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Microwave Synthesis and Characterisation of Coumarin Based Ligands and their Metal Chelates

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ABSTRACT

Ti(III), Mn(III) & Co(III) complexes of schiff bases derived from condensation reaction of 3-(2-amino-4-thiazolyl)coumarin with 2-hydroxybenzaldehyde, 2-hydroxy-3-methoxy benzaldehyde and 2-hydroxy-1-naphthaldehyde have been prepared and characterised. All the three ligands function as uninegative bidentate coordinating ligands with metal ions through phenolic oxygen and azomethine nitrogen. The complexes have been characterised by analytical data, molar conductance, magnetic susceptibility, electronic and infra red spectra. Based on these studies octahedral geometry has been proposed for these complexes.

Key words: Schiff base, Chelates, Octahedral, Coumarin.

INTRODUCTION

Coumarin, 2H-1-benzopyran-2-one, is a natural product found widely in plant kingdom. Coumarin derivative with hydroxy, acetyl and amino substituents have proved to be potential chelating agents¹. Coumarin attracts an immense interest due to its pharmacological applications². Owing to the importance associated with this class of compounds, the present paper reports the synthesis and characterisation of metal complexes of coumarin based schiff bases.

MATERIAL AND METHODS

All the chemicals used were of A.R. or B.D.H. grade. 3-(2-Amino-4-thiazolyl)coumarin and

the ligands HB ATC, HMATC and HNATC were prepared by reported methods^{3,4}. Ti(III) chloride was prepared by standard method, while Mn(III) chloride and Co(III) chloride were used as such.

Preparation of metal complexes

The metal complexes were prepared using required quantities for 1:2 molar ratio. The mixture was refluxed on water bath for 2,3h. The solid that separated was filtered off, washed with methanol and ether and dried in air. The complexes were characterised by the determination of melting point, molar conductance, magnetic susceptibility and recording of electronic and I.R. spectra.

RESULTS AND DISCUSSION

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 give satisfactory C,M,N and M analyses corresponding to 1:2 metal organic ligand stoichiometry.

The ligands HBATC, HMATC and HNATC show somewhat a broad, small or medium intensity band around 3400cm^{-1} that has been assigned to O-H. This band disappears in the spectra of their complexes indicating that the deprotonation of the group has taken place. A small or medium intensity band around 1250cm^{-1} in the ligands assignable to C-O has undergone a positive shift by $12-32\text{cm}^{-1}$ in the complexes suggesting coordination through phenolic oxygen⁵. The ligands display a strong absorption band around 1720cm^{-1} due to $\nu\text{C=O}$ of lactone and this remains unshifted in the spectra of the complexes indicating non-participation of oxygen of this group in coordination. A strong band that shows up in the ligands at 1605cm^{-1} due to $\nu\text{C=N}$ has been found lower shifted by about 20cm^{-1} in the complexes suggesting the involvement of azomethine nitrogen in coordination⁶. Further, the presence of a broad band around 3400cm^{-1} in the complexes points to the presence of coordinated water in them which is further confirmed by the appearance of a non-ligand band at 833cm^{-1} assignable to rocking mode of coordinated water⁷. The coordination through phenolic oxygen and

azomethine nitrogen of the ligands is further evidenced by the appearance, in all the complexes of non-ligand bands in the far infrared region around 540 and 420cm^{-1} assignable respectively to $\nu\text{M-O}$ and $\nu\text{M-N}$ vibrations⁸.

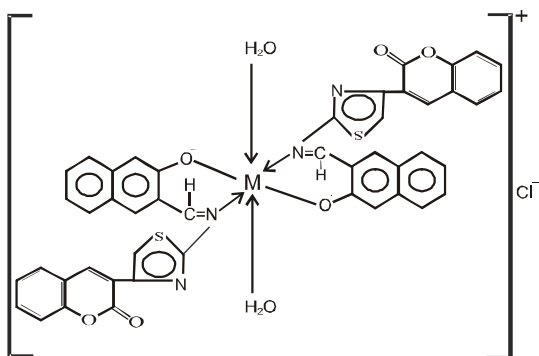
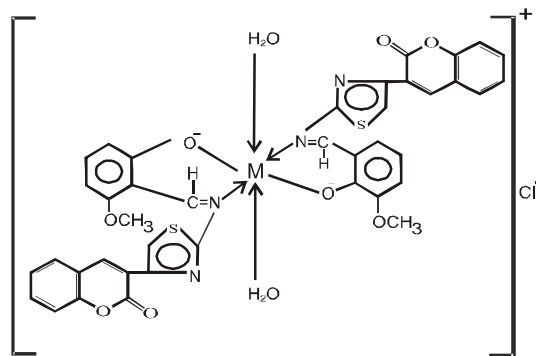
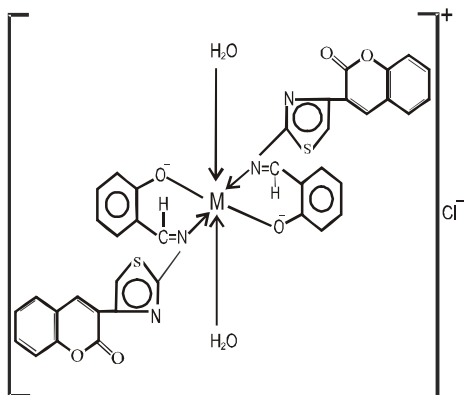
Thus the ligands function as mononegative bidentate ones coordinating with the metal ions through deprotonated phenolic oxygen and azomethine nitrogen atoms.

The observed value of magnetic susceptibility was used to calculate the spin only value of magnetic moment which came out to be 1.68 B.M. This value suggested paramagnetic nature of the complex and that Ti(III) has not been oxidised to Ti(IV) during or after complexation. The electronic spectrum of the complex has shown a single broad band at 19500cm^{-1} which has been assigned to ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ for octahedral symmetry⁹. The μ_{eff} value for the complex is 4.98 B.M. which is in good agreement with manganese(III) complexes¹⁰. The complex Mn(III) has a 5D electronic ground state is pure octahedral symmetry. In the electronic spectrum of this complex exhibits two bands at 19800 and 13000cm^{-1} assignable to ${}^5\text{B}_1$ ${}^5\text{B}_2$ and ${}^5\text{B}_1$ ${}^5\text{E}_g$ transitions respectively and are characteristic of octahedral geometry⁹.

The Co(III) complex is diamagnetic in nature as expected for a low spin d^6 ion. The electronic spectrum of the cobalt(III) complex displays bands at 15200 , 21100 and 23400cm^{-1} which may be assigned as ${}^1\text{A}_{1g} \rightarrow {}^3\text{T}_{2g}$, ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$ and

Table 1: Analytical, Physical data and IR bands (cm^{-1}) the complexes

Compound	m.p. (°C)	Elemental analyses % Found (calculated)						Mag. moment B.M.	Molar conductance $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$	
		C	H	N	S	Cl	Metal		DMSO	DMF
Ti Yellow	350	56.72 (56.85)	1.80 (1.87)	6.85 (6.98)	7.80 (7.98)	4.30 (4.42)	5.82 (5.98)	1.68	50	70
Mn Brown	275	56.29 (56.36)	1.72 (1.85)	6.86 (6.92)	7.78 (7.91)	4.32 (4.38)	6.66 (6.79)	4.98	55	65
Co pinkish yellow	300	56.00 (56.08)	1.76 (1.84)	6.76 (6.88)	7.75 (7.87)	4.32 (4.36)	7.12 (7.25)	diamagnetic	53	68



${}^1A_{1g} \rightarrow {}^3T_{2g}$ transitions respectively. These are similar to those reported for other six coordinated Co(III) complexes.

CONCLUSION

On the bases of the studies performed all the complexes may be assigned octahedral geometry and may be represented as :

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