

Synthesis and Characterization of 1-(2', 4' dihydroxy-5-nitrophenyl)-3-(pyridin-3-yl)-propane-1, 3-dione and its metal complexes

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Abstract: 1-(2', 4' dihydroxy-5-nitrophenyl)-3-(pyridin-3-yl)-propane-1, 3-dione **4** and its metal complexes have been synthesized. The β -diketone **4** is afforded by employing Baker-Venkataraman rearrangement on 2-acetyl-4-nitro-5-hydroxyphenyl nicotinate **3**. The synthesized compound have been characterized by physical, spectral and analytical data. The functionalized β -diketone compound acts as bidentate ligand and co-ordinate with the transition metal atom through β -diketo system. The synthesized compounds have also been screened for in vitro antibacterial activity.

Keywords: β -diketones, Baker-Venkataraman rearrangement, metal complexes, antibacterial activity.

INTRODUCTION

The chemistry of 1,3-diketones and its metal complexes has attracted the attention of scientists for almost a century. Diketones are key intermediates for the synthesis of core heterocycles such as pyrazole^[1], isoxazole^[2], triazole^[3], flavones^[4], benzodiazepine^[5] and pyrimidine^[6].

In the last decades, β -diketones and their metal complexes have been used as chelating ligands for lanthanides and transition metals.^[7] β -diketones are bidentate ligands with the possibility of complexation with almost all the metal ions.^[8] The nature of bonding and chelation was elucidated by Werner and Morgan.^[9] A wide variety of β -diketones with different substituents and their complexes have been synthesized and their properties such as volatility, Lewis acidity or aggregation state, standard molar enthalpies of

formation, standard molar enthalpies of sublimation, vapour pressures, enantioselective catalytic property etc have been studied.^[10]

β -diketones are clinically important molecules since they exhibits some biological activities, such as antiviral, insecticidal, antioxidants, antitumors, anticancer^[11] and antibacterial activities and are also key intermediates to various heterocyclic compounds.^{[12]-[15]}

β -diketone like Anabaena β -diketone hydrolase also possesses some enzymatic activities^[16], Rare earth doped β -diketone complexes were studied as promising high-density optical recording materials for blue optoelectronics^[17]. Lanthanide complexes of β -diketones are vastly studied for their optical properties like electroluminescence^[18] and fluorescence^[19,20].

Metal 1, 3-diketonates have been used in the production of laser devices^[21] and as NMR shift reagents^[22]

The lanthanides are also known to form stable complexes with different β -diketonates^[23], which in the last three decades have been intensively studied due to their potential applications in design of chelate lasers^[24], efficient organic light emitting diodes (OLEDs)^[25], polymer light emitting diodes (PLEDs)^[26], as NMR shift reagents^[27], in analytical applications and as a modern antibody catalysts in biochemistry.^[28]

Some β -diketonates are also used in UV sunscreen cosmetics that filters certain ultraviolet rays to protect skin.^[29] β -diketonate in its keto-enol form is also an important pharmacophore of HIV-1 integrase inhibitors.^[30] It is also used as extractants for lanthanide ions.^[31]

In present work, we have synthesized and studied some properties of 1-(2', 4' dihydroxy-5-nitrophenyl)-3-(pyridin-3-yl)-propane-1, 3-dione and its metal complexes. The title compound was synthesized from 2-acetyl-4-nitro-5-hydroxyphenyl nicotinate by employing Baker-Venkataraman rearrangement^[32] which was previously synthesized by Nitroresacetophenone. The synthesized compounds were characterized by analytical techniques and screened for antibacterial study.

EXPERIMENTAL AND METHOD:

p-Nitroresacetophenone 2:

5.5g of dry resacetophenone was dissolved in 25ml H₂SO₄ by heating it at 60-65^o for 15min. Then the reaction mixture was cooled below 10^oC and a cold nitrating mixture (4ml HNO₃ and 5ml H₂SO₄) was added into it in small portions maintaining the temperature of system below 10^oC. It was kept for 15min at 0-10^oC and then poured into crushed ice

with constant stirring and washed with cold water. Yield: 5.3g (74%) m.p. 142^oC

2-acetyl-4-nitro-5-hydroxyphenyl nicotinate 3:

3.94g (0.02mol) of p-nitroresacetophenone **2** and 2.46g (0.02mol) of nicotinic acid were dissolved in 10ml dimethylformamide and cooled in ice bath. To that 3ml POCl₃ was added dropwise with constant stirring maintaining the temp below 10^oC. After 2 hr the reaction mixture was poured on crushed ice with stirring. White solid compound separated out which was then washed with cold water. The product was filtered and recrystallized from alcohol. Yield: 5.19g (86%); m p: 180^oC

1-(2',4'dihydroxy-5-nitrophenyl)-3-(pyridin-3-yl)-propane-1, 3-dione 4:

6.04g (0.02mol) of 2-acetyl-4-nitro-5-hydroxy-phenyl nicotinate **3** was dissolved in 18ml of dry dimethyl sulfoxide in a 50ml bolt-necked flask and heated to 50^oC. 1.7g (0.03mol) of potassium hydroxide was added with mechanical stirring which was powdered rapidly in a mortar preheated in an oven at 100^oC and was stirred for 15min. The reaction mixture was then cooled to room temperature and acidified by adding 25ml of 10% aqueous acetic acid with stirring. The yellow coloured compound so obtained was filtered and recrystallized from ethanol. Yield: 4.77g (79%); m.p.220^oC.

Bis(β -diketonato) Cu(II) complex 5a:

Complexes of β -diketonate compound **4** have been synthesized by dissolving compound **4** and copper acetate in 2:1 mole in ethanol. The olive green solid **5a** precipitated was filtered and washed with hot ethanol Yield: 93%. Similarly, the complexes of Cobalt, Nickel, Manganese and Zinc were prepared.

Table 1: Physical properties and elemental analyses of the ligand and its metal complexes

	Color	Yield%	Elemental Analyses found (calculated)			
			%C	%H	%N	%M
Ligand(L)	Yellow	73	55.13 (55.63)	3.39 (3.31)	9.63 (9.27)	--
[Mn.2L.2H ₂ O]	Orange	89	48.11 (48.34)	3.02 (2.88)	8.19 (8.08)	7.69 (7.90)
[Co.2L.2H ₂ O]	Rosewood	71	48.35 (48.06)	2.52 (2.86)	7.64 (8.01)	8.70 (8.43)
[Ni.2L.2H ₂ O]	Brown	64	48.14 (48.06)	2.98 (2.86)	8.40 (8.01)	8.48 (8.40)
[Cu.2L]	Olive Green	86	50.06 (50.29)	2.86 (2.99)	8.13 (8.38)	9.36 (9.51)
[Zn.2L]	White	81	50.63 (50.22)	3.16 (2.99)	8.73 (8.37)	9.39 (9.27)

Table 2: Infrared data of the ligand and its metal complexes (cm⁻¹)

	-C=O	-OH	-C-H Aromatic	C=C	-C=N	C-NO ₂	-CH ₃ ester	M-O	H-O-H Coordinated water
Anhn 3	1736	3450	3042	1630	1589	1501	2972	-	-
Ligand(L)	1736	3440	3045	1641	1589	1501	-	-	-
[Mn.2L.2H ₂ O]	1682	3440	3058	1636	1588	1508	-	415	754
[Co.2L.2H ₂ O]	1697	3484	3029	1625	1576	1508	-	458	752
[Ni.2L.2H ₂ O]	1657	3390	3065	1621	1581	1522	-	465	762
[Cu.2L]	1696	3430	3034	1630	1585	1508	-	443	-
[Zn.2L]	1662	3450	3029	1626	1601	1508	-	410	-

anhn= 2-acetyl-4-nitro-5-hydroxyphenyl nicotinate

RESULTS AND DISCUSSION

The elemental analyses were done using the Perkin Elmer 2400 CHN analyzer. FT-IR spectra were recorded using (KBr) disc on Perkin-Elmer spectrum Rx-I spectrometer. ¹H NMR were recorded on Bruker AC-300 F (300 MHz) NMR spectrometer using DMSO-*d*⁶ and CDCl₃ as solvent and tetramethylsilane as an internal standard. Mass spectra were recorded on 70-S Mass spectrometer using m-nitro benzyl alcohol (NBA) matrix.

The synthesized ligand and its metal complexes were characterized by their physical properties, elemental analyses, IR Spectra, ¹H NMR, mass spectra, electronic and magnetic spectra.

Physical properties and elemental analyses of the ligand and its metal complexes have been tabulated in **Table 1**. The elemental analyses of the ligand and its metal complexes were found in good agreement with the calculated data.

The characteristic infrared spectral assignment of ligand and its complexes have been reported in **Table 2**. The presence of broad band at 3450 cm⁻¹ in the infrared spectra may be due to the -OH group. The band appearing at 1736 cm⁻¹ in the spectra of ligand assigned due to the carbonyl group (C=O), exhibited a lower shift in metal complexes. This shift indicates that the beta-diketo functionality in ligand coordinated with the transition metal ion. All the above evidences were further supported by the emergence of new bands at 410-465 cm⁻¹ due to the metal-oxygen vibrations. These new bands were only observed in the spectra of the transition metal complexes only.

2-acetyl-4-nitro-5-hydroxyphenyl nicotinate **3** undergoes Baker-Venkataraman rearrangement to afford bright yellow needles of 1-(2', 4' dihydroxy-5-nitrophenyl)-3-(pyridin-3-yl)-propane-1, 3-dione **4**. The negative test for ester confirms that it is devoid of ester group. The elemental analysis and

characteristic infrared spectral assignment of this compound is reported in Table 1 and Table 2 respectively. The structure was further confirmed by the other spectral analysis: ¹H NMR (DMSO-*d*₆) : 15.72 (s, 1H), 12.02 (s, 1H), 4.76(s, 1H), 8.89(s, 1H), 8.84 (s, 1H), 7.10-8.17 (d, 2H), 7.26 (d, 1H), 6.92 (d, 1H), 7.02 (s, 1H); MS (EI, 70eV): m/z (%) 302 (M⁺, 100), 303 (M⁺, 32), 137 (55). In the ¹H NMR Spectra it gives characteristic peak at 15.72 which corresponds to enolic proton and at 12.02 which is being due to phenolic proton adjacent to carbonyl group. It confirms the formation of -diketones. The compound in enolic form is more stable than that of ketonic one.

The complex of synthesized compound **4** gives green colored Cu (II) -diketonate **5a** in high yield. The elemental analysis and characteristic infrared spectral assignment of this compound is also reported in Table 1 and Table 2 respectively. The structure was then further confirmed by the spectral analysis: ¹H NMR (DMSO-*d*₆): 12.56 (s, 2H), 4.99(s, 2H), 8.79(s, 2H), 8.78 (d, 4H), 7.67-8.21 (m, 4H), 7.67 (d, 2H), 7.02 (d, 2H), 7.09 (s, 2H); MS (EI, 70eV): m/z (%) 668 (M⁺, 100), 669(M⁺,12), 137(62).

Similarly, other transition metal complexes were prepared by the same method. The ligand and its metal complexes are quite stable. All the complexes are insoluble in water but soluble in acetone, Methanol and DMSO. The complexes are non-electrolytic in nature.

Magnetic and electronic spectral studies of Ligand and its metal complexes

[Mn.2L.2H₂O] complex shows two bands at 19.76kK and 28.73kK which may be due to ⁴T_{2g}, ⁶A_{1g} and ⁴A_{1g}, ⁴E_g, ⁶A_{1g} for octahedral geometry^[33]. The [Co.2L.2H₂O] complex exhibited the bands at 21.74kK and 10.38kK, which may be due to ⁴T_{1g}(P), ⁴T_{1g}(F) and ⁴T_{2g}(F), ⁴T_{1g}(F) transition

respectively, having distorted octahedral geometry^[34]. For [Ni.2L.2H₂O] complex, the bands observed at 15.87kK and 24.89kK which may be assigned to ³T_{1g}(F) ³A_{2g} and ³T_{1g}(P) ³A_{2g} transition respectively indicates octahedral geometry^[35], while Cu.2L complex exhibited two bands at 14.10kK and 19.80kK which may be due to ²E_g ²B_{1g} and Charge Transfer respectively for square planar geometry^[36]. Since Zn.2L complex is a d¹⁰ system and hence is diamagnetic in nature, however, on the basis of other spectral data, its most probable geometry is suggested to be tetrahedral^[37].

The magnetic susceptibility measurements of all the complexes were carried out at room temperature by the Gouy's method. (Hg[Co(NCS)₄]) was used as reference material. Molar susceptibilities were corrected for diamagnetism of the component atom using pascal's constant^[38]. The magnetic moments (μ_{eff}) and electronic spectral data of all the complexes have been reported in **Table 3**.

Antibacterial screening

The synthesized compounds were screened for antibacterial activities against bacteria, such as

E.coli, *P. aeruginosa* (Gram-negative), *P. vulgaris*, *B. subtilis* and *S. aureus* (Gram-positive) using filter paper disc diffusion method (Peach and Traey, 1950). Antibiotic drugs such as Streptomycin and Amoxicillin were used as reference drugs. Selected pathogenic bacteria were maintained on nutrient agar medium for 36 hrs. Old bacterial culture were inoculated into nutrient broth and incubated at 37 ± 2⁰c on a rotary shaker at 100 rpm. After 36 hrs incubation, the bacterial suspensions were used for further tests.

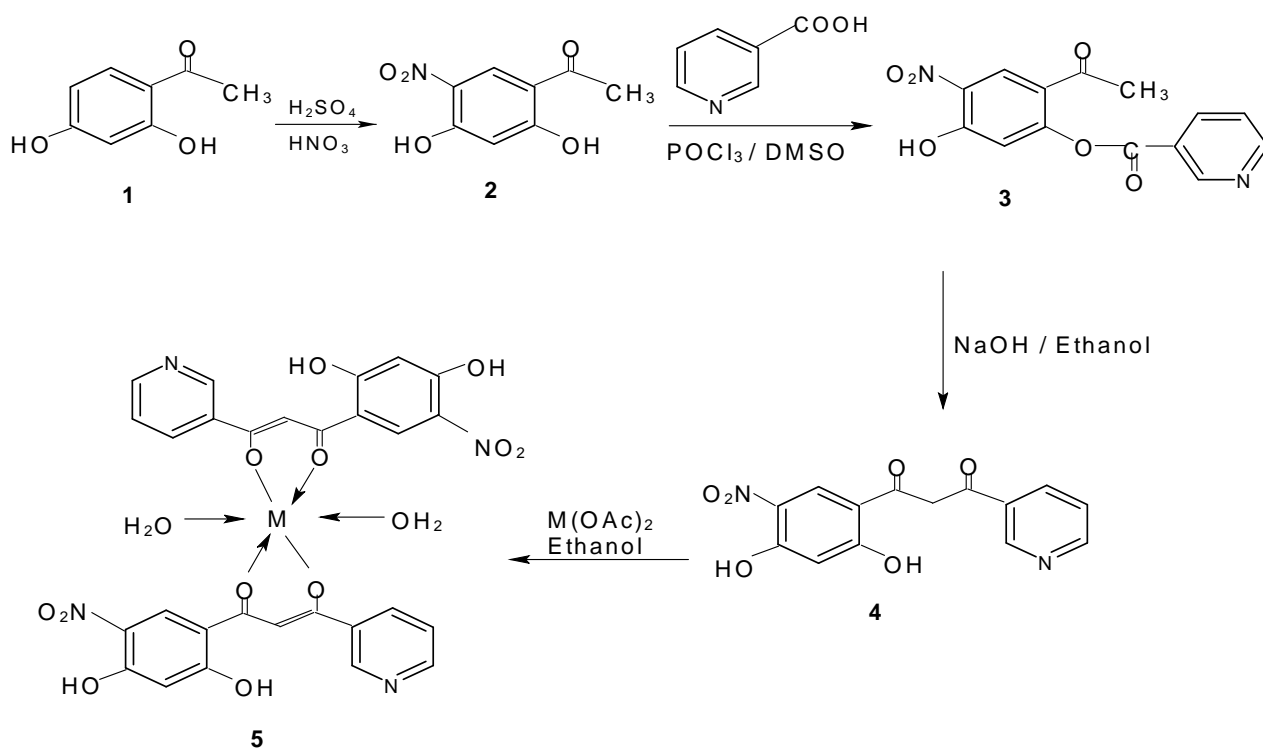
Antibacterial activity was then carried out using 100µg/mL of synthesized compounds. Filter paper disc soaked in solvent was used as negative controls while the discs soaked in standard broad-spectrum antibiotic solution (Streptomycin and Amoxicillin) were used as positive control. The results of tested compounds against these bacteria have been shown in **Table 4** given below. The Screening result indicates that the compounds showed moderate to excellent antibacterial activities.

Table 3: Magnetic and electronic spectral data of Ligand and its metal complexes

	Effective Magnetic Moment (μ_{eff})	Absorbance (kK)	Assignments	Stereochemistry
[Mn.2L.2H ₂ O]	5.82	19.76 28.73	⁴ T _{2g} ⁶ A _{1g} ⁴ A _{1g} ⁴ E _g ⁶ A _{1g}	Octahedral
[Co.2L.2H ₂ O]	5.02	10.38 21.74	⁴ T _{2g} (F) ⁴ T _{1g} (F) ⁴ T _{1g} (P) ⁴ T _{1g} (F)	Distorted octahedral
[Ni.2L.2H ₂ O]	3.63	15.87 24.89	³ T _{1g} (P) ³ A _{2g} ³ T _{1g} (P) ³ A _{2g}	Octahedral
[Cu.2L]	1.78	14.10 19.80	² E _g ² B _{1g} CT	Square planar
[Zn.2L]	diamagnetic	--	--	Tetrahedral

Table 4: Antibacterial activity of compounds:

	Source	Solvent	Minimum Inhibitory Concentration (MIC) µg mL ⁻¹ Diameter of Inhibition Zone (in mm)				
			Gram-negative		Gram-positive		
			<i>E. coli</i>	<i>P. aeruginosa</i>	<i>P. vulgaris</i>	<i>B. subtilis</i>	<i>S. aureus</i>
1.	Ligand 4	H ₂ O	11	14	12	31	33
2.	Mn(II) complex	DMSO	28	12	13	30	--
3.	Co(II) complex	DMSO	41	--	--	--	--
4.	Ni(II) complex	DMSO	24	15	19	21	11
5.	Cu(II) complex	DMSO	31	26	27	32	27
6.	Zn(II) complex	DMSO	09	--	25	--	26



$\text{M} = \text{Co}(\text{II}), \text{Ni}(\text{II})$ and $\text{Mn}(\text{II})$ where water of coordination present however in case of $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$, water of coordination is absent.

Scheme: Synthesis of ligand and its metal complexes

CONCLUSION

In the present work 1-(2', 4' dihydroxy-5-nitrophenyl)-3-(pyridin-3-yl)propane-1, 3-dione 4 was prepared by employing Baker-Venkataraman Transformation and its transition metal complexes were also synthesized. Their structures were elucidated on the basis of spectral analysis such as elemental analysis, IR, NMR, mass, electronic and magnetic spectra. The spectra revealed that the prepared compounds possess characteristic peaks due to the presence of enolic proton and phenolic

proton adjacent to carbonyl group. These synthesized compounds were screened for in vitro antibacterial activity and found to be promising candidates as new antibacterial agents.

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