INTRODUCTION

Coumarin, 2H-1-benzopyran-2-one, is a natural product found widely in the plant kingdom. Coumarin derivative with hydroxy, acetyl and amino substituents have proved to be potential chelating agents\(^1\). Coumarin attracts immense interest due to its pharmacological applications\(^2\). 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 2.3 h. 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.

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-napthaldehyde 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.
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 some what a broad, small or medium intensity band around 3400 cm⁻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 1250 cm⁻¹ in the ligands assignable to C-O has undergone a positive shift by 12-32 cm⁻¹ in the complexes suggesting coordination through phenolic oxygen. The ligands display a strong absorption band around 1720 cm⁻¹ due to νC=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 1605 cm⁻¹ due to νC=N has been found lower shifted by about 20 cm⁻¹ in the complexes suggesting the involvement of azomethine nitrogen in coordination. Further, the presence of a broad band around 3400 cm⁻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 833 cm⁻¹ assignable to rocking mode of coordinated water. 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 420 cm⁻¹ assignable respectively to νM-O and νM-N vibrations.

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 19500 cm⁻¹ which has been assigned to 2T₂g → 2Eg for octahedral symmetry. The μeff value for the complex is 4.98 B.M. which is in good agreement with manganese(III) complexes. 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 13000 cm⁻¹ assignable to 5B_{1g} → 5E_{g} and 5B_{2g} → 5E_{g} transitions respectively and are characteristic of octahedral geometry.

The Co(III) complex is diamagnetic in nature as expected for a low spin d6 ion. The electronic spectrum of the cobalt(III) complex displays bands at 15200, 21100 and 23400 cm⁻¹ which may be assigned is 1A_{1g} → 3T_{2g}, 1A_{1g} → 1T_{1g} and Table 1: Analytical, Physical data and IR bands (cm⁻¹) the complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>m.p. (°C)</th>
<th>Elemental analyses % Found (calculated)</th>
<th>Mag. Molar moment condutance ohm⁻¹ cm² mol⁻¹</th>
<th>B.M. DMSO DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti Yellow</td>
<td>350</td>
<td>C 56.72 (56.85) H 1.80 (1.87) N 6.85 (6.98) S 7.80 (7.98) Cl 4.30 (4.42)</td>
<td>1.68 50 70</td>
<td></td>
</tr>
<tr>
<td>Mn Brown</td>
<td>275</td>
<td>C 56.29 (56.36) H 1.72 (1.85) N 6.86 (6.92) S 7.78 (7.91) Cl 4.32 (4.38)</td>
<td>4.98 55 65</td>
<td></td>
</tr>
<tr>
<td>Co pinkish yellow</td>
<td>300</td>
<td>C 56.00 (56.08) H 1.76 (1.84) N 6.76 (6.88) S 7.75 (7.87) Cl 4.32 (4.36)</td>
<td>diama-53 68 gnetic</td>
<td></td>
</tr>
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</table>

A1g → T2g 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 octaedral geometry and may be represented as:

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REFERENCES