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ORIGINAL ARTICLE

Synthesis and Characterization of Oxovanadium (II), Cobalt (II), Nickel (II), Copper (II) and Palladium (II) Complexes of Schiff Bases of Coumarin Derivatives

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ABSTRACT

The complexes of VO^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Pd^{2+} of Schiff bases derived from the condensation reaction of 3-(2-amino-4-thiazolyl) coumarin with 2-hydroxybenzaldehyde, 2-hydroxy-3-methoxybenzaldehyde and 2- hydroxyl naphthaldehyde have been prepared and characterized, All the three ligands function as uninegative, bidentate coordinating ligands with metal ions through phenolic oxygen and azomethine nitrogen. The geometry and the bonding characteristics of the complexes have been derived from the electronic and ESR spectral data.

Key words: *Schiff base, coumarin derivatives, transition metal ions*

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INTRODUCTION

Coumarin, 2H-1-benzopyran-2-one, is a natural product found widely in the plant kingdom, Coumarin derivatives with hydroxy, acetyl, amino, etc, substituents have proved to be potential chelating agents. Metal complexes of vari ous coumarin derivatives have been synthesized and characterized [1]. Coumarins attract an immense interest because of their diverse pharmacological applications [2]. Owing to the importance associated with this class of compounds, we present, herewith the synthesis and characterization of VO^{2+}, Co^{2+} , Ni^{2+}, Cu^{2+} and Pd^{2+} complexes of coumarin based Schiff bases namely 3-[2-(2-hydroxybenzylidene amino)-4-thiazolyl coumarin (HBATC), 3-[2-(2-hydroxy-3-methoxybenzylidenc amino) 4-thiazolyl coumarin (HMATC) and 3-[2-(2-hydroxy-1-naphthylmethyleneamino)-4-thiazolyl coumarin (HNATC).

MATERIALS AND METHODS

All the chemicals used were of A.R. or B.D.H. grade. 3-(2-Amino-4-thiazolyl) coumarin [3] and the ligands HBATC, HMATC and HNATCH were prepared as reported earlier. VO^{2+} complexes of the ligands were prepared taking vanadyl sulphate, Co^{II}, Ni^{II} and Cu^{II} complexes taking respective metal acetates and Pd^{II} complexes using palladium chloride. In the preparation of the metal complexes, the metal and the ligand were combined in 1:2 mole ratio using required quantities of methanol or water for the metal salts and methanol or methanol-DMF (20:1) for the ligands so as to effect their solubility. The contents were refluxed on a water bath for 2-3 h, the solid that separated was filtered, washed with water, hot methanol and ether and dried in air.

The elemental analyses of the complexes were carried out employing Elemental analyzer, model Carlo Erba 1108. Conductance measurements were made in DMF at 10^{-3} M concentration on a Digisun digital conductivity meter, DI 909 model. Magnetic measurements on complexes were made at room temperature using CAHN instrument model 7550-03 and diamagnetic corrections were calculated from Pascal's constants [4]. The IR spectra of the ligands and the metal complexes in KBr were recorded in the range 4000-400 cm- using JASCO FT/IR 5300 spectrophotometer. The electronic spectra of the metal complexes were recorded on Shimadzu UV-VIS spectrophotometer UV-160A and JASCO 7800 UV-VIS spectrophotometer. The Varian E-4 X-band spectrophotometer operating in the frequency range 8.8-9.6 GHz was employed in recording ESR spectra of the VO^{2+} and Cu^{II} complexes in DMF at LNT. The metal content in the complexes, after decomposition with conc. HNO_3, was determined by standard procedures- V by colorimetry, Co by complexometry, Ni and Pd by gravimetry and Cu by iodometry [5].

RESULTS AND DISCUSSION

All the metal complexes are stable at room temperature and are non hygroscopic. They are insoluble in water, slightly soluble in methanol and fairly soluble in DMF and DMSO. All the metal complexes which are non-electrolytic in DMF give satisfactory C, H, N and M corresponding to 1:2 metal organic ligand stoichiometry. The magnetic studies reveal that VO^{2+}, Co^{II}, Ni^{II} and complexes of all the three ligands are paramagnetic to the extent of one, three, two and one unpaired electrons respectively and that Pd^{II} complexes are diamagnetic.

The ligands HBATC, HMATC and HNATC show some what a broad, small or medium intensity band around 3400 cm^{-1} that has been assigned to VO-H. This band appears in the spectra of their complexes indicating that the deprotonation of the group has taken place. A small or medium intensity band around 1250 cm^{-1} in the ligads assignable to νc=0 has undergone a positive shift by 12-32 cm^{-1} in the complexes suggesting coordination through phenolic oxygen [6]. The ligands display a strong absorption band around 1720 cm^{-1} due to νc=0 of lactone and this remains unshifted in the spectra of the complexes indicating nonparticipation of oxygen of this group in coordination. A strong band that shows up in the ligands at 1605 cm^{-1} due to νc=N has been found lower shifted by about 10 cm in the complexes suggesting the involvement of azomethine nitrogen in coordination [7]. Further, the presence of a broad trough around 3400 cm^{-1} in the Co^{II} and Ni^{II} complexes points to the presence of coordinated water in them which is further confirmed by the appearance of a nonligand band at 833 cm^{-1} assignable to rocking mode of coordinated waters [8]. A sharp band which appears at 970 cm^{-1} in the VO^{2+} complexes has been assigned to νc=0 [9]. The coordination through phenolic oxygen and azomethine nitrogen of the ligands is further evidenced by the appearance in all the complexes of nonligand bands in the far infrared region around 540 and 420 cm^{-1} assignable respectively to VM-O and VM-N vibrations [10]. Thus, the ligands function as mononegative, bidentate ones coordinating with the metal ions through phenolic oxygen and azomethine nitrogen atoms.

The present VO^{2+} complexes, each show in their electronic spectra, three peaks around 14500, 16600 and 25500 cm^{-1} which may be assigned respectively to the transitions $^2B_2 \rightarrow {}^2E_2$, $^2B_2$, $^2B_2$ and $^2B_2 \rightarrow {}^2A_2$ of square- pyramidal geometry [11]. The Co^{II} complexes each show three peaks around 9300 (V_1), 16700 (V_2) and 22200 (V_3) cm^{-1} assignable respectively to the transitions ^4T_1g (F) $^4T_{2g}$ (F), $4T_{1g}$. (F) → $^4A_{2g}$ (F) and $^4T_{1g}$ (F) $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) and similarly Ni complexes three peaks around 9500 (V),14200 (V_2) and 24400 (V_3) cm^{-1} due to $^3T_{2g}$ (F)- $^3A_{2g}$(F), ^3A_2g (F) + $^3T_{1g}$ (F) and ^3A_2g (F) + $^3T_{1g}$ (P) of octahedral geometry [11] The Racah interelectron repulsion parameter (β), ligand field splitting energy (10 Dq) and nephelauxetic parameter (β) for the Co^{II} and Ni^{II} complexes have been evaluated [12] and results are shown in Table-1. Based on the values obtained, the Co^{II} and Ni^{II} complexes may be arranged with respect to orbital overlap and extent of covalency as follow:

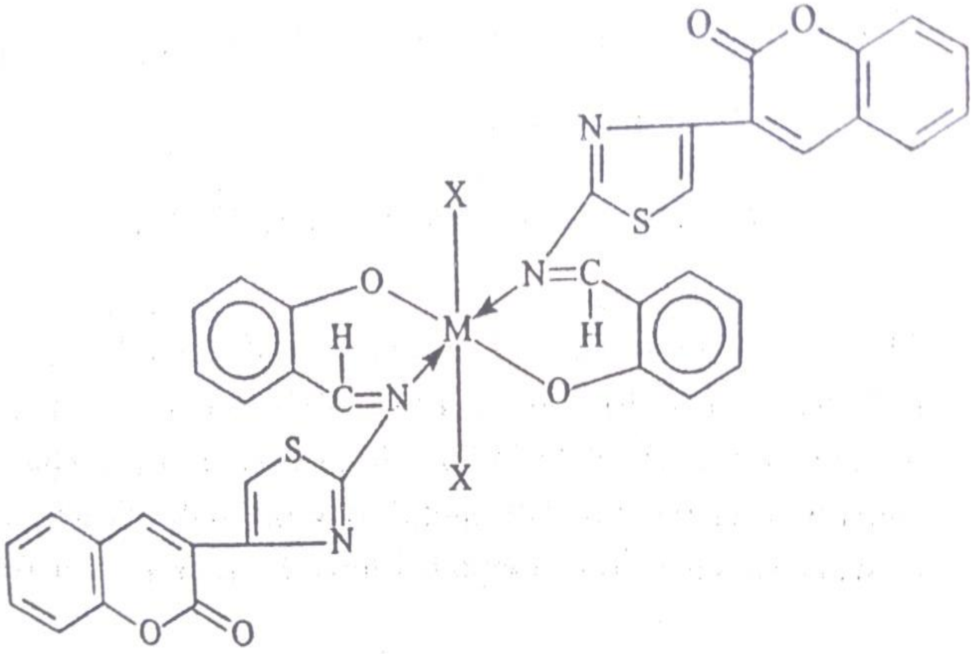
M-HNATC > M-HBATC > M-HMATC
(where M = Co, Ni)

The Cu^{II} complexes show each two peaks around 16400 and 20000 cm^{-1} that could be assigned respectively to $^{2}B_{1}g \rightarrow {}^{2}B_{2}g$ and $^{2}B_{1}g \rightarrow 2Eg$. Based on these observations and the analytical data, the complexes have been assigned a square planar structure [12]. The Pd^{II} complexes show each three peaks around 14000, 16600 and 25000 cm^{-1} that could be assigned in the increasing order of frequency, to the transitions $^{1}A_{1}g \rightarrow {}^{1}A_{2}g$, $^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ and $^{1}A_{1g}$ - $^{1}E_{g}$ of square planar geometry [12].

Table 1: Electronic spectral data of Co^{II} and Ni^{II} complexes

Metals Complex	Frequency (cm^{-1})			β	10Dq	β
	V_1	V_2	V_3	(cm^{-1})	(cm^{-1})	
$Co(HBATC-H)_2(H_2O)_2$	9350	16750	22220	729	7400	0.750
$Co(HMATC-H)_2(H_2O)_2$	9320	16630	22800	766	7312	0.789
$Co(HNATC-H)_2(H_2O)_2$	9370	16800	22180	728	7426	0.748
$Ni(HBATC-H)_2(H_2O)_2$	9520	14290	24390	676	9520	0.656
$Ni(HMATC-H)_2(H_2O)_2$	9380	14120	24500	699	9380	0.679
$Ni(HNATC-H)_2(H_2O)_2$	9530	14200	24300	662	9530	0.646

The schematic drawing of metal complexes formed with the representative ligand HBATC is shown in Fig.



M = VO Co Ni Cu Pd
X = - H_2O H_2O - -

Fig. 1: Chemical Structure of Metal (M) Schiff's base Complex

The ESR spectra of representative VO^{2+} and Cu^{II} complexes are reproduced and the parameters calculated for all the complexes using appropriate equations [13] are presented in Table- 2. The ESR spectra of VO^{2+} complexes are appropriately resolved with parallel and perpendicular components corresponding to hyperfine coupling with vanadium nucleus of I = 7/2. The spectra of Cu^{2+} complexes are of anisotropic nature in that each of them has two peak envelopes, one of small intensity towards low field and the other of large intensity towards high field. The small intensity envelope towards low field has been resolved into two to four peaks due to hyperfine interaction with copper nucleus (I= 3/2) while the large intensity peak towards high field remains unresolved. The parameters calculated for the complexes using appropriate equations are presented in Table- 2. The g and A values observed for the VO^{2+} complexes are in agreement with those generally observed for a vanadyl complex with a square pyramidal geometry [14] For all the complexes, $g_{II} < g_1 < g_e$ (where g_e is free electron value equal to 2.0023) which indicates that the unpaired electron is in the d_{xy} orbital with ^2B as the ground state[15].

Table 2: ESR data of VO^{2+} and Cu^{II} complexes

Metal Complex	**g_{11}**	**g_1**	**g_{av}**	**$A_{11} \times 10^4$**	**α^2(cm^{-1})**	**β^2(cm^{-2})**	**γ^2**
$Co(HBATC\text{-}H)_2(H_2O)_2$	9350	16750	22220	-	728	7400	0.750
$Co(HMATC\text{-}H)_2(H_2O)_2$	9320	16630	22800	-	765	7312	0.788
$Co(HNATC\text{-}H)_2(H_2O)_2$	9370	16800	22180	-	725	7426	0.747
$Ni(HBATC\text{-}H)_2(H_2O)_2$	9520	14290	24390	-	675	9520	0.655
$Ni(HMATC\text{-}H)_2(H_2O)_2$	9380	14120	24500	-	698	9380	0.678
$Ni(HNATC\text{-}H)_2(H_2O)_2$	9530	14200	24300	-	661	9530	0.642

In the Cu^{II} complexes, it is found that $g_{11} > g_1 > 2$ indicating that the unpaired electron lies in $d_{x^2-y^2}$ orbital with $^2B_{1g}$ as the ground state. The α^2, β^2 and γ^2 values for the complexes are in the ranges 0.66-0.68, 0.86-0.93 and 0.67-0.87 suggesting appreciable/moderáte/weak in-plane α −bonding, inplane π −bonding and out of plane π-bonding respectively [13].

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