



SYNTHESIS AND PHYSICOCHEMICAL STUDY OF COMPLEXES WITH SOME TRANSITION METAL ION WITH NEWLY DERIVED CONDENSED SULFA DRUGS

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ABSTRACT:

New complexes of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} with Newly synthesized N-saliylaldehyede (Benzene sulfonamido-thiazolyl) carbaiminis (SbstC) and N-saliylaldehyede (Benzene sulfonamido-5-methyl-1-2-oxazolyl) carbaiminis (SbsmoC) as ligands have been prepared and characterized on the basis of elemental analyses, magnetic measurements, electronic, I.R spectra and. thermogravimetric analyses. The results are discussed.

INTRODUCTION:

Ligands derived from the reaction of aromatic aldehydes and aromatic amines or amides represent an important series of widely studied organic ligands. The relevant transition metal complexes are still found to be of great interest in inorganic chemistry, although this subject has been studied extensively [1-3]. A combination of distinctly different metal ion binding sites within one ligand can lead to materials with interesting new properties [4,5], e.g. specific sensors, molecular wires, and magnetic and optical devices. In continuation of unpublished work; we report here the synthesis and physicochemical characterization of manganese (II), iron (II) cobalt (II), nickel(II), copper(II), and zinc(II), with N-salicylaldehyde (Benzene sulfonamido-thiazolyl) carbaimines (SbstC) and N-salicylaldehyde (Benzene sulfonamido-5-methyl-1,2-oxazolyl) carbaimines (SbsmoC).

Physical Measurements :

The magnetic moments have been obtained by Gouy's method using mercurytetrathiocyanato cobaltate-(II) as a calibrant ($\chi_g = 16.44 \times 10^{-6}$ c.g.s. units at 25°C). Diamagnetic correction were made using Pascal's constants. I.R. spectra were recorded on

FTIR spectrophotometer at CDRI Lucknow. Electronic spectra of the complexes were recorded in the 270-1200 nm range on GB cintra spectrophotometer. The elemental analyses of the carbon, hydrogen and nitrogen were performed at RSIC Chandigarh. Sulphur estimation was done by standard messenger's method. The metal contents of the complexes were analyzed by EDTA titration [7]. Thermogravimetric analyses (t.g.a) were obtained by-2 Perkin Elmer computer controlled thermogravimetric analyzer model TGS-2 at RSIC Nagpur.

MATERIAL AND METHOD:

Preparation of the organic ligands

The organic ligands, N-salicylaldehyde (Benzene sulfonamido - thiazolyl) carbaimines (SbstC) and N-salicylaldehyde (Benzene sulfonamido-5-methyl-1,2-oxazolyl) carbaimines (SbsmoC) were synthesized by condensation reaction.

N-salicylaldehyde (Benzene sulfonamido-thiazolyl) Carbaimines (SbstC)

The preparation of SbstC was carried out by refluxing a solution of 10 mmol of sulphathiazole (4g) in DMF with a solution of salicylaldehyde in 1:1 molar proportion and acidic condition was made by adding 2-3 drops

of concentrated hydrochloric acid for 1-2 hrs at 140°C-160°C with controlled temperature. The reaction mixture was then allowed to cool to room temperature and add distilled water in small installment with constant and vigorous stirring yellow turbid solution part was removed and thick liquid stuck to beaker was left over and was treated with water in small installment with stirring near about 20-30 min, orange coloured substance was formed filter and dried, in air, and recrystallized from EtOH. Yield 3.90g (90%), m.p : 260°C. Same procedure used for (SbsmoC)

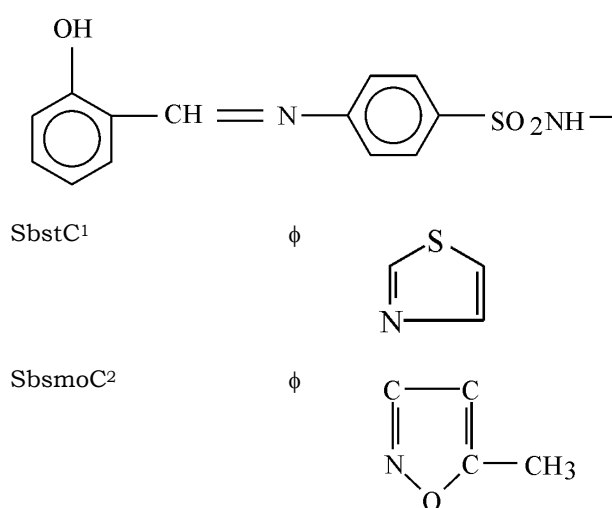


Fig. 1 : Structure of the ligands

Preparation of the complexes :

The SbStC-M^{II} or SbsmoC-M^{II}, [M=Mn^{II},Fe^{II},Co^{II},Ni^{II},Cu^{II}, and Zn^{II}] complexes were synthesized by a following method.

Metal and ligands were taken in the molar ratio 1:2 for reaction except Fe^{II}. Metal and ligand was dissolved in minimum quantity of distilled water and DMF separately. Then the solution was warmed in water bath. Both the solution were mixed in warm condition with constant stirring then the mixture was digested for few minutes with constant stirring. Add aqueous ammonia (50%) drop by drop precipitate was formed at pH 6-7 and the solid complex collected was washed with hot double distilled water to remove excess of metal present in the reaction.

In case of Fe^{III} complexes, metal and ligands, were taken in the molar ratio 1:2 for reaction metal and ligand was dissolved in minimum quantity of distilled water and DMF separately. Then the reaction mixture was digested for few minutes adjust the pH- 2.50. This solution was refluxed for 2-3 hour's. Red-brown coloured precipitated was formed. The solution was filtered and collected the coloured complex so obtained was washed with hot double distilled water 2-3 times to remove excess of metal present in the reaction.

RESULT & DISCUSSION

Elemental analysis data, formula weights, colours, percentage yields, melting points and magnetic moments are given in Table-1. The results of the elemental analyses of the organic ligands sbstC, SbsmoC and its complexes are in good agreement with those required by the proposed formula.

I.R Spectra :

The i.r. spectra of the complexes, in comparison with those of the free ligands, display certain changes which give an idea about the type of bonds and their structure. The ligands SbStC and sbsmotC, exhibit a broad bands in the region 3200-3500 may be assigned to ν (OH) stretching vibration[8]. It is further observed that bands in the region 3200-3500 cm⁻¹ are in the same region in coordination complexes. This indicates non participation of phenolic group in complexatio [9,10,11]. In the free ligands indicates bands around the region 1260-1180 cm⁻¹ and 1390-1330 cm⁻¹ which may be assigned for ν (C-O) stretching and ν (O-H) bending in phenol [8,12]. In case of complexes all these bands observed in the same range indicating no coordination through phenolic group. The ν (CH=N) frequency of SbStC and SbsmtC occurs at 1630-1680 cm⁻¹. This band shifts to lower energy by 10-20 cm⁻¹ in the complexes, indicating coordination through the azomethine nitrogen [13]. The frequencies in the 450-460 and 410-420 cm⁻¹ ranges are attributed

to $\nu(\text{M-N})$ [14,15]. The persual of the i.r. of SbstC & SbsmoC ligands indicates sharp bands around $1370\text{-}1320\text{-}1\text{cm}^{-1}$ which may be $\text{SO}_2\text{-NH}$ stretching vibration [16]. This bands shifts to lower or higher energy $10\text{-}15\text{ cm}^{-1}$ in all the complexes, indicating that the participation of oxygen in coordination with metal ion which further supported by $\nu(\text{M-O})$ [8,17]. In ligand SbstC bands in the range $1610, 1500, 1380, \text{cm}^{-1}$ indicate presences of Thiazole group and in ligand SbsmoC bands in the range $1460, 1360\text{ cm}^{-1}$ indicates presences of Oxazole group [18].

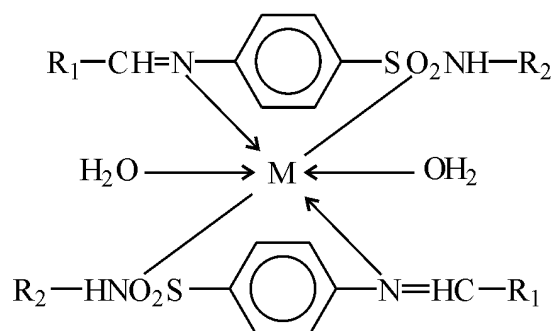
The magnetic moments of the complexes are given in Table 1 the values for the manages(II) complexes are 6.30 and 6.07 B. M, which are slightly greater than the spin-only value (5.92 B. M), but within the limits of the spin-free value for five unpaired electron, indicating that the complexes are high-spin and six-coordinated [19] the magnetic moments of the Iron(II) complexes are 5.27 and 5.01 B. M which suggest high spin octahedral geometry [20]. The magnetic moments, of cobalt(II) complexes are 3.08 and 3.09 B. M., which suggest an octahedral geometry [21,22]. The magnetic moments of the nickel(II) complexes are 2.67 and 4.59 B. M. indicating that these complexes are octahedral [23].

The magnetic moments of the copper(II) complexes are 2.01 and 2.59 B. M, consistent with an octahedral geometry [24]. The magnetic moment determination shows that zink(II) complexes are diamagnetic.

Electronic Spectra :

The electronic spectra of the complexes were recorded in the $400\text{-}1200\text{ nm}$ range. The electronic spectra of the manganese (II) complexes exhibit absorption band at 22.20 kK and 22.72 kK , which are assigned to the transition ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}, {}^4\text{E}_g(\text{G})$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}, {}^4\text{E}_g(\text{G})$ respectively for SbstC and SbsmoC complexes suggesting octahedral geometry [25]. The spectra of the Iron (II) complexes exhibit two bands at 20.83 kK and $16.88, 18.88\text{ kK}$ which

may be due to the transitions $t_{2g} \rightarrow \pi^*$ or charge transfer (C.T) transitions and suggesting an octahedral geometry [26].



Where

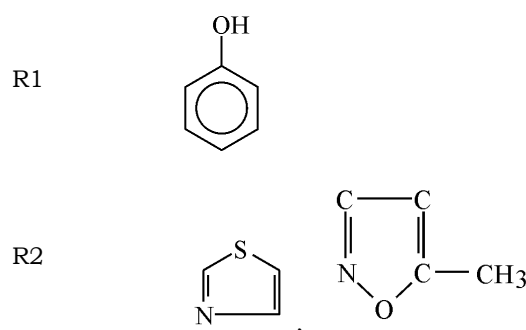


Fig. 2 : Suggested structure of the complexes

The cobalt(II) complexes exhibit two bands of 8.60 kK , 16.49 kK and 17.26 kK which may be assigned to transitions ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$, and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ respectively, and suggested an octahedral geometry [27]. The spectra of the nickel(II) complexes exhibits two bands at 23.80 kK and 24.60 kK which may be due to the transitions ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ respectively and suggests an octahedral geometry [28]. The electronic spectra of the copper (II) complexes exhibit bands at 16.84 kK , 20.50 kK and 23.52 kK . The transition can be assigned for these bands as ${}^2\text{B}_{1g} \rightarrow \text{B}_{2g}$ and charge transfer. Which are characteristic of distorted octahedral geometry [29].

Thermogravimetric analyses

It has been observed that all of the complexes show a loss in weight between $120\text{-}290^\circ\text{C}$, indicating that presences of crystal water and coordinated water molecule in the complexes. It is observed from the t.g. curves

after the loss of hydrated and coordinated water molecule that the decomposition of organic ligands species from 300^o-700^oC in two or three step's. In all cases the remaining residues are metal oxides. These results (Table-2) are in good agreement with the composition of the complexes. The suggested structure for the complexes is shown in figure 2.

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