

# Synthesis and Photophysical Investigations of Novel Transition Metal Complexes of Pyridine Tetrazole Ligands

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Two bidentate pyridine-tetrazole ligands *viz*. pyridine tetrazole (Hpytz) and pyridine tetrazole-N-oxide (Hpytzo), which are integrated *in vitro* from pyridine carbonitrile by thermal cycloaddition reaction with sodium azide for complexation with transition metals (Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup> and Ru<sup>3+</sup>) to improve sophisticated photonic appliances in them as perceived in Ln (III) complexes. The configuration investigation of *bis* and *tris*-complexes was studied in solution by UV, FTIR and <sup>1</sup>H NMR techniques. The hetero-nuclear pyridine tetrazole metal complexes display a close performance concerning the photo-physical properties as displayed by lanthanide(III) complexes and conventional carboxylate analogous.

Keywords: Transition metal complexes, Pyridine tetrazole ligands, Spectroscopy.

#### INTRODUCTION

The utmost success in the tetrazole chemistry is the innovative creation of organometallic derivative of tetrazole which escalating precipitously [1]. The elevated physiological activity and low toxicity of tetrazole marks, it feasible to these metal complexes as affluence of attractive biochemical and pharmaceutical activities. More than 20 biological activities of tetrazole are recognized. Tetrazole derivatives "antennae" have better ability to custom the complexes with *d*- and *f*-metal ions. These complexes displayed the curious photophysical properties. Thus, chemical properties revealed by them are very parallel due to roughly alike ionic radius and only separated by ion-exchange method at greater ease.

The photophysical properties revealed by transition metal and inner transition metal complexes are due to by d-d and f-f transitions, a fascinating or attractive property of these complexes. This performance is owed by accessibility of bare d-orbitals and f-orbitals on absorption of light. The metal center get animated to higher energy state *i.e.*, splitting of d-orbitals and f-orbitals will ensue, triggering the creation of two sets of energy levels in which transition of electron takes place from lower to higher energy state. The current work with lanthanide salts have been made with novel organic tetrazole centered

ligands in which nitrogen and oxygen acts as donor atoms [2,3]. The lanthanide complexes made are very effective and increases spectroscopic assets with these ligands. The novel assembly of these two bide-ntate [4] organic pyridine tetrazole ligands "antennae" surviving a good chromophores which sensitizing lanthanide (III) centered emission and well screening the metal center intensely by non-radioactive deactivation progressions like O-H vibrators in the vicinity of metal center [5-8]. These lanthanide(III) complexes have amplified in numerous applications ranging from biomedical diagnosis to photonic devices and solar energy renovations [9-15]. These pyridine tetrazole ligands "antennae effect" are vital for increased molar absorption coefficient and for rising excitation wavelength. Thus, well design novel ligand architecture shows elevated radiation quantum yield, extensive luminescence and lifetime [16,17]. These organic ligands acts as chromophores capable of triggering the lanthanide center efficiently. The characteristic action of transition metals offer a route to coordination chemistry for the synthesizing of novel compounds with (Hpytz ) and (Hpyto) ligands in which nitrogen and oxygen atoms acts as moral donor atoms [18]. The metal-center elected for making of new modules of metal complexes was performed with some transition metals  $(Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Ru^{3+})$ . The attractive properties of transition metals are revealed by *d*-*d* transition on absorption

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of light in UV-visible region. This absorption band was boosted by using such organic ligands "antennae effect" in which pyridine and tetrazole rings together acts as chromophore unit, thus upsurges its absorption spectra. The configuration of these transition metal complexes intensifies an innovative idea in coordination chemistry as revealed by lanthanide(III) complexes and carboxylate analogous, which differ from usual coordination chemistry as they are distant from these innate properties such as: luminescence efficiency, medicinal property (disease diagnosis), high quantum yield, sharp radiation spectra, optical property, long-lived luminescence-lifetime, biomedical appliances [9,12,14,19].

The promoted molecule can emit the absorbed energy by diverse routes which merely depend on the lifetime of metal complex (stability) in the excited state. In case of lanthanide complexes singlet<sup>1</sup>-triplet<sup>3</sup> inter-system crossing is more preferential due to L-S coupling which strongly evidences the configuration of triplet<sup>3</sup> state [20]. The tetrazole centered lanthanide complexes aids the antenna center (antenna effect) for changing the light in UV-visible range which offers coloured vision (OLEDS, waveguides) [21,22]. The replacement by highly conjugated tetrazole constructed novel organic ligands promote these complexes for absorption of the visible region [23]. This is an innovative feature of these complexes that specifies an incredible awareness in biomedical purposes such as MRI in which black and white images are supplanted by coloured images that aids in surgical diagnosis. Hence, such remarks supports the arrangement of transition metals with pyridine tetrazole organic ligands.

The lanthanide complexes so far holding following ligands namely pyridine tetrazole, pyridine *bis*-tetrazolate and terpyridine tetrazolate (pentadentate). It was observed with the expansion in denticity of ligands the complex formation tendency drops and also due to elevated cost of lanthanide salts their accessibility becomes harder. Since transition metals and inner transition metal complexes are very close in their properties. Nowa-days, a remarkable field of complexation of these tetrazole based organic ligands with transition metals arise, which are inexpensive and easily accessible. The varieties of ligands used containing heteronuclear tetrazole part *viz*., pyridine tetrazole and pyridine tetrazole-N-oxide [24].

#### **EXPERIMENTAL**

UV spectrum: Shimadzu UV-1800 series, IR spectrum: FTIR-8400S Shimadzu, <sup>1</sup>H NMR spectrum: Bruker Avance-II 400 NMR Spectrometer using TMS as internal standard (DMSO- $d_6$ ) are used to determine the structures of the metal complexes and photophysical spectroscopic properties.

**Synthesis of pyridine tetrazole (Hpytz):** 2-Cyanopyridine (10 mmol) in 300 mL of toluene, 130 mmol of sodium azide and 130 mmol of triethylamine were mixed together followed by the addition of 130 mmol of conc. HCl with constant stirring for 30 min and then refluxed for 12-16 h. Now, addded 30 mL of water and stirred for 30 min resulted in the formation of two layers. Separate the aqueous layer by adding 10 to 100 mmol of acetic acid, after few minutes white crystals were obtained [25,26]. Yield (7.5 g, 65 %); .m.w. 147; m.p. 215-220 °C.

**Synthesis of pyridine tetrazole-N-oxide (Hpytzo):** Hpytz (1 mmol) and 2.5 mmol of Mcpba were added in 180 mL of ethanol and then stirred at room temperature. Haziness occurs after 30 min which indicated the formation of white precipitate of crystals of pyridine tetrazole-N-oxide (**Scheme-I**). Yield (2.55 g, 70 %); .m.w. 163; m.p. 255-260 °C.



Scheme-I: Synthesis of pyridine tetrazole-N-oxide

Synthesis of *bis*- and *tris*-pyridine tetrazole metal complexes: Metal salt (1 mmol) was dissolved in 2 mL ethanol and then added (2/3mmol) of Hpytz and (2/3mmol) of triethylamine mixture in 20 mL ethanol in 250 mL round bottom flask and then refluxed the mixture for 12-16 h (Scheme-II). The coloured precipitate of metal complex was washed by ethanol followed by cold distilled water and finally again with ethanol (m.p. > 360 °C).





Synthesis of *bis*- and *tris*-pyridine tetrazole-N-oxide metal complexes: Hpytz-N-oxide (2/3 mmol) and triethylamine (2/3 mmol) are mixed in 20 mL of ethanol followed by the addition of 1mmol of metal salt dissolved in 2 mL of ethanol and then refluxed the mixture for 12-16 h (Scheme-III). The coloured precipitate was collected and washed first by ethanol followed by cold distilled water and finally again with ethanol (m.p. > 360 °C).



M = Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Ru<sup>3+</sup>



**Synthesis of [M(pytz)<sub>2</sub>(TPPO)<sub>2</sub>]:** Triphenylphosphine oxide (TPPO, 1.5 mmol) dissolved in 30 mL of ethanol was added to 0.5 mmol of [M(pytz)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] dissolved in 2 mL of ethanol reflux and then stirred the mixture for 12-16 h (**Scheme-IV**). The coloured precipitate was collected and washed similarly as described about and dried at room temperature (m.p. > 360 °C).



#### **RESULTS AND DISCUSSION**

**Absorption spectroscopy:** The solubility and immersion spectra of all the *bis*- and *tris*-metal complexes of Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup> and Ru<sup>3+</sup> was taken in subsequent diluents methanol, ethanol, acetonitrile and DMSO. From the immersion spectra all the complexes, it was marked that there was sizeable bathochromic shift in the absorption maxima in all complexes owed by unsaturation or prevalence of conjugated aromatic pyridine and tetrazole rings, with the consequences a shift was perceived in the wavelength on complex formation, portraying that the complexation has ensued in the vicinity of metal center. This bathochromic shift in the absorption band can be distinctly seen from the succeeding data of all the complexes, which was a close semblance of the spectroscopic assets of lanthanide (III) complexes [27-30].

The ligands (Hpytz, Hpytzo) display proficient absorption in UV-region from 400 to 800 nm of absorption band, two sorts of peaks are perceived 269 nm peak of extensive wavelength and also peaks 239, 240 nm of smaller wavelength. This designates the system is extremely conjugated due to existence of unsaturated tetrazole and pyridine rings (for pyridine 256 nm), from this surveillance these ligands boosts the absorption interface for spectroscopic assets in the metal complexes [20].

**Iron complexes:** The pyridine tetrazole complexes of iron display eclectic array of absorption spectra from 269 to 357 nm on complexation with these ligands (Table-1). The *bis*- complexes of iron { $[Fe(pytzo)_2(H_2O)_2]$  and  $[Fe(pytzo)_2(H_2O)_2]_2$ } with ligands (Hpytz and Hpytzo) are impressively inclined on absorption of light in UV-region to 354 nm, 357 nm as related to *tris*-complexes of iron { $[Fe(pytzo)_3]$  and  $[Fe(pytz)_3]$ } to 272 and 275 nm. Hence, these ligands display better absorption spectra on configuration of *bis*-iron complexes rather than *tris*- complexes.

TABLE-1 UV DATA OF LIGANDS AND METAL COMPLEXES				
Ligands & Complexes	Wavelength (nm)			
Hpytz	239, 269			
Hpytzo	240, 269			
$[Fe(pytz)_2(H_2O)_2]$	271, 357			
[Fe(pytz) <sub>3</sub> ]	242, 275			
$[Fe(pytzo)_2(H_2O)_2]$	240, 354			
[Fe(pytzo) <sub>3</sub> ]	237, 272			
$[Co(pytz)_2(H_2O)_2]$	288			
[Co(pytz) <sub>3</sub> ]	244, 282			
$[Co(pytzo)_2(H_2O)_2]$	288			
[Co(pytzo) <sub>3</sub> ]	244, 282			
$[Ni(pytz)_2(H_2O)_2]$	287			
[Ni(pytz) <sub>3</sub> ]	236, 288			
$[Ni(pytzo)_2(H_2O)_2]$	240, 252			
[Ni(pytzo) <sub>3</sub> ]	242, 272			
$[Zn(pytz)_2(H_2O)_2]$	205, 241			
[Zn(pytz) <sub>3</sub> ]	245, 273			
$[Zn(pytzo)_2(H_2O)_2]$	274, 667			
[Zn(pytzo) <sub>3</sub> ]	272, 273			
$[Ru(pytz)_2(H_2O)_2]$	242, 271			
[Ru(pytz) <sub>3</sub> ]	242, 272			
$[Ru(pytzo)_2(H_2O)_2]$	240, 288			
[Ru(pytzo) <sub>3</sub> ]	271, 412			

**Cobalt complexes:** The pyridine tetrazole complexes of cobalt indicate inclusive sort of absorption spectra from 269 to 288 nm on complexation with these ligands (Table-1). The *bis*-complexes of cobalt { $[Co(pytz)_2(H_2O)_2]$  and  $[Co(pytz)_2(H_2O)_2]$ } with ligands (Hpytz and Hpytzo) are insignificantly induced on absorption of light in UV region to 288 nm both as competed to *tris*-complexes of cobalt { $[Co(pytz)_2(H_2O)_2]$  and  $[Co(pytz)_3]$  to 282 nm. Hence, these ligands confirms well absorption spectra to specific degree on arrangement of *bis*-cobalt complexes moderately than tris- complexes.

**Nickel complexes:** The pyridine tetrazole complexes of nickel illustrates comprehensive scope of absorption spectra from 269 to 288 nm on complexation with these ligands (Table-1). The *bis*-complexes of nickel { $[Ni(pytzo)_2(H_2O)_2]$  and  $[Ni(pytz)_2(H_2O)_2]$ } with ligands (Hpytz and Hpytzo) are persuaded reduced range on absorption of light in UV- region to 287 nm but *tris*-

complexes of nickel display proficient absorption {[Ni(pytzo)<sub>3</sub>] and [Ni(pytz)<sub>3</sub>]} to 288 nm as rivalled to *bis*-nickel complexes. Hence, these ligands performs efficient absorption spectra on formation of tris-nickel complexes reasonably than bis-complexes.

Zinc complexes: The pyridine tetrazole complexes of zinc demonstrates extensive range of absorption spectra from 269 to 667 nm on complexation with these ligands (Table-1). The bis complexes of zinc { $[Zn(pytz)_2(H_2O)_2]$  and  $[Zn(pytzo)_2(H_2O)_2]_2$ } with ligands (Hpytz and Hpytzo) are deeply manipulated on absorption of light in UV-region to 667 nm as related to triscomplexes of zinc  $\{[Zn(pytzo)_3] \text{ and } [Zn(pytz)_3]\}$  to 273 nm. Henceforth, these ligands expresses better absorption spectra on construction of bis-zinc complexes slightly than tris-complexes. Also bis complex of zinc [Zn(pytzo)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] with Hpytzo indicates inordinate boost in UV-absorption spectra to 667 nm.

Ruthenium complexes: The pyridine tetrazole complexes of ruthenium demonstrates varied range of absorption spectra from 269 to 412 nm on complexation with these ligands (Table-1). The bis complexes of ruthenium  $\{[Ru(pytz)_2(H_2O)_2]$  and  $[Ru(pytzo)_2(H_2O)_2]$  with ligands (Hpytz and Hpytzo) are a bit induced on absorption of light in UV region to 288 nm as rivalled to tris-complexes of ruthenium {[Ru(pytzo)<sub>3</sub>] and [Ru(pytz)<sub>3</sub>]} to 412 nm. Hereafter, these ligands spectacles better absorption spectra on arrangement of tris-ruthenium complexes slightly than bis-complexes. Also tris-complex [Ru(pytzo)<sub>3</sub>] with Hpytzo spectacles boundless improvement in UV-absorption spectra to 412 nm.

From the above observations, bis- and tris-metal complexes of transition metals (Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup> and Ru<sup>3+</sup>) with pyridine tetrazole and pyridine tetrazole-N-oxide ligands can subsidize almost equally for photophysical spectroscopic assets in the UV-region of absorption band, also a bathochromic shift was noted that was severely due to a conformational change during complex formation and consequently triggers the coloured vision (Table-1). The same marks was perceived with lanthanide (III) complexes with bis-tetrazole pyridine, bipyridine and terpyridine tetrazole ligands.

FTIR studies: From FTIR data (Table-2), the key bands of ligand configuration (Hpytz, Hpytzo) were predicted by the remark of subsequent peaks of stretching frequencies C-H, N=N, C=C,C-N in the range of 3093-3084, 1481,1612-1396, 1159 cm<sup>-1</sup>, respectively and metal complex formation by obtaining the metal-nitrogen, metal-oxygen peaks of stretching frequencies. For iron [Fe(pytzo)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], [Fe(pytz)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (390, 418 cm<sup>-1</sup>), (390, 410 cm<sup>-1</sup>) Fe-O, Fe-N str. for bis-complexes similarly for tris-complexes [Fe(pytzo)<sub>3</sub>], [Fe(pytz)<sub>3</sub>] (395, 412.7 cm<sup>-1</sup>), (412, 410 cm<sup>-1</sup>) Fe-O, Fe-N. There are also stretching frequencies of O-H, C-N, C=C, N=N, C-H (3416-3394, 3093-3022, 1481-1437 and 1614-1396 cm<sup>-1</sup>). The stretching frequency of 3396-3416 cm<sup>-1</sup> is due to the presence of water molecule in bis-complexes and also due to trapped water molecules in tris-complexes. Similarly, the key bands of other bis and tris-metal complexes are shown in Table-2. The TPPO complexes of Fe, Co, Ni and Zn are blended by substitution of water molecules by triphenyl phosphine oxide. From IR analyses, it was perceived that the O-H peaks of stretching frequency 3396-3416 cm<sup>-1</sup> was found to be lacking which may be attributed due to deactivation of non-radiative process.

<sup>1</sup>H NMR studies: <sup>1</sup>H NMR spectrum of all the synthesized complexes was taken in DMSO at 298 K. The <sup>1</sup>H NMR spectrum of  $[Zn(pytzo)_3]$  following peaks are observed;  $\delta$  ppm 8.45, (*meta*, 2H) and  $\delta$  ppm 7.5 (*para*, 1H) due to aromatic protons

TABLE-2 KEY BANDS (cm <sup>-1</sup> ) OF LIGANDS AND THEIR METAL COMPLEXES								
Ligand/Complexes	ν(C–H)	$\nu(N=N)$	ν(M–N)	v(M–O)	ν(C=C)	ν(C–N)	ν(O–H)	
Hpytz	3093	1481	-	-	1396	1159	-	
Hpytzo	3084	1481	-	-	1410	1159	-	
$[Fe(pytz)_2(H_2O)_2]$	3065	1437	418.0	390	1612	1163	3416	
[Fe(pytzo) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3059	1437	410.0	390	1612	1159	3394	
[Fe(pytz) <sub>3</sub> ]	3022	1437	412.7	395	1614	1163	-	
[Fe(pytzo) <sub>3</sub> ]	3065	1450	412.0	410	1612	1165	-	
[Fe(pytz) <sub>2</sub> (Tppo) <sub>2</sub> ]	3059	1437	403.0	391	1612	1163	-	
$[Co(pytz)_2(H_2O)2]$	3059	1462	418.0	390	1396	1163	3423	
$[Co(pytzo)_2(H_2O)2]$	3059	1456	412.0	385	1431	1159	3394	
[Co(pytz) <sub>3</sub> ]	3059	1462	418.0	395	1396	1163	-	
[Co(pytzo) <sub>3</sub> ]	3101	1450	412.0	395	1431	1165	-	
[Co(pytz) <sub>2</sub> (Tppo)2]	3059	1464	416.0	391	1431	1163	-	
$[Ni(pytz)_2(H_2O)_2]$	3059	1462	418.0	385	1431	1163	3423	
[Ni(pytzo) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3059	1456	412.0	385	1450	1159	3391-3059	
[Ni(pytz) <sub>3</sub> ]	3100	1462	418.0	395	1431	1163	-	
[Ni(pytzo) <sub>3</sub> ]	3101	1450	412.0	395	1431	1163	-	
[Ni(pytz) <sub>2</sub> (TPPO) <sub>2</sub> ]	3059	1464	416.0	395	1431	1165	-	
$[Zn(pytz)_2(H_2O)_2]$	3059	1435	416.0	390	1610	1160	3200	
$[Zn(pytzo)_2(H2O)_2]$	3059	1437	410.0	395	1620	1159	3387	
$[Zn(pytz)_3]$	3022	1437	418.5	395	1614	1163	-	
$[Zn(pytzo)_3]$	3225	1433	416.0	408	1612	1165	-	
$[Zn(pytz)_2(TPPO)_2]$	3059	1443	418.0	391	1610	1161	-	
$[Ru(pytz)_2(H_2O)_2]$	3097	1442	452.0	381	1386	1159	3394	
$[Ru(pytzo)_2(H_2O)_2]$	3097	1442	452.0	381	1386	1159	3412	
[Ru(pytz) <sub>3</sub> ]	3091	1438	422.0	395	1614	1159	-	
[Ru(pytzo) <sub>3</sub> ]	3095	1440	424.0	399	1614	1165	_	
$M = Fe_{c} Co_{c} Ni_{c} Zn_{c} Ru$								

TABLE-2	
KEY BANDS (cm <sup>-1</sup> ) OF LIGANDS AND THEIR METAL COMPLEXE	ES

of pyridine ring,  $\delta$  ppm 2.5-3.5 (DMSO) and  $\delta$  3.52-4.00 ppm due to trapped water molecules in the metal complex, counter ion (NHEt<sub>3</sub>)  $\delta$  2-2.5 ppm. In <sup>1</sup>H NMR spectrum of  $[Co(pytz)_2(H_2O)_2]$  bis-complex, first set of signals,  $\delta$  ppm 8.6, (meta, 2H) and  $\delta$  ppm 7.6 (para, 1H) due to aromatic protons of pyridine ring; second set of signals,  $\delta$  3.52 ppm (due to proton of water) and third set of signals,  $\delta 2.5$  ppm (due to DMSO) was observed, which confirms the complexation has occurred in the vicinity of metals. Similarly in [Zn (pytz)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] biscomplex, the incidence of three sets of signals, first set corresponding due to the aromatic protons of pyridine ring  $\delta$ ppm 8.34, (*meta*, 2H) and  $\delta$  ppm 7.65 (*para*, 1H), second set ( $\delta$  3.52 ppm) corresponds to water molecule, coordinated to the metal centre in all bis complexes and the third peak corresponds to solvent (DMSO) at  $\delta$  2.5 ppm). In <sup>1</sup>H NMR analysis of [Ru(pytz)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] bis complex following peaks are observed; ( $\delta$  3.5-4 ppm, H<sub>2</sub>O) has coordinated to the metal centre and ( $\delta$ 2.5 ppm, DMSO). The peaks due to aromatic protons of pyridine ring,  $\delta$  ppm 8.55, (*meta*, 2H) and  $\delta$  ppm 7.75 (*para*, 1H).

### Conclusion

A series of bidentate pyridine organic ligands Hpytz, Hpytzo are combined in vitro by conservative routine and then used for coordination with transition metals. The ratio of ligands used to synthesize a series of *bis* and *tris* (pytz, pytzo) complexes with Fe, Co, Ni, Zn and Ru metal ions. The assembly investigation and representative descriptions are determined by several spectroscopic techniques like UV, FTIR, and <sup>1</sup>H NMR. The absorption window was greatly increased from 269 to 412 nm [Ru(pytzo)<sub>3</sub>], 667nm [Zn(pytzo)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] as observed in zinc, ruthenium metal complexes, alike observation was seen in terpyridine lanthanide(III) complexes because of d-d transitions and L-S coupling (singlet-triplet state) which tunes them in photonic applications. From these observations, the transition metal complexes can show an impressive substitution for photophysical spectroscopic properties as shown by lanthanides and orthodox carboxylate complexes.

## **CONFLICT OF INTEREST**

The authors declare that there is no conflict of interests regarding the publication of this article.

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