



STUDIES OF SOME HYDRAZONE DERIVATIVES AND THEIR TRANSITION METAL COMPLEXES

Vijay Kumar Tiwari^{1*}, Anupa Kumari Dubey² and S. N. Dikshit³

^{1,2,3}Department of Chemistry, S.M.S Govt. Model Science College, Gwalior, MP., India.

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*Corresponding Author

Vijay Kumar Tiwari

Department of Chemistry,
S.M.S Govt. Model
Science College, Gwalior,
MP., India.

ABSTRACT

The new series of two new hydrazone derivatives and their vanadium complexes have been synthesized bearing the formula $V[DPTDH](BF_4)_2$ and $V[DCTDH](BF_4)_2$, where $M=V$, $DPTDH=2,6$ -diacetyl pyridine- $N-N'$ -dithiodiacetyl dihydrazone and $DCTDH=2,6$ -pyridine diacarbonyl dichloride- $N-N'$ -dithiodiacetyl dihydrazone and $(BF_4)=$ Tetrafluoroborate. The complexes were characterized on the basis of various spectroscopic techniques like FT-IR, UV & elemental analysis, and conductivity measurements. The octahedral geometry of synthesized complexes confirms by electronic data and IR spectra. The compounds were subjected to antimicrobial screening of ligand and

hydrazone derivatives and their vanadium complexes against bacteria and fungi shows the complexes have been found to be manifold active biologically than the ligand.

KEYWORDS: Hydrazone derivatives, Ligand, vanadium complexes, FT-IR, spectral and biological studies.

INTRODUCTION

Transition metals are particularly suitable for this purpose because they adopt a wide variety of coordination numbers, geometries and oxidation states in comparison with carbon and other main group elements.^[1] The d-block metal ions have tendency to form the complexes. A series of transition metal complexes with Schiff bases, aromatic hydrazones^[2-5] have been quite extensively investigated. The chemistry of hydrazone complexes involving O, N, S donor ligands has received special attention because of their coordination capability, their pharmacological activity^[6-10] and their uses in analytical chemistry as metal extracting agents. It has recently been shown that the metal complexes are more potent and less toxic in many cases as compared to the parent compound.

EXPERIMENTAL

MATERIALS & METHODS

All the chemicals and solvents used of A.R. grade, purchased from Aldrich, Himedia, Merck were used as received.

Synthesis of Ligand

1:2 stoichiometric quantities of thiodiacetic acid ester (1.78 gm., 0.01M) and hydrazine hydrate (0.83cm³, 0.02M) were mixed in 20ml. ethyl alcohol with continuous stirring. The obtained solution was refluxed over a water bath at 40-50°C for around 5-6 hours. Thereafter, obtained light-yellow crystal in bottom round flask was concentrated to one-third of its original volume. Then, the obtained solution was cooled overnight and light-yellow crystals were filtered, washed with alcohol and ether then dried in vacuum over anhydrous CaCl₂ in a desiccator.

Synthesis of 2,6-diacetyl pyridine-N-N'-thiodiacetyl dihydrazone

1:1:1 stoichiometric quantities of thiodiacetic acid dihydrazide (1.78gm, 0.01M), vanadium acetate (1.85 gm, 0.01M) and 2,6-diacetyl pyridine (1.63 gm., 0.01M) were mixed in 20ml. ethanol with continuous stirring. The dark greenish-brown solution thus obtained was refluxed over a water-bath for around 6-7 hours. Thereafter, it was concentrated to one-third of its original volume. It was subjected to addition of a small quantity of sodiumtetrafluoroborate and solution was cooled overnight when light-brown crystal separated out. The crystals were filtered, washed with alcohol and ether and dried in vacuum over anhydrous CaCl₂ in a desiccator.

Synthesis of 2,6- pyridine dicarbonyl di chloride-N-N'-thiodiacetyl dihydrazone

1:1:1 stoichiometric quantities of thiodiacetic acid dihydrazide (1.78 gm., 0.01M), vanadium acetate (1.85 gm., 0.01M) and 2,6-pyridine dicarbonyldichloride (1.90 gm., 0.01M) were mixed in 25ml. Ethanol with constant stirring. The solution obtained was refluxed over a water-bath for around 6-7 hours. Thereafter, it was concentrated to one-third of its original volume. Then, a small amount of sodiumtetrafluoroborate was added and solution was cooled overnight when chocolate-brown crystals separated out. The crystals were filtered, washed with alcohol and ether and dried in vacuum over anhydrous CaCl₂ in a desiccator.

ANALYTICAL AND PHYSICAL MEASUREMENTS

The elemental analysis helps in fixing the stoichiometric composition of the ligand and hydrazone derivatives and their vanadium complexes. The carbon, hydrogen, nitrogen, oxygen analyzed by sophisticated analytical instrument facility such as Elemental Analyzer (*Thermo Scientific 338 35210*) and for weighing by micro balance (*Mettler Toledo Model XP₆*). melting point determine by (*Make-VEEGO, Model- VMP-PM*). For metal estimation, using gravimetric method of analysis *Vogel's Quantitative Inorganic Analysis (seventh edition) revised by G.SVEHLA*. Infra-red spectra of synthesized compounds were recorded on (*Perkin-Elmer, Model No.- C91158*) in the range 4000-400 cm^{-1} . The electronic spectra of complexes in DMSO were recorded on a UV-VIS-NIR (*Cary5E*) spectrophotometer at room temperature.

Table: 1 Elemental Analysis and Molar Conductivity Data of the Ligand and Newly Synthesized hydrazone derivatives and their vanadium complexes

Compound	M.P. (°C)	Color	Yield	Molecular Weight [F/(c)]	Percentage Composition (F/c)				Molar Conductivity ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)
					C	H	N	M	
TDADH	176	Light-Yellow	2.55gm	178.13 (178.21)	26.94 (26.96)	5.61 (5.66)	31.43 (31.44)	-	-
V(II)[DPTDH](BF ₄) ₂	209	Light-Brown	1.98gm	531.89 (531.92)	29.32 (29.35)	3.19 (3.22)	13.16 (13.17)	9.45 (9.58)	113.35
V(II)[DCTDH](BF ₄) ₂	239	Chocolate-Brown	1.89gm	572.70 (572.76)	23.04 (23.07)	1.92 (1.94)	12.22 (12.23)	8.76 (8.89)	113.66

INFRA-RED DATA

The band due to the $-\text{NH}_2$ group disappeared completely in the complexes. The band due to the $-\text{NH}$ group did not show any change in the spectra of complexes, confirming that the Nitrogen of $-\text{NH}$ group did not take part in reaction whereas a sharp band was seen in the range of 1350cm^{-1} proving that $-\text{NH}_2$ group is present in the ligand. Some entirely new absorption band appeared in the spectra of complexes viz. band around $560\text{--}550\text{cm}^{-1}$ due to M-N group, a band around $440\text{--}430\text{cm}^{-1}$ due to M-O group and a band around $340\text{--}320\text{cm}^{-1}$ due to presence of M-S group. These new band confirmed the coordination of nitrogen and sulphur with the metal atom in the complexes.

Table: 2: Infra-red Spectral Data of Ligand and Newly Synthesized hydrazone derivatives and their vanadium complexes

S. No.	FUNCTIONAL GROUPS	TDADH	V(II)[DPTDH](BF ₄) ₂	V(II)[DCTDH](BF ₄) ₂
1.	-CH ₂	2930	2880	2870
2.	-NH ₂	1350	-	-
3.	-NH	3420	3410	3400
4.	N-N	980	930	940
5.	>C=N	-	1590	1580
6.	>C=O	1730	1690	1670
7.	M-N	-	560	550
8.	M-O	-	440	430
9.	M-S	-	340	320

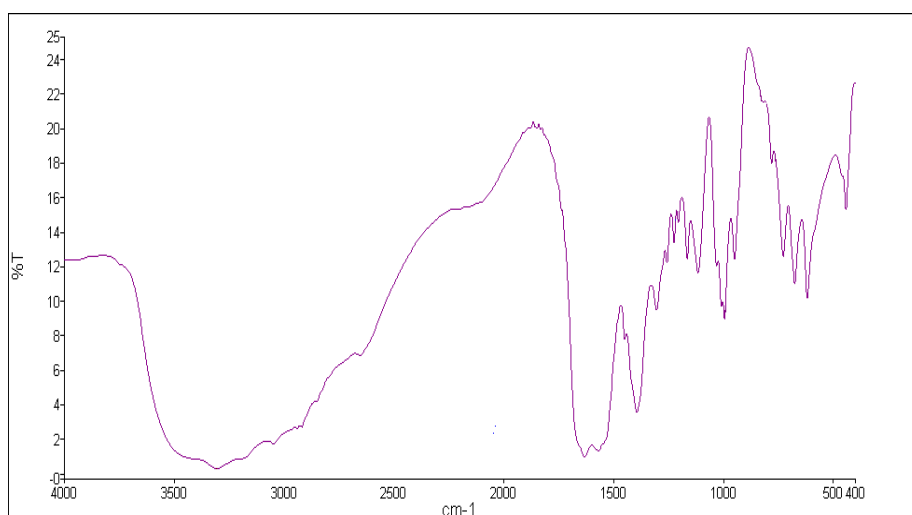


Figure 1: Infra-red Spectrum of Ligand (TDADH)

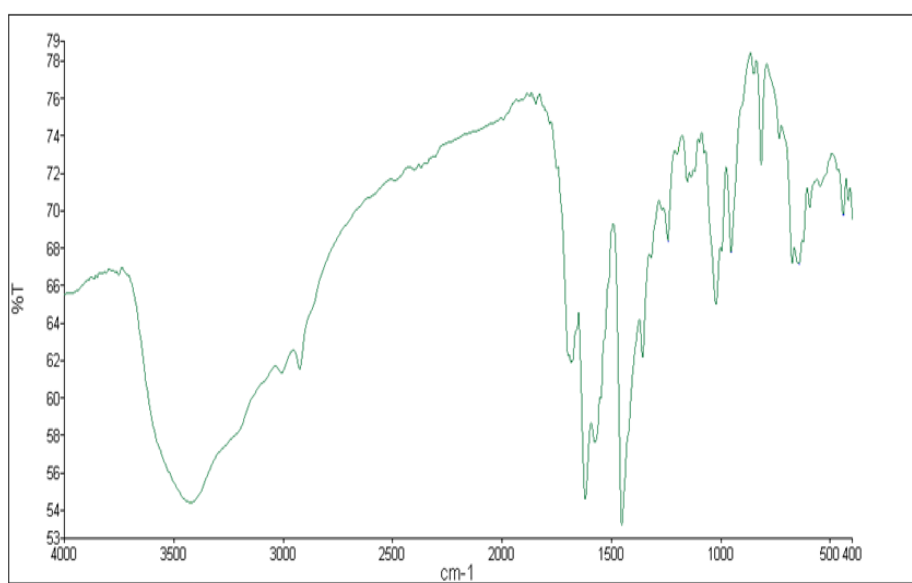


Figure 2: Infra-red spectrum of synthesized complex V(II)[DPTDH](BF₄)₂

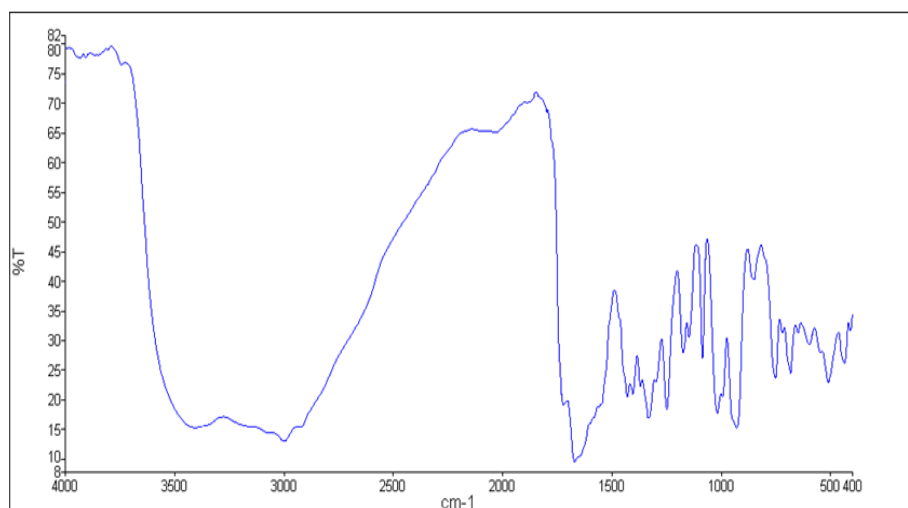


Figure: 3 Infra-red Spectrum of Synthesized Complex V(II)[DCTDH](BF₄)₂

ELECTRONIC DATA

The synthesized hydrazone derivatives and their vanadium complexes are stable in air, completely insoluble in water and common organic solvents, but they are soluble in DMSO. The electronic spectra of the complexes recorded in DMSO (HPLC grade). All the absorption bands in electronic spectra were found for complexes in the range of 11,550–11,500 cm⁻¹ attributed to ²E_g→²T_{2g} transition and in the range of 24,250–24,200cm⁻¹ attributed to L→M charge transfer transition. These transition confirmed the octahedral geometric of the complexes.

Table 3: Absorption Bands (in cm⁻¹) of hydrazone derivatives and their vanadium complexes

S. No.	Complexes	Transition (cm ⁻¹)	
		² E _g → ² T _{2g}	L→M
1.	V(II)[DPTDH](BF ₄) ₂	11500	24250
2.	V(II)[DCTDH](BF ₄) ₂	11550	24200

ANTIMICROBIAL ACTIVITY

Agar Well Diffusion Method

The antimicrobials present in the compound are allowed to diffuse out into the medium and interact in compound and sealed with test microorganism. The resulting zone of inhibition will be uniformly circular as there will be a confluent lawn of growth.

Minimum Inhibitory Concentration (MIC)

The MIC values determine by the sets to of “two fold serial dilution method”. In this method 1 ml. of seeded broth (obtained by 1:100 dilution of the indicated micro-organism in broth)

was taken in ten well sterilized tubes (3x100mm. size) keeping the first test tube empty 2ml. of each of the seeded broth was prepared having 100 μ g/ml. and test compound in two tubes. A and B respectively (prepared by dissolving 0.2 ml. and 0.3 ml. of the stock solutions (1 μ g/ml.) in 1.8 ml. and 1.7 ml of broth respectively). Contents of the tube A were placed in the first empty tube using a fresh sterilized pipette. 1 ml. contents from the B tube were withdrawn and added to second tube and mixed well. Similarly, 1 ml. contents from the first tube were withdrawn and added into the third tube and mixed well. 1ml. contents from the third tube were pipette out with other fresh sterilized pipette and added into fourth tube and shaken well. This gradient dilution process was continued for all the ten test tubes using a fresh pipette each time. 1ml. contents were taken out from the tenth tube and rejected. All the test tubes were labeled with 100 μ g/ml., 75 μ g/ml., 50 μ g/ml., 25 μ g/ml., 12.5 μ g/ml., 6.25 μ g/ml., 3.125 μ g/ml., 1.562 μ g/ml., 0.78 μ g/ml. and 0.39 μ g/ml. respectively. 1ml. of each of the seeded broth and broth was placed in two separate tubes for the control of culture and control of broth media respectively in each set of above experiments simultaneously. All the above sets of tubes were incubated in BOD incubator for the respective indicated micro-organisms. The tube having the highest dilution showing no visible turbidity was chosen. The amount of the test compound in this tube was the minimum inhibitory concentration.

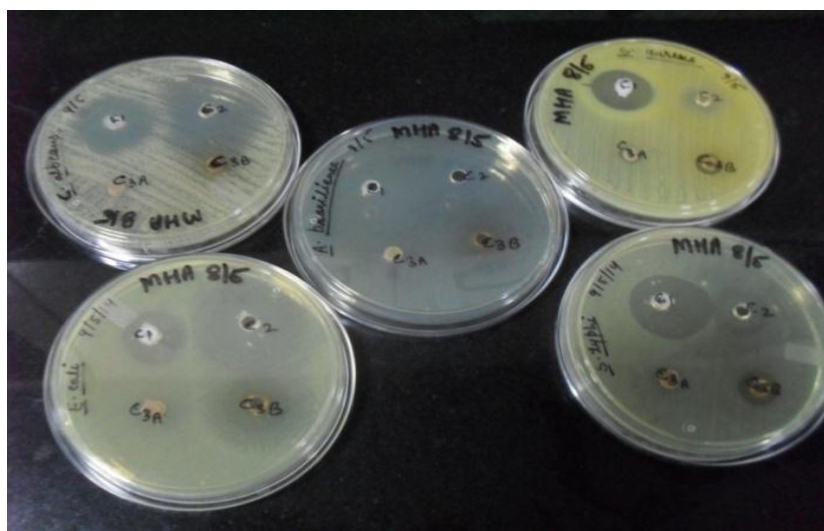


Figure 4: Antimicrobial activity determination of Micro-organism in Mueller Hinton Agar (Well Method)

Table 4: Minimum inhibitory concentration (MIC) value in Molar Concentration [$\times 10^{-4}$] of ligand and newly synthesized hydrazone derivatives and their vanadium complexes

Compounds	Activity against bacterial strain			Activity against fungal strain	
	<i>E. coli</i> (Gram Negative)	<i>Salmonella</i> (Gram Negative)	<i>S. aureus</i> (Gram Positive)	<i>A. brasiliensis</i>	<i>C. albicans</i>
TDADH	0.599	0.589	0.627	0.578	0.595
V(II)[DPTDH](BF ₄) ₂	0.235	0.221	0.241	0.230	0.220
V(II)[DCTDH](BF ₄) ₂	0.221	0.219	0.239	0.221	0.210

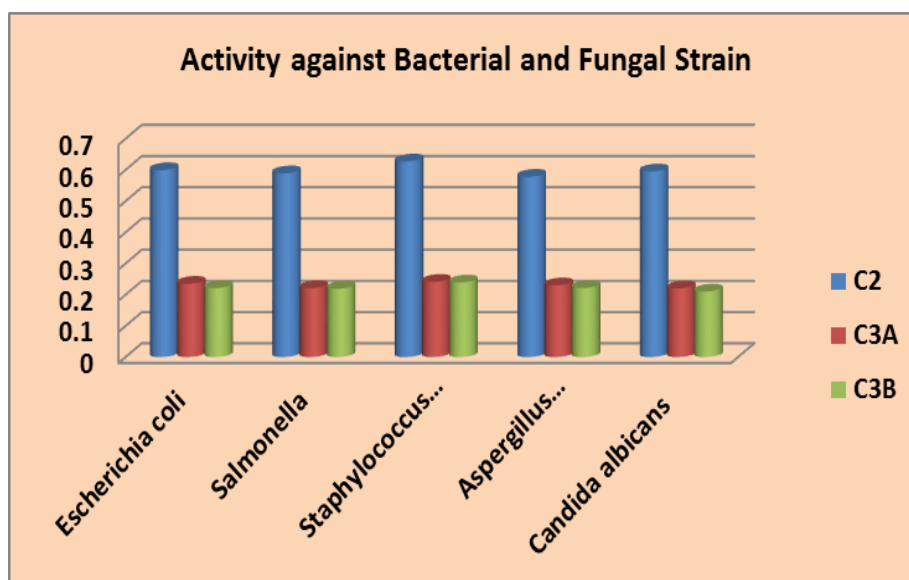


Figure 5: Activity against bacterial and fungal strain

Abbreviation

C2- TDADH

C3A- V(II)[DPTDH](BF₄)₂

C3B- V(II)[DCTDH](BF₄)₂

CONCLUSION

In the present paper, we have synthesized and characterized hydrazone derivatives and their vanadium complexes, formulated as V(II)[DPTDH](BF₄)₂ and V(II)[DCTDH](BF₄)₂ both the complexes are solid and colored. The complexes are stable at room temperature. The ligand and hydrazone derivatives and their vanadium complexes are light-yellow, light brown, chocolate-brown in color and are soluble in DMSO and DMF. All compounds give satisfactory elemental analyses results as are shown in the Table-1. According to infra-red spectral graph and data in Figure-1, 2, 3 and Table-2, nitrogen, oxygen and sulphur are

suitably placed for coordination towards the metal ion which has been proposed for both complexes. It is absent in ligand and present in both complexes confirms an octahedral geometry of complex I and complex II. On the basis of all analytical and spectral data both complexes having octahedral geometry as evidences by the electronic spectral and infra-red spectral results. Electronic spectra data of ligand and hydrazone derivatives and their vanadium complexes are shown in Table-3. The Minimum Inhibitory Concentration (MIC) value in molar concentration of ligand and hydrazone derivatives and their vanadium complexes are shown in Figure-4, 5 and Table-4. The antimicrobial screening data confirms that the metal complexes exhibit a higher inhibitory effect than the free ligand. Present observations may serve as a guide for studying the control release of these complexes that could be a promising future in the field of infectious diseases.

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