

Metal Complexes of 3-[3-(4-Nitro-phenyl-4-hydroxy-6-methyl-pyran-2-one)] Synthesis, Spectral, Magnetic and Fungicidal Study



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Abstract

The metal complexes of Ti(III), V(III), Ru(III), Mo(V) & (VI), UO₂(VI), Ru (II) and Pd (II) were synthesized, using 3-[3-(4-Nitro-phenyl)-4-hydroxy-6-methyl-pyran-2-one] as ligand. These complexes were characterised by elemental analyses, conductometry, thermal analysis, magnetic, IR, UV-vis and NMR spectral studies. The ligand has behaved as O,O donor. All complexes have been found to have 1:2 (Metal : Ligand) stoichiometry.

The ligand and its metal complexes have been screened in vitro for their antifungal activities against *Aspergillus-flavus*, *Curvularia Lunata* and *Penci-lium notatum*.

Keywords: Dehydroacetic Acid, Piperidine, Transition Metal Complexes and Antifungal Study.

Introduction

The detailed survey of chemical literature has revealed that unsaturated Ketones are gaining importance as reactive intermediates and are used to obtain the biologically important heterocycles. This class of compounds exhibits wide spectrum of Pharmaceutical and biological properties¹⁻³. It has been shown that the prime cause of these activities, is the presence of α , β unsaturated ketonic system.⁴ The fungal and bacterial activities of such unsaturated ketones are also enhanced by the substitution of halogen groups.⁵ It is well known from the literature that dehydroacetic acid (3-acetyl-6-methyl-2H-Pyran 2,4 (3H)-dione), a biologically active compound has shown to have good antibiotic and antifungal effects, besides showing strong antiseptic properties.⁶⁻⁹

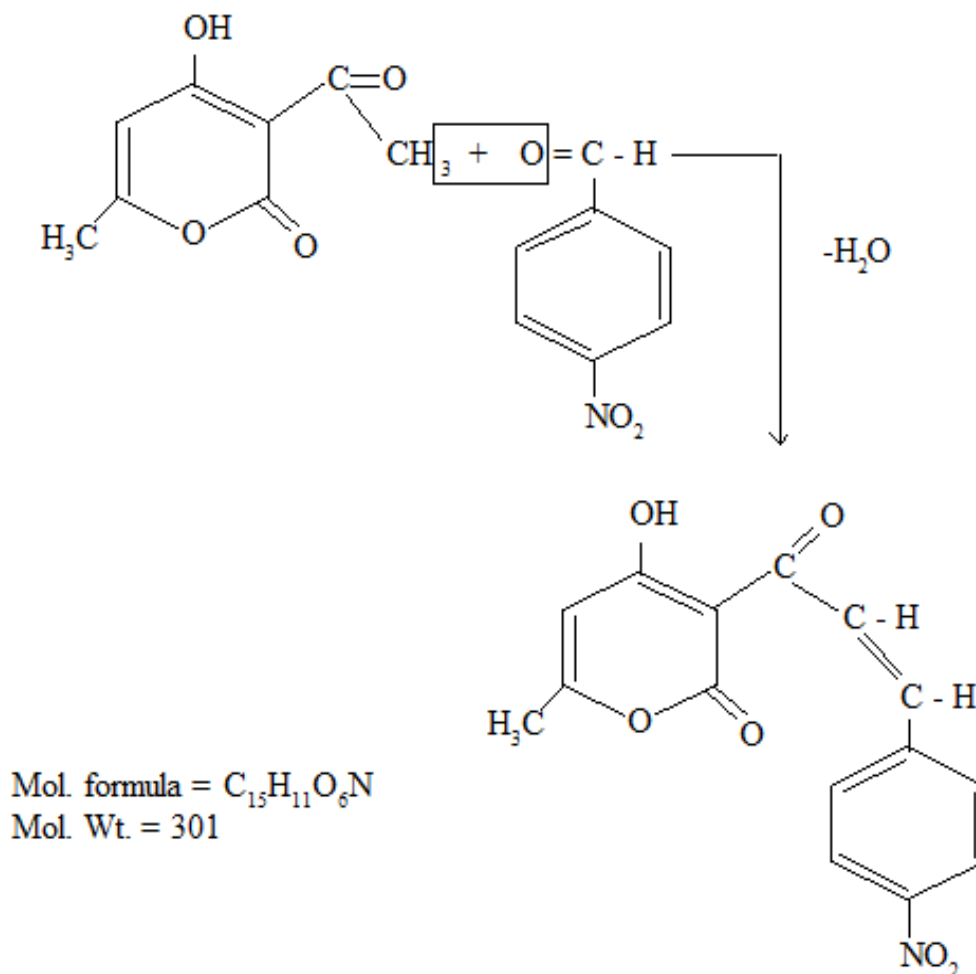
Experimental

Dehydroacetic acid, piperidine p-Nitrobenzaldehyde and chloroform were from Merck and Aldrich respectively. 12% solution of Ti(III) chloride was procured from BDH. and TiCl₃ was prepared in the lab using reported method. All other metal salts were of A.R. Grade. The Carbon, hydrogen and sulphur content in each sample were measured on Perkin-Elmer (2400) CHNS analyzer. The UV-vis spectra of the complexes were recorded on a Shimadzu UV-1601 spectro photometer. Magnetic susceptibility measurement of complexes were carried out using a Gouy balance at room temperature and Hg [Co(SCN)₄] as calibrant. Molar conductivity was measured on an Elico CM 180 conductometer with a dip-type cell using 10⁻³ M solution of complexes in DMF.

IR spectra (V-max, cm⁻¹) were recorded on Shimadzu 820 IPC. FT-IR spectrometer in KBr discs. The solvent used were ethanol (distilled), methanol, benzene, Chloroform, T.H.F., DMSO and DMF. All the solvents were of highest purity.

Preparation of The Ligands

A solution of 3.4g (0.02 mol) of dehydroacetic acid, 10 drops of piperidine and 2.9g (0.02 mol) p-nitrobenzaldehyde in 25 ml chloroform was refluxed for 8-10h. 10ml of the chloroform-water azeotrope mixture was separated by distillation. Crystals of product were separated on slow evaporation of the remaining chloroform and recrystallised from ethanol. The purity of the sample was checked by TLC.



Preparation of Titanium (III) Chloride

The 200 ml. solution of Titanous chloride (12.5% W/V) containing HCl was taken in a conical flask, dry hydrogen chloride was passed in the flask for ten minutes to saturate the solution. 5gm of Titanium metal sponge was added to it. The flask was then heated to initiate reaction of metal with the gas to produce titanous chloride and evolving hydrogen. The solution was covered with a layer of toluene in order to avoid oxidation. It was then cooled in freezing mixture and was saturated with HCl gas till the violet Crystals of $TiCl_3 \cdot 6H_2O$ separated out.

Synthesis of Metal Complexes

To a chloroform solution (30ml) of the ligand 10(m.mol), methanolic solution 20(ml) of metal salts. 5 (m. mol) was added with constant stirring. The pH of the reaction mixture was maintained around 7.5 by adding 10% methanolic solution of ammonia. It was then refluxed for 2h. The resulting metal complex was filtered in hot condition and washed with chloroform, methanol, pet-ether and dried over calcium chloride in vacuum desiccator.

Result and Discussion

The elemental analyses show 1 : 2 (Metal : Ligand) Stoichiometry for all the complexes. The analytical data of the ligand and complexes are given in Table. It corresponds well with the general formula $[ML_2(H_2O)_2]$ where M = Ti(III), V(III), MoO(V), Ru(III),

Ru(II). All the complexes contain water molecules except Pd(II), MoO(VI) & UO₂(VI) complexes.

IR Spectra

The IR spectrum of the ligand shows bands at 3120, 1722, 1680 and 1232 cm^{-1} assigned to ν_{OH} (intermolecular hydrogen bonded) $\nu_{C=O}$ (Lactone-carbonyl), $\nu_{C=O}$ (acetyl carbonyl) and ν_{C-O} (Phenolic) respectively.⁹ In the IR spectra of all the metal chelates. No band is observed in the region of 3112 cm^{-1} , suggesting the cleavage of intramolecularly hydrogen bonded OH and participation of oxygen of phenolic group in co-ordination¹⁰. This is supported by an upward shift in ν_{C-O} (Phenolic)¹⁰ to the extent of 30-60 cm^{-1} . The $\nu_{C=O}$ (acetyl carbonyl) is shifted to the lower energy with respect to the free ligand, suggesting the participation of $\nu_{C=O}$ (acetyl carbonyl) in co-ordination.¹¹ In the IR spectra of some of the chelates a broad trough appeared around 3500-3200 cm^{-1} , which is due to ν_{OH} of co-ordinated water. This is supported by presence of non ligand band¹² around 820-840 cm^{-1} . The presence of new bands in the region 600-450 cm^{-1} can be assigned to ν_{M-O} vibrations.¹³

A very strong band found at 950 cm^{-1} in the spectra of Mo(V) complexes corresponds to Mo=O

stretching frequency. The strong bands exhibited by the dioxomolybdenum(VI) complexes in the region 950-970 and 910 cm^{-1} are attributed to $\nu_{\text{sym}}(\text{O}=\text{Mo}=\text{O})$ and $\nu_{\text{asym}}(\text{O}=\text{Mo}=\text{O})_{\perp}$ respectively of cis-MoO₂ configuration due to the maximum utilization of the available π orbitals for bonding with the oxogroups.¹⁴ The complex trans-[UO₂] shows a strong IR band at 920 cm^{-1} assigned to as (UO₂) of the trans-O-U-O group.¹⁵

¹H NMR Spectrum

The ¹H NMR spectrum of the ligand was recorded in CDCl₃. The spectrum shows peaks at $\delta = 2.28$ (3H, s, C₆-CH₃), 5.96 (1H, s, C₅-H) for dehydroacetic acid moiety, $\delta = 7.2-8.32$ (7H, M) for aromatic and olefinic protons and $\delta = 17.75$ (1H, s, C₄-OH) due to strong intramolecular phenolic hydrogen.

Electronic Spectra

The Ti(III) complex shows magnetic moment of 1.96 B.M. for one unpaired electron. The higher value may be due to the orbital contribution. The electronic spectra of the chelate shows a single broad band has been observed at 19230 cm^{-1} , for Ti(III) complex derived from the transition ${}^2T_{2g} \rightarrow {}^2E_g$ for an octahedral symmetry¹⁶. This band is unsymmetrical in shape and is indeed made up to two closely shaped bands. The second band appears as a hump and which is due to the presence of Jahn Teller distortion in the complex.

The magnetic moment of the Vanadium (III) complex is 2.94 B.M. which is nearly equal to the calculated value for d₂ system like V(III). The electronic spectrum of V(III) complex exhibited a band at 16000 cm^{-1} with a shoulder at 20500 cm^{-1} . The low energy band has been assigned to ${}^3T_{1g} \rightarrow {}^3T_{2g}$ and the high energy band to ${}^2T_{1g} \rightarrow {}^3T_{1g}$ (p) transitions respectively. These bands are characteristic of octahedral geometry.¹⁷

The electronic spectrum of oxomolybdenum (V) complex suggested that the complex may be considered as octahedral with a strong tetragonal

distortion resulting from Mo = O bond¹⁸. The spectrum exhibited three distinct absorption bands in the ligand field region. The low intensity band at 13000 cm^{-1} in the long wavelength region is possibly due to first crystal field transition ${}^2B_2 \rightarrow {}^2E$ (d_{xy}, d_{yz}, d_{xz}). The second crystal field transition at 19000 cm^{-1} is assignable to ${}^2B_2 \rightarrow B_1$ (d_{xy} \rightarrow d_{x²-y²}). The third peak was observed at 30000 assignable to ${}^2B_2 \rightarrow {}^2A_1$ (d_{xy}-d_{z²}). Its magnetic moment is 1.96 B.M.

The electronic spectrum of MoO₂ (VI) complex has a single band due to charge transfer transition. It is diamagnetic in nature.

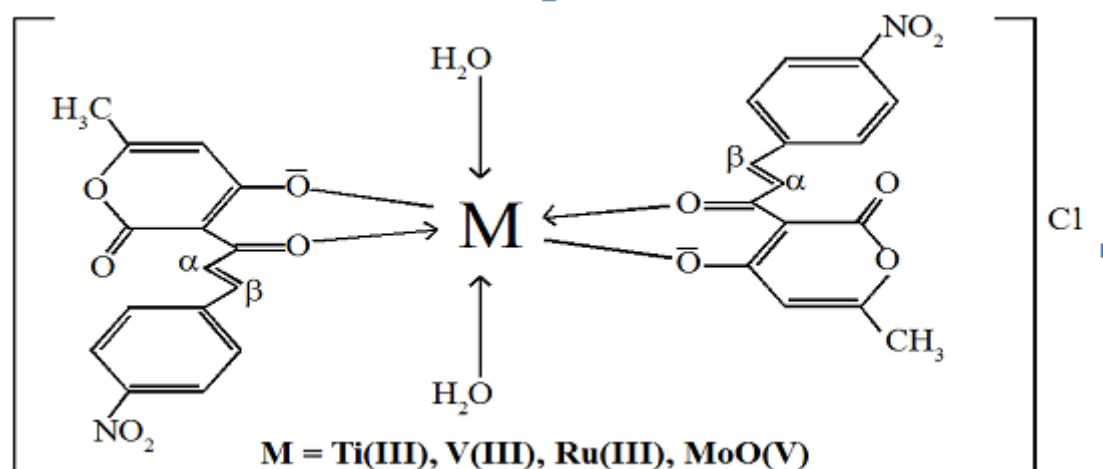
The UO₂(VI) complex does not exhibit any characteristic transition except the charge transfer bands. It is diamagnetic in nature.

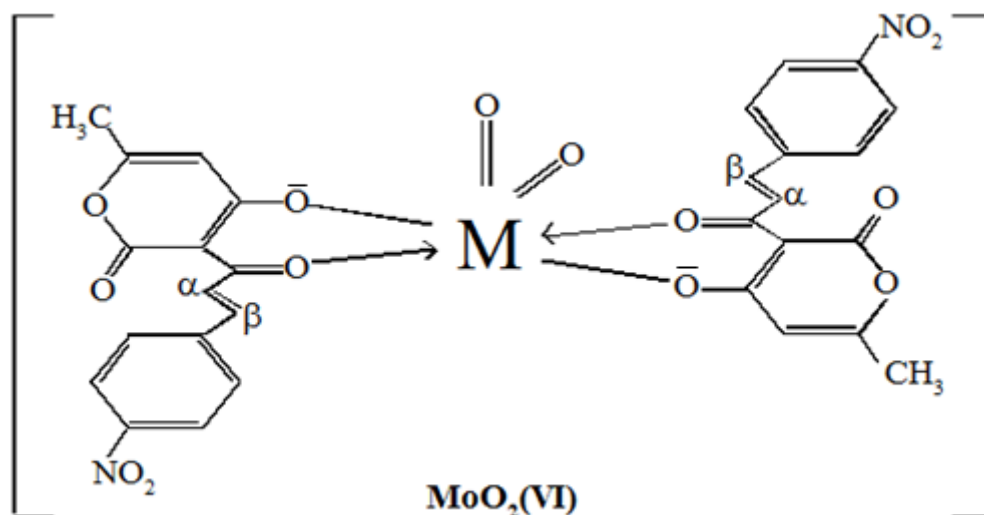
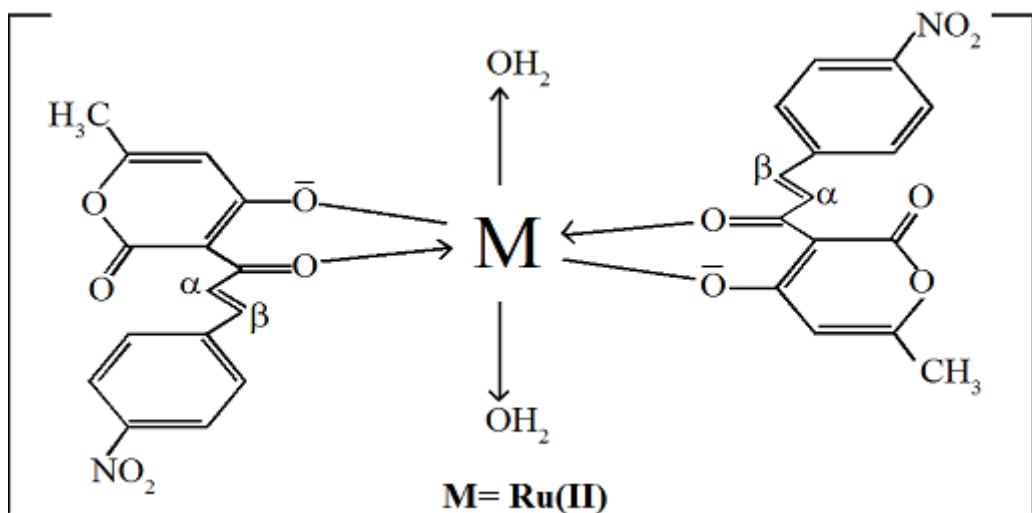
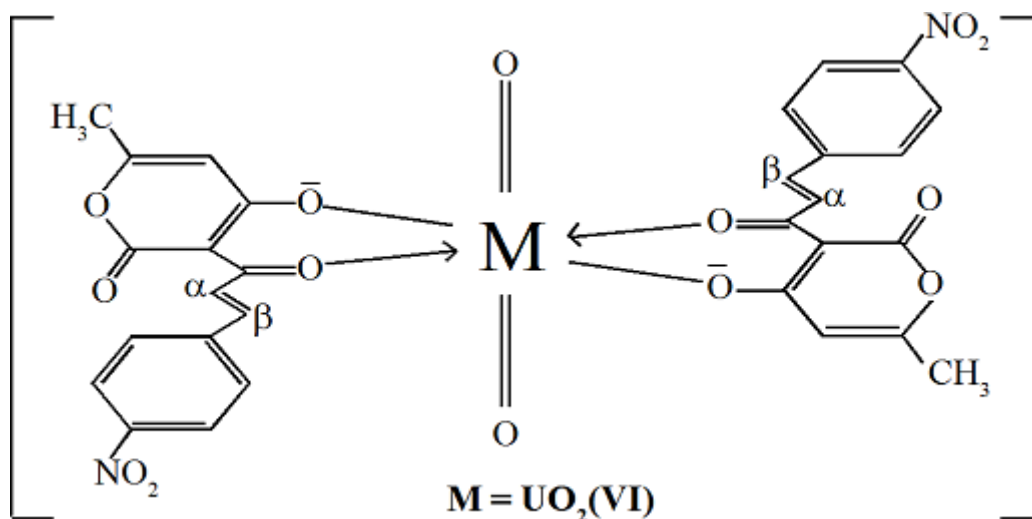
The magnetic moment for the complex is 2.10 B.M. which is nearly the same as reported for other Ru(III) complexes.¹⁹ Three transitions are observed, the first two bands are assigned to ${}^2T_{2g} \rightarrow {}^4T_{1g}$ and ${}^2T_{2g} \rightarrow {}^4T_{2g}$ transitions and the third one to ${}^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$ levels respectively.¹⁹ These are characteristic of octahedral symmetry.

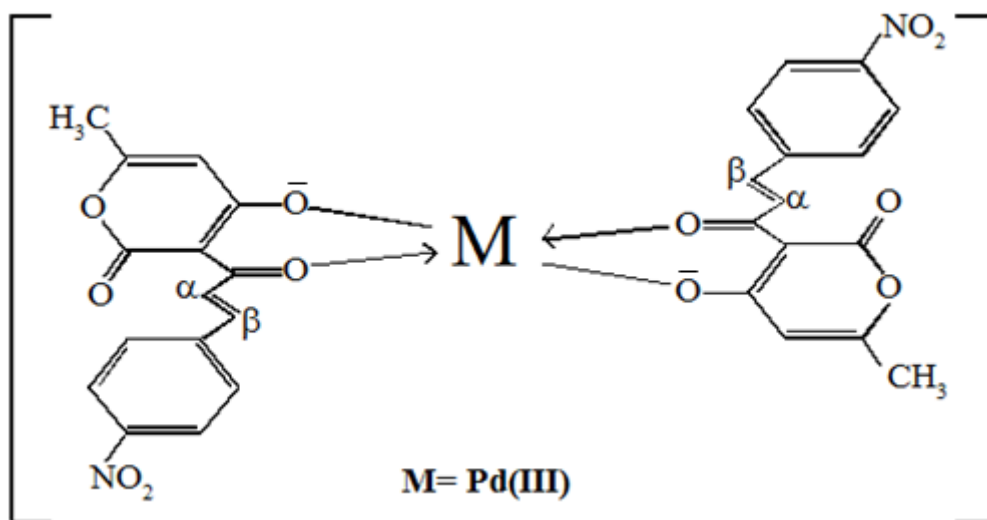
The Ru (II) complex is diamagnetic in nature. The electronic spectrum of the complex in CH₂Cl₂ shows a band assigned to the charge transfer transition arising from the excitation of an electron from the metal T_{2g} level to the unfilled molecular orbitals derived from the $\rightarrow \pi^*$ level of the ligand in accordance with the assignments made for other similar octahedral ruthenium (II) complex.²⁰⁻²²

The Pd(II) complexes show three peaks around 14000, 16600 and 25000 cm^{-1} that could be assigned, in the increasing order of frequency, to the transitions ${}^1A_{1g} \rightarrow {}^1A_{2g}$, ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1E_g$ of square planer geometry.²³

Based on the studies performed an octahedral geometry has been proposed for all the complexes except Pd(II) which is square planer.







Aim of the Study

The Present Project Is Undertaken for Synthesis of Various Shift Bases and Their Complexes and there after to find out Its Biological activities after through examination.

Fungicidal Activity

To evaluate fungicidal activity of the ligand and its corresponding metal complexes, their effect on the growth of *Aspergillus flavus*, *Curvularia lunata* and *Penicillium notatum* was studied. The ligand and its corresponding metal chelates in DMF were screened by mycelia dry weight method in vitro for their fungicidal activity in glucose nitrate media. The ligand exhibited 20-25 and 30-35% inhibition for 125 and 250 ppm concentration respectively. It is observed that the metal complexes show enhanced antifungal activity as compared to the ligand. This is because of chelation, which reduces the polarity of metal ion due to partial sharing of its positive charge with donor groups and also due to delocalization of pi electrons over whole chelate ring.

Conclusion

Thus chelation increase lipophilic character in the complexes and results in the enhancement of activity.²⁴ The inhibition by metal complexes has been increased by 30-65% and 40-70% for 125 and 250 ppm concentration respectively. The order of inhibition with respect to metal ions is $Mo(V) > V > Ti > Pd > Ru$.

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Table
 Characteristics of Ligand & Metal Chelates Prepared
 The Molar Conductance and Characteristic IR Frequencies of the Ligand and its Metal Complexes

S. No.	Formula of the Ligand & Complex & Molecular Weight	Colour	M.P./ Decom Temp. °C	Elemental Analyses					IR frequencies (in cm ⁻¹)					Electrolyte Type	Magnetic moment
				%C	%H	%N	%Cl	%M	□ OH	□ C=O (lactone carbonyl)	□ C=O (acetyl-carbonyl)	□ CO (Phenolic)	□ M-O/ □ M-N		
1.	C ₁₅ H ₁₁ O ₆ N Mol. Wt. = 301	Yellowish Orange	168	59.14 (59.80)	3.27 (3.65)	4.61 (4.65)	-	-	3120(b)	1722(m)	1680(m)	1232(m)	-	-	-
2.	[(C ₁₅ H ₁₀ O ₆ N) ₂ Ti.2H ₂ O]Cl Mol. Wt. = 719.367	Yellow	240	50.01 (50.04)	3.12 (3.33)	3.65 (3.89)	4.71 (4.93)	6.54 (6.65)	3175(b)	1720(m)	1680(m)	1235(m)	495	1:1	1.96 B.M.
3.	[(C ₁₅ H ₁₀ O ₆ N) ₂ V.2H ₂ O]Cl Mol. Wt. = 722.441	Yellow	255	49.53 (49.83)	3.14 (3.32)	3.60 (3.87)	4.74 (4.91)	7.01 (7.05)	3172(b)	1725(m)	1685(m)	1232(m)	535	1:1	2.94 B.M.
4.	[(C ₁₅ H ₁₀ O ₆ N) ₂ MoO.2H ₂ O]Cl Mol. Wt. = 765.44	Light Yellow	260	47.01 (47.03)	2.52 (2.87)	3.31 (3.65)	4.26 (4.63)	12.14 (12.46)	3122(b)	1725(m)	1685(m)	1240(m)	505	1:1	1.96 B.M.
5.	[(C ₁₅ H ₁₀ O ₆ N) ₂ MoO ₂] Mol. Wt. = 727.96	Cream	245	49.45 (49.63)	2.74 (2.91)	3.84 (3.98)	-	13.18 (13.36)	3125(b)	1722(m)	1682(m)	1246(m)	510	Non electrolyte	Dia magnetic
6.	[(C ₁₅ H ₁₀ O ₆ N) ₂ UO ₂] Mol. Wt. = 870	White	265	41.37 (41.56)	2.29 (2.83)	3.21 (3.54)	-	27.35 (27.41)	3132(b)	1724(m)	1686(m)	1255(m)	520	Non electrolyte	Dia magnetic
7.	[(C ₁₅ H ₁₀ O ₆ N) ₂ Ru(III).2H ₂ O]Cl Mol. Wt. = 772.6	Green	242	46.60 (46.71)	2.58 (2.91)	3.62 (3.89)	4.59 (4.71)	13.07 (13.19)	3160(b)	1726(m)	1681(m)	1281(m)	515	1:1	2.10 B.M.
8.	[(C ₁₅ H ₁₀ O ₆ N) ₂ Ru(II).2H ₂ O] Mol. Wt. = 737.1	Light Green	248	48.84 (48.92)	2.71 (2.81)	3.79 (3.93)	-	13.70 (13.92)	3166(b)	1723(m)	1684(m)	1285(m)	530	Non electrolyte	Dia magnetic
9.	[(C ₁₅ H ₁₀ O ₆ N) ₂ Pd] Mol. Wt. = 706.4	White	250	50.96 (50.99)	2.83 (2.93)	3.96 (3.98)	-	15.01 (15.07)	3171(b)	1724(m)	1665(m)	1290(m)	570	Non electrolyte	Dia magnetic

Values given in the brackets are observed values.