

## 4'-(4-Pyridyl)-2,2':6',2''-Terpyridine (Pyterpy) as Ligand in the Gadolinium (III) Complex, [Gd(Pyterpy) (NO<sub>3</sub>)<sub>3</sub>] and Preparation Nano Complex

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**Abstract:** 4'-(4-Pyridyl)-2,2':6',2''-terpyridine (pyterpy) as ligand and Gadolinium (III) complex of it that abbreviated as pyterpy and [Gd(pyterpy)(NO<sub>3</sub>)<sub>3</sub>] were synthesized. The pyterpy has been prepared by reaction of methyl-2-pyridyl ketone in methanol, hydroxid sodium, 4-pyridin carbaldehydewith ammonium acetateand the [Gd(pyterpy)(NO<sub>3</sub>)<sub>3</sub>]has been prepared by reaction of Gadolinium oxide, acid nitric with pyterpy. The authenticity of these ligand and complex was established by elemental analyses, as well as spectroscopic (IR and <sup>1</sup>HNMR), TG, DTA.

**Key words:** 4'-(4-Pyridyl)-2 · 2':6', 2''-Terpyridine (Pyterpy) · Gadolinium (Iii) Complex · Ir · Synthesis

### INTRODUCTION

Gadolinium was first detected spectroscopically in 1880 by de Marignac who separated its oxide and is credited with its discovery. It is named for gadolinite, one of the minerals in which it was found, in turn named for chemist Johan Gadolin. The metal was isolated by Lecoq de Boisbaudran in 1886. 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 agents in 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. Gadolinium combines with most elements to form Gd (III) derivatives. Nitrogen, carbon, sulfur, phosphorus, boron, selenium, silicon and arsenic at elevated temperatures, forming binary compounds. Unlike other rare

earth elements, metallic gadolinium is relatively stable in dry air. However, it tarnishes quickly in moist air, forming a loosely adhering gadolinium(III) oxide (Gd<sub>2</sub>O<sub>3</sub>), which spalls off, exposing more surfaces to oxidation. Gadolinium is a silvery-white malleable and ductile rare-earth metal. It crystallizes in hexagonal, close-packed α- form at room temperature, but, when heated to temperatures above 1235°C, it transforms into its β- form, which has a body-centered cubic structure [1]. Gadolinium-157 has the highest thermal neutron capture cross-section among any stable nuclides: 259,000 barns. Only xenon-135 has a higher cross section, 2 million barns, but that isotope is unstable [2]. Gadolinium is ferromagnetic at temperatures below 20°C (68°F) and is strongly paramagnetic above this temperature [3]. Gadolinium demonstrates a magnetocaloric effect whereby its temperature increases when it enters a magnetic field and decreases when it leaves the magnetic field. The temperature lowered to (5°C (41°F)) for the gadolinium alloy Gd<sub>85</sub>Er<sub>15</sub> and the effect is considerably stronger for the alloy Gd<sub>5</sub>(Si<sub>2</sub>Ge<sub>2</sub>), but at a much lower temperature (<85 K (-188.2°C; -306.7°F)) [4,5]. Individual gadolinium atoms have been isolated by encapsulating them into fullerene molecules and visualized with transmission electron microscope [6]. Individual Gd atoms and small Gd clusters

have also been incorporated into carbon nanotubes [7]. Terpyridine (2,2';6',2''-terpyridine) is a heterocyclic compound derived from pyridine. This colourless solid is used as a ligand in coordination chemistry. Terpyridine is a tridentate ligand that binds metals at three meridional sites giving two adjacent 5-membered  $MN_2C_2$  chelate rings [8]. Gadolinium combines with most elements to form Gd(III) derivatives. nitrogen, carbon, sulfur, phosphorus, boron, selenium, silicon and arsenic at elevated temperatures, forming binary compounds [9]. Terpyridine forms complexes with most transition metal ions as do other polypyridine compounds, such as 2,2'-bipyridine and 1,10-phenanthroline. Complexes containing two terpyridine complexes, i.e.  $[M(\text{terpy})_2]^{n+}$  are common. They differ structurally from the related  $[M(\text{bipy})_3]^{n+}$  complexes in being achiral. Terpyridine complexes, like other polypyridine complexes, exhibit characteristic optical and electrochemical properties: metal-to-ligand charge transfer (MLCT) in the visible region, reversible reduction and oxidation and fairly intense luminescence. Because they are pi-acceptors, terpyridine and bipyridine tend to stabilize metals in lower oxidation states. For instance in acetonitrile solution, it is possible to generate the  $[M(\text{terpyridine})_2]^+$  ( $M = \text{Ni}, \text{Co}$ ). In recent years considerable attention has been drawn to the polymetallic coordination architectures maintained by covalent and non-covalent (supramolecular) interactions in the solid-state [10]. The N-donor ligands have been either exo-bidentate (divergent) [2–9] or chelating bis-bidentate [10]. In this paper we report preparation of a new complex

of 4'-(4-Pyridyl)-2, 2':6', 2''-terpyridine (pyterpy) with Gadolinium (III) and identification them with IR,  $^1\text{H NMR}$ , TG and DTA

## MATERIALS AND METHODS

All reagents were supplied by Merck and were used without further purification. The FT-IR spectra were recorded in the range  $400\text{--}4000\text{ cm}^{-1}$  by KBr disk using a Bruker Tensor 27 M 420 FT-IR spectrophotometer.

### Synthesis of the 4'-(4-pyridyl)-2, 2':6', 2''-terpyridine

**(Pyterpy):** The ligand pyterpy was prepared by a reported method [11]. Yield: 85%. M.p.  $230\text{--}232^\circ\text{C}$ , IR (KBr,  $\text{cm}^{-1}$ ): 3050 (aromatic C-H stretch), 1475, 1585 (aromatic C=C stretch), 1390 (C=N stretch).  $^1\text{H NMR}$  (300 MHz, DMSO, ppm):  $\delta$  7.54 (dd,  $J = 4.8, 6.15\text{ Hz}$ , 2H,  $H_i$ ), 7.94 (d,  $J = 4.8\text{ Hz}$ , 2H,  $H_b$ ), 8.04 (t,  $J = 7.8\text{ Hz}$ , 2H,  $H_c$ ), 8.68 (d,  $J = 7.8\text{ Hz}$ , 2H,  $H_d$ ), 8.76 (s, 2H,  $H_e$ ), 8.76–8.77 (4H,  $H_a, H_d$ ). UV-Vis ( $\text{H}_2\text{O}$ ,  $\lambda_{\text{max}}/\text{nm}$ ): 198, 238, 272, 312. (Fig 1, 2, Table1).

### Synthesis of the $[\text{Gd}(\text{pyterpy})(\text{NO}_3)_3]$ complex

**Reflux method:** At first Gadolinium oxide (0.25 mmol, 0.091 g) reacted with nitric acid (1.5 mmol) to be converted to gadolinium nitrate (0.5 mmol) were dissolved in ammoniac and the below complex was formed. The resulting product was heated until gadolinium nitrate completely dry. Then the resulting product was dissolved in methanol (2 ml). At the next stage pyterpy (0.05 mmol, 0.016 g) was dissolved in

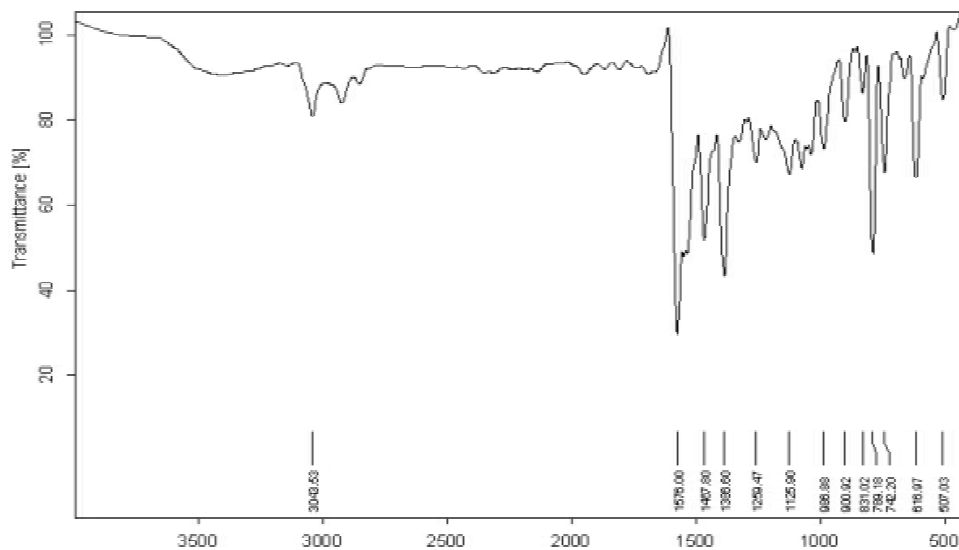


Fig. 1: FTIR spectrum of pyterpy (KBr Disk)

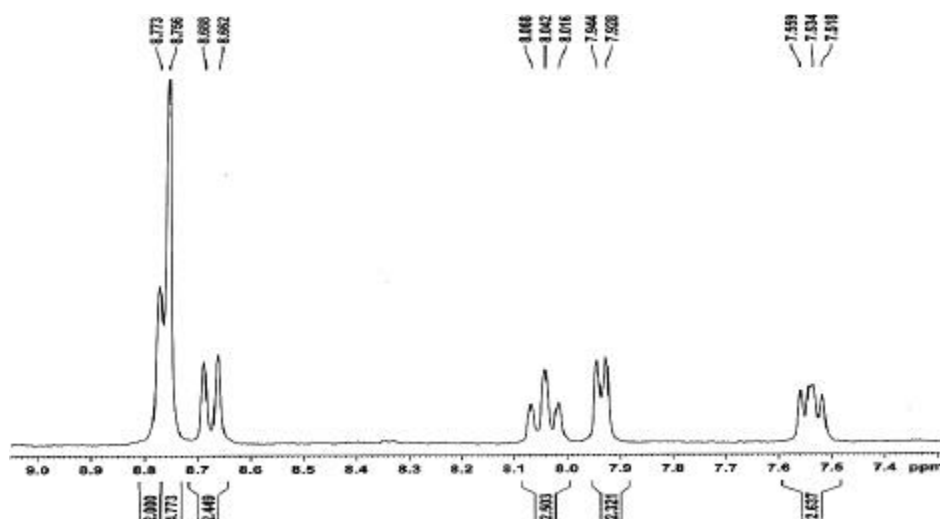


Fig 2: <sup>1</sup>H NMR spectrum of pyterpy(in DMSO)

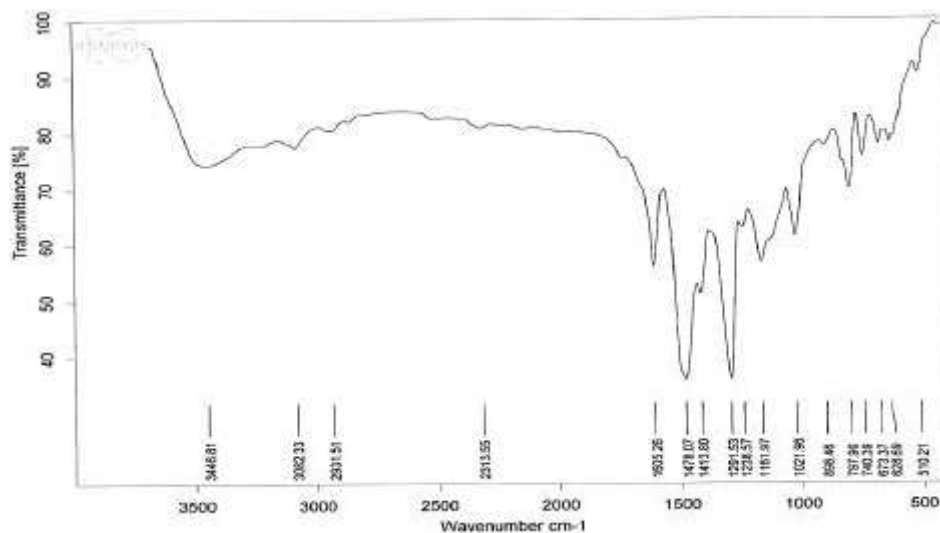


Fig. 3: FTIR spectrum of [Gd(pyterpy)(NO<sub>3</sub>)<sub>3</sub>] (KBr Disk)

Table1: FTIR spectral data (cm<sup>-1</sup>) of pyterpy

$\nu(\text{cm}^{-1})$	Vibration	Intensity
3050	$\nu_{\text{C-H}}$	w
1475	$\nu_{\text{C=C}}$	M
1585	$\nu_{\text{C=C}}$	s
1390	$\nu_{\text{C=N}}$	s

Table 2: FTIR spectral data (cm<sup>-1</sup>) of [Gd(pyterpy)(NO<sub>3</sub>)<sub>3</sub>]

$\nu(\text{cm}^{-1})$	Vibration	Intensity
3085	$\nu_{\text{C-H}}$	w
1605	$\nu_{\text{C=C}}$	M
1478	$\nu_{\text{C=C}}$	s
1413	$\nu_{\text{C=N}}$	w
1291	$\nu_{(\text{NO}_3)}$	s

methanol and added to the first solution. The resulting solution was refluxed at 65°C and after one hour the resulting white precipitate was filtered. Yield 55%, M.P.>300°C, white solid; IR (Kbr,  $\nu/\text{cm}^{-1}$ ): 3082 (C-H arom), 1605, 1478 (aromatic C=C stretch), 1413 (C=N stretch), 1291 (NO<sub>3</sub>), 1161, 1021, 797. UV-Vis (H<sub>2</sub>O,  $\lambda_{\text{max}}/\text{nm}$ ): 201, 240, 276, 287, 331. (Fig 3, 4, Table2).

**Ultrasonic methods:** To prepare this complex, 4'-(4-Pyridyl)-2, 2':6', 2''-terpyridine (pyterpy) was dissolved in methanol- dichloromethane (3:1) and was added to gadolinium nitrate in ethanol. Reaction mixture was placed in the ultrasonic bath, after 5 hour the resulting white precipitate was filtered. Complex nanoscale was approved by SEM images.

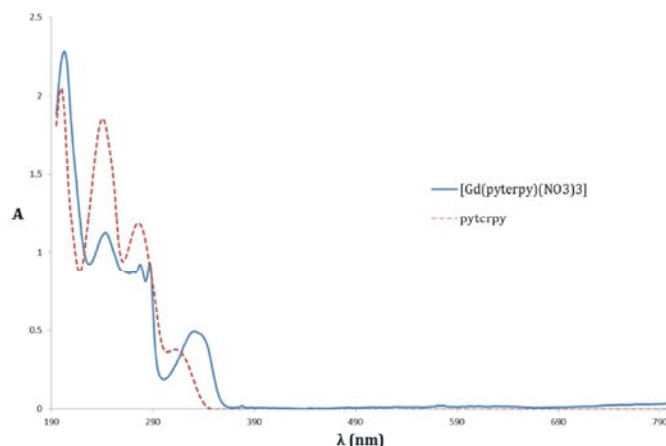


Fig. 4: UV/Vis spectrum of  $[Gd(pyterpy)(NO_3)_3]$  and pyterpy (in acetonitrile,  $C=1 \times 10^{-3} M$ )

## RESULTS AND DISCUSSION

The purpose of building this complex is synthesis of a new compound of gadolinium and study on its characterization is in line with the transparency factor. This is due to the constant presence of aromatic rings in the structure factor enhance transparency and improve efficiency. In this work, ligand is considered to be comprised of four rings Pyridine. Interesting properties, electronic, photonic, magnetic and structural and reactivity of the ligand in the metal complex of the ligand is an important factor. This ligand was soluble in solvents such as diethyl ether, ethanol, ethyl acetate, hexane, acetone and water and soluble in dichloromethane. This complex was insoluble in solvents such as diethyl ether, ethyl acetate, hexane, acetone and water and soluble in ethanol and THF.

In this paper, a direct, simple and one step method has been used to synthesize these compounds. The advantages of the method are; that there is no side product, the reaction is quite fast, there are mild conditions. This complex was obtained in relatively high yield, 75%. The infrared spectrum of these compounds was obtained. The IR spectra of the pyterpy show characteristic bands due to  $\nu$  (CH),  $\nu$  (C=C) and  $\nu$  (C=N) in the region  $3050$ ,  $1475$ ,  $1585$  and  $1390$   $cm^{-1}$  respectively. In the case of  $[Gd(pyterpy)(NO_3)_3]$  complex we observed characteristic bands due to  $\nu$  (CH),  $\nu$  (C=C),  $\nu$  (C=N) and  $\nu$  ( $NO_3$ ) in the region  $3085$   $cm^{-1}$ ,  $1605$   $cm^{-1}$ ,  $1478$   $cm^{-1}$ ,  $1413$   $cm^{-1}$  and  $1291$   $cm^{-1}$  respectively. The  $^1H$ -NMR spectra of pyterpy compound displays a signal at  $7.54$  ppm which is assigned to protons of  $H_a$ , a signal at  $7.94$  ppm which was assigned to two protons of  $H_b$ , a signal at  $8.04$  ppm which is assigned to two protons of  $H_c$ .

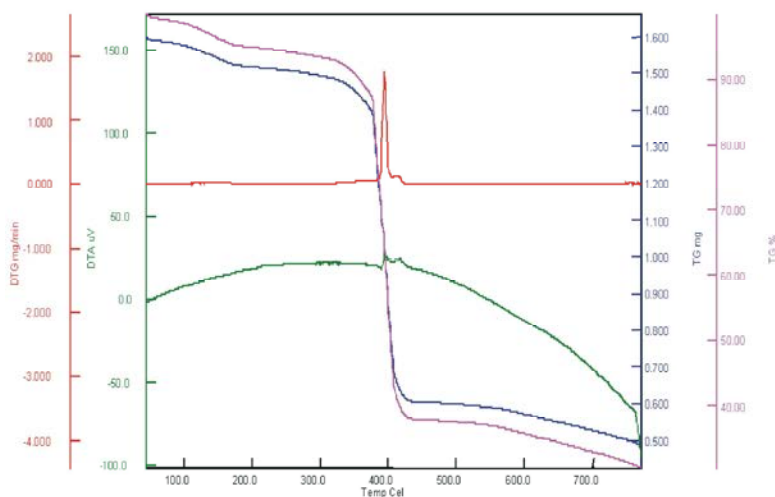


Fig. 5: Thermal analysis data of  $[Gd(pyterpy)(NO_3)_3]$  complex

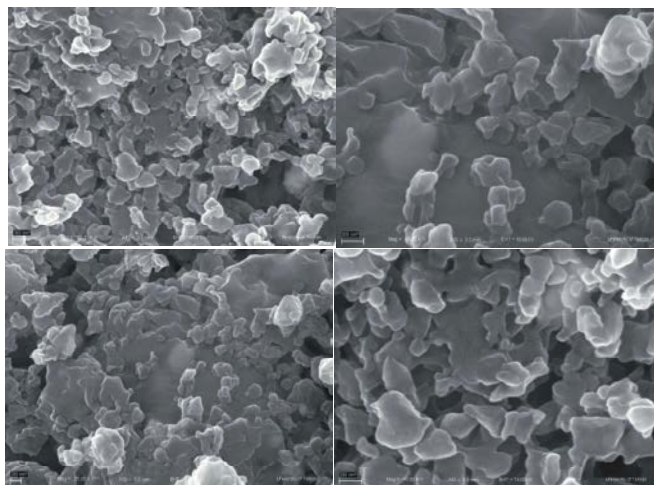


Fig 6: [Gd(pyterpy)(NO<sub>3</sub>)<sub>3</sub>] morphology

**Thermogravimetric Analyses:** The thermal properties of [Gd(pyterpy)(NO<sub>3</sub>)<sub>3</sub>] was investigated by thermograms (TG/ DTA). Figure 5 shows TGA and DTA curves for [Gd(pyterpy)(NO<sub>3</sub>)<sub>3</sub>]. In the temperature range 420°C, a weight losing was observed which was related to the degradation and evaporation of pyterpy.

**SEM Pictures:** Scanning Electron Microscope image of [Gd(pyterpy)(NO<sub>3</sub>)<sub>3</sub>] with different magnification has been shown (Fig 6).

### CONCLUSION

In summary, the synthesis and characterization of complexes have been described pyterpy and [Gd(pyterpy)(NO<sub>3</sub>)<sub>3</sub>] was synthesized simply. These compounds was characterized by IR and <sup>1</sup>HNMR, UV-Vis and TG/DTA.

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