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Study on the synthesis and characterization of Cobalt (II) complexes with Schiff bases 1-(O-hydroxybenzylidine) amino-2-(O-hydroxybenzylidine) aminomethyl-5-mercapto-1,3,4-triazole

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Abstract: Cobalt(II) chloride has been reacted with Schiff bases 1- (o-hydroxybenzylidine)amino-2-(o-hydroxybenzylidine) aminomethy-l, 5- mercapto-1,3,4-triazole to obtain the complexes of 1:1 stoichiometry. The infrared spectral studies suggest that the-OH group and C=N are involved in co-ordination. The magnetic and electronic spectral data favours the tetrahedral configuration for these complexes.

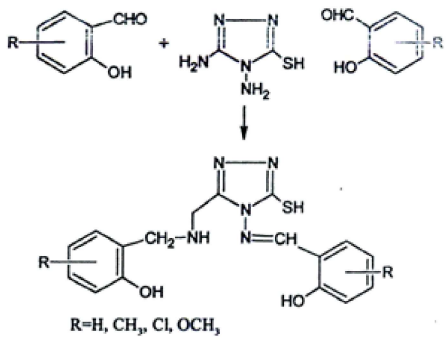
(Keywords : Infrared, magnetic, electronic spectra tetrahedral configuration)

Introduction

Various metal complexes with various Schiff bases have been synthesized and Schiff base may be obtained by the interaction of o-hydroxybenzaldehyde and 1-amino-2-aminomethy-1,1,2,3-triazole which may act a very good ligand for the complexation with metal ions and complexes will be synthesized and charaterised by physico chemical methods.

It has been corroborated spectrochemically and magnatochemically that both Cu(II) and Ni(II) complexes have square planar configuration. The literature records no attempt on the complexation of such ligand with Cu(II).

In the present investigation, we have prepared Co(II) complexes with the following ligands and characterized them by spectral and magnetic data.



Experimental

Synthesis of ligand and complexes

The chemicals used for preparing ligand and complexes were of reagent grade, substituted salicylaldehydes were prepared according to known standard method[5]. 2-Aminomethyl-edinemino-5-mercapto- 1, 3. 4-triazole was prepared as the reported earlier method[1-6]. Schiff bases were prepared by condensing this triazole with substituted salicylaldehydes.

Co(II) complexes were synthesized by heating Co(II) chloride (0.01m) and ligand (0.01m) in ethanol medium. The reaction mixture was refluxed for about an hour. Consequently, to the reaction mixture was added 2g of sodium acetate

and refluxed was continued for 2-3 hours. The precipitation of complex was initiated by adding little water. Thus, the separated complex was filtered, washed with water and dried in vacuum over fused calcium chloride.

Analysis

Cobalt in the complexes was estimated[7] gravimetrically as 8-hydroxyquinolinate and sulphur was estimated as $BaSO_4$ after oxidizing sulphus to sulphate Table I. The values in parenthesis are calculated values.

Physical measurements

The magnetic moments of the complexes are determined at room temperature on Gouy balance using $Hg[Co(SCN)_4]$ as calibrant. The electronic spectral measurements were made with an Elico-CI-24-spectrophotometre in the 350-900 nm region. The I.R. spectra of these complexes were recorded on Perkin-Elmer in 4000-400 cm^{-1} region.

Results and Discussion

All the complexes are dark-brown in colour analyzed for 1:1 stoichiometry of the type Co-L (Table-1). The complexes are insoluble in common organic solvents. However, they are soluble to a limited extent in DMF and DMSO. The molar conductance values 10-20 ohm^{-1} cm^{-2} mol are too small to account for any dissociation. Hence, these complexes are regarded as non electrolytes in DMF.

Table - I

Ligand No.	Complex No.	Empirical formula	% metal	% Sulphus	% Nitrogen
I	1	$(C_{17}H_{15}N_5O_2S)Co$	17.12 (17.67)	7.62 (7.75)	16.80 (16.75)
II	2	$(C_{19}H_{17}N_5O_2S)Co$	14.20 (14.15)	7.00 (7.10)	15.32 (15.25)
III	3	$(C_{17}H_{11}N_5O_2SCl_2)Co$	13.98 (13.90)	6.51 (6.58)	14.21 (14.30)
IV	4	$(C_{19}H_{17}N_5O_4S)Co$	13.50 (12.57)	7.10 (7.25)	15.50 (15.38)

I.R. spectra of ligands

The triazoles are known to exhibit thiol-thiol tautomerism[4]. The condensation of such triazoles with aldehydes and ketones cannot modify the behavious, i.e., ligand to exhibit tatutomerism and can expect both V(SH) and V(CZS) vibrations.

It is well established that Schiff bases containing o-hydroxy groups can form intramolecular hydrogen bonding.[8] The ligand exhibits a broad weak bond with fine structure around 2700cm^{-1} attributable to intramolecular hydrogen boded-OH in analogy with previous assignments[9].

In addition to this a medium intensity band observe around 3250 cm^{-1} is assigned to V(SH) vibration.

As the ligands contain (NCHS) or (NHCS) groups the band due to thiamide vibration are excepted taking into consideration the

previous assignments[10], the medium to high intensity band around 1520 cm^{-1} observed in the ligands may be assigned to V(C=N) vibrations.

A group of medium to high intensity bands in the region 1580-1490 cm^{-1} can be regarded as due to as C=N of triazole ring and C=C aromatic ring vibrations. High intensity bands in the region 1080-1020 cm^{-1} are due to thiamide (III) vibrations. The thiamide (IV) bands mainly due to V(C=S) vibration and is expected around 780cm^{-1}. Therefore the high intensity band in the region 780-740 cm^{-1} is assigned thiamide (IV) vibration.

Spectra of complexes

In cobalt (II) complexes, we observed the following changes in the characteristics frequencies which make the complex formation.

(i) A broad weak bond with fine structure appearing around 2700cm^{-1} in ligand disappears in the complexes. The shifting of phenolic (C=O) (1280 cm^{-1} to higher frequency side (1320 cm^{-1}) suggests the coordination to the metal in through the oxygen via deprotonation.

(ii) The bands due to V(C=N) appearing in the region 1640 cm^{-1} in the ligands shifts towards lower frequencies and appear around 1620 cm^{-1} in the complexes. This indicates that coordination takes place through azomethine nitrogen.

(iii) The band due to V(C=S) in the region 780-740 cm^{-1} of the ligand has remained unperturbed in the complexes suggesting non-involment of sulphur atom in co-ordination.

Assignment in the lower region is tentative because various skeletal vibrations of ligand appear as high intensity bands in the reigon and sometimes they associated with metal-ligands vibrations. Hence, these arrangements are purely tentative and based on the previous assignments[11]. The bands around 540 and 502 cm^{-1} and 500-400 cm^{-1} can be assigned to V (Co-N) and V (Co-O) vibrations.

Magnetic susceptibility

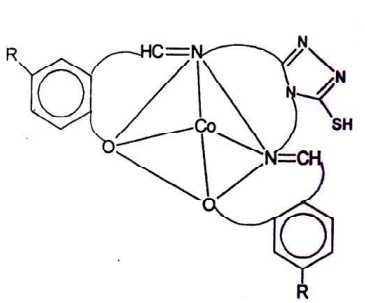
All the complexes show magnetic moment in the ragne of 4.44-4.47 B.M. The values are well with in the range expected for tetrahedral Co (II) complexes, i.e., 4.4 B.M. The observed values are little higher than the spin only values of 3.89 B.M. This may be due to the orbital angular momentum. It may, therefore, be concluded that Co (II) complexes have tetrahedral configuration. This is further supported by electronic spectra.

Electronic spectra

The Co (II) complex under present investigation exhibits high intensity multi-component band in the region 17555-15680 cm^{-1} due to $4A_2$-$4T_1$ (p). Another weak multicomponent band in the region 7860-7488 cm^{-1} which can be attributed $4A_2$-$4T_1$ (F) transition. Hence these complexes can be regarded to have tetrahedral configuration. These observations support the conclusion achieved in the magnetic data.

With the help of analytical magnetic and spectral data, it may be suggested that Co(II) has co-ordination number of four in the complexes and has tetrahedral configuration.

All the observation combined together project the following probable structure for these complexes



R=H, CH_3Cl, OCH_3

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