (0.068) at room temperature. The compound was refluxed for 3 hours to ensure the completion and precipitation of the formed complex. The precipitated solid complex was filtered and washed several times with hexane and ether to remove any traces of the unreacted starting materials. Anal. Calcd of $(C_{20}H_{13}N_2O_2)Gd$; C; 51.09, H; 2.76, N; 5.95; found: C; 51.16, H. 2.84, N; 5.99. Mp: 197°C. FT-IR (KBr, cm^{-1}): 3432.22 (ν OH of phenol), 1623.88 (ν C=N of immine), 1384.15 (ν C=C of Ar ring), 115.03 (ν C-O), UV/Vis:380(250) [ε, M^{-1} cm^{-1}], 338(1334) [ε, M^{-1} cm^{-1}], 320(1417) [ε, M^{-1} cm^{-1}], 228(1367) [ε, M^{-1} cm^{-1}], 282(1350) [ε, M^{-1} cm^{-1}], 268 (1125) [ε, M^{-1} cm^{-1}].

RESULTS AND DISCUSSION

The chemistry of Schiff bases is a field that is beingnoticed. Schiff bases are potentially capable of forming stablecomplexes with metal ions.Schiff bases derived from the reaction of aromatic aldehydes and aliphatic or aromatic amines represent animportant series of widely-studied organic ligands.Schiff bases form a significant class of compounds in medicinal and pharmaceutical chemistry with several biological applications that include antibacterial, antifungaland antitumor activity.The ligandand complex are stable at room temperature.

The Advantages of the Newmethod Are:

- There are no sides products,
- The reaction are quite fast, mild conditions and
- The accompanied color change that providing visual means for ascertaining the progress of the reaction.

Preparation of Ligand and Complex: In this paper, we report a new method of the synthesis of N, N'- bissalicylidene- 1, 2-phenylenediamine (I) (salophene) andN, N'- bissalicylidene- 1, 2-phenylenediamine (I) (salophene) galodinium. The reaction between 1,

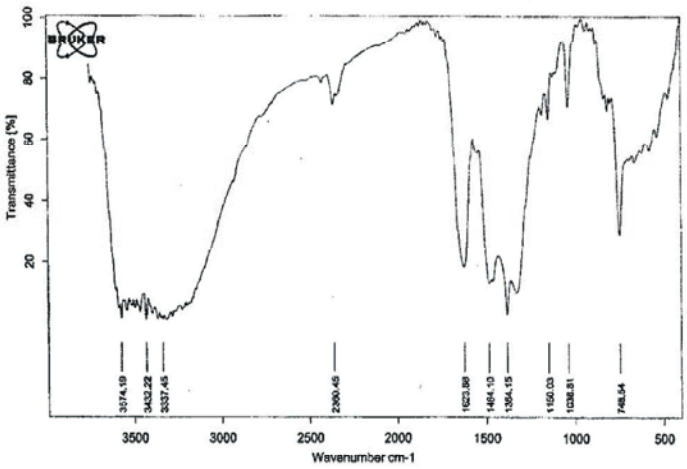

Fig. 1: FTIR spectrum of SPDAS (KBr Disk)

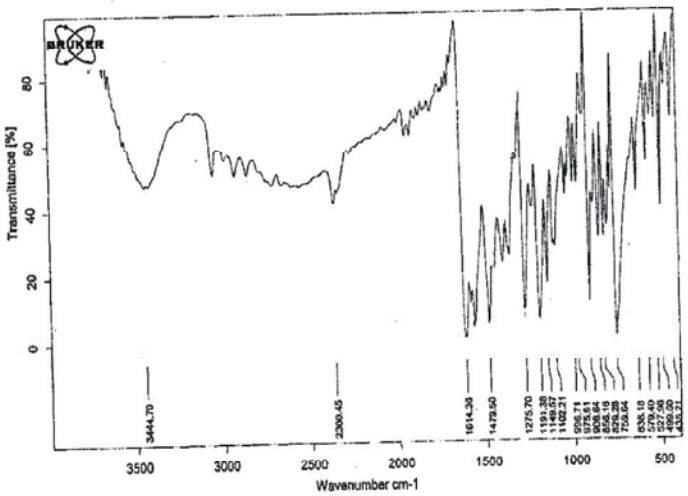

Fig. 2: FTIR spectrum of Gd ($C_{20}H_{13}N_2O_2$) (KBr Disk)

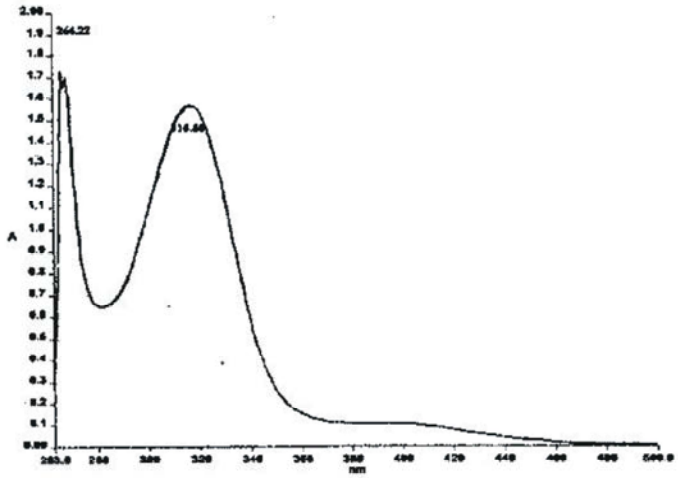

Fig. 3: UV/ Vis spectrum of SPDAS

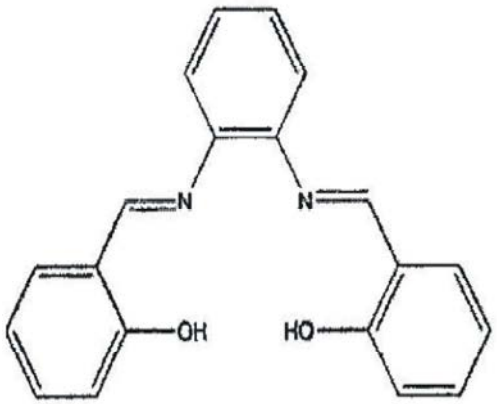

Fig. 4: Chemical structure of SPDAS

2-phenylenediamine, salicylaldehyd, SPDAS and $Gd(NO_3)_3.6H_2O$produced two new galodiniumcompoundand was synthesized through a one-step reaction. Our procedure for producing compound has some advantages. For example, there is no side product in preparing SPDASandGd ($C_{20}H_{13}N_2O_2$) in our method, the reaction is quite fast and does not require any severe conditions such as high pressure or high temperature. These compounds were characterized by FT-IR and UV/Visible techniques. The SPDASand Gd ($C_{20}H_{13}N_2O_2$) have 163-165and 197°C melting points respectively. SPDAS is soluble in DMF, Acetonitrile, methanol, hexane, ethanol, chloroform, dichloro methane and DMSO and insoluble in water and Gd ($C_{20}H_{13}N_2O_2$) is soluble in acetone, THF and DMSO and insoluble in water, chloroform, ethanol and dichloro methane.The spectral data of the complexes have good relationship with the literature data. In the case of SPDASwe observed the following changes. The bands appeared around 3444.70, 1614.36, 1479.50 and 1275.70cm^{-1} due to ν OH of phenol, ν C=N of immine, ν C=C of Ar ring, ν C-O of phenol. In the case of Gd ($C_{20}H_{13}N_2O_2$) we observed the following changes. The bands appeared around 3432.22, 1623.88, 1384.15 and 115.03cm^{-1} due to ν OH of phenol, ν C=N of immine, ν C=C of Arringandν C-O (Figures1-4).

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