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MAGNETIC AND SPECTRAL STUDIES OF COPPER(II) COMPLEXES WITH SCHIFF BASES DERIVED FROM *o*-AMINO-BENZOYL HYDRAZIDE

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INTRODUCTION

THE transition metal complexes with hydrazones have been investigated during the past few years¹. However, there is not much work on the complexes of transition metals with bis(salicylidene)-*o*-amino-benzoylhydrazones². In this communication we wish to report the synthesis and spectral properties of a few copper(II) complexes with the Schiff bases derived from *o*-aminobenzoylhydrazide. Following aldehydes were used for the preparation of hydrazones.

1. Salicylaldehyde, 2. 5-Methyl salicylaldehyde, 3. 2-Hydroxynaphthaldehyde and 4. Acetylacetone.

EXPERIMENTAL

Methyl anthranilate and hydrazine hydrate used were of reagent grade. Substituted aldehydes were prepared by Duff's method³. *o*-Amino-benzoylhydrazide was prepared by the standard method⁴. The respective hydrazones were prepared following known methods⁵.

Copper acetate and hydrazones in 1 : 1 molar ratio were refluxed in ethanol medium for about five hours. The separated copper complexes were filtered, washed with ethanol and soxhleted using ethanol. They were then dried in vacuum over fused calcium chloride,

The metal and nitrogen content in these complexes, were analysed and are indicated in Table I.

TABLE I

Elemental analysis, magnetic data and electronic spectra of copper(II) complexes with hydrazones of salicylidene methyl anthranilate:

Sl. No.	Empirical formula of complexes	% Cu	% N	μ_{eff} (B.M.)	λ_{max} (nm)
1.	(C ₂₁ H ₁₅ N ₃ O ₃) Cu	14.91 (15.10)	10.07 (9.99)	1.81	650 350
2.	(C ₂₂ H ₁₇ N ₃ O ₃) Cu	14.00 (14.16)	9.52 (9.36)	1.80	630 375
3.	(C ₂₉ H ₁₉ N ₃ O ₃) Cu	12.31 (12.11)	7.82 (8.01)	1.89	675 412
4.	(C ₁₇ H ₂₁ N ₃ O ₃) Cu	16.55 (16.78)	11.00 (11.09)	1.99	660 380

Note : (i) The values in the parenthesis are the calculated values.

(ii) Electronic spectra of the complexes are taken in Nujol Mull.

RESULTS AND DISCUSSION

The elemental analysis (Table I) indicates 1:1 stoichiometry for these copper(II) complexes. The complexes are brownish green in colour and insoluble in common organic solvents.

Infrared Spectra

The infrared spectra of the ligands and the complexes (4000–400 cm^{-1}) were recorded on a Beckmann I.R.-12 spectrometer.

The important infrared frequencies are listed in Table II along with their assignments. The high intensity bands observed in the regions 1653–1639 cm^{-1} and 1620–1600 cm^{-1} , attributable^{6,7} respectively to the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ vibrations, show considerable shift to the lower frequency, suggesting the coordination of C=O and C=N respectively through oxygen and nitrogen. The absence of intramolecularly hydrogen bonded OH and the appearance of phenolic C–O in the region 1360–1320 cm^{-1} indicate deprotonation of the ligands and formation of metal-oxygen bonds. The band due to the $\nu(\text{NH})$ in the region 3350–3200 cm^{-1} also appears in the complexes. These observations make it obvious that in the complexes, ligands preserve keto form.

TABLE II

Important infrared frequencies (in cm^{-1}) of the ligands and their copper(II) complexes with hydrazones of salicylidene methyl anthranilates

Sl. No.	Assignments	V	VI	VII	VIII
1.	(NH) stretch	3350brm 3200m	3300brm 3200m	3350brm 3250m	3350m 3250m
2.	H bonded OH stretch
3.	(C=O) stretch	1610s	1610s	1600s	1600m
4.	(C=N) stretch	1585s	1580m	1580s	1575s
5.	Phenolic C–O stretch	1325s	1325s	1325s	1360s
6.	(Cu–N) stretch	490m	490brm	485m	480s
7.	(Cu–O) stretch	455m	450m	460s	450s

Note :— w = weak; m = medium; s = strong; br = broad.

In the ligands NH stretch is observed at 3300–3200 cm^{-1} range, C=O stretch around 1653–1639 cm^{-1} , C=N stretch between 1620–1600 cm^{-1} and the intramolecularly hydrogen bonded OH stretch around 2632 cm^{-1} .

With the help of ^{14}N – ^{15}N and ^{63}Cu – ^{65}Cu isotopic shift study, Nakamoto *et al.*^{8a} have assigned i.r. active Cu–N band at 483 cm^{-1} in the case of Cu(II)-glycino complexes. In view of these assignments, we have assigned a band of medium intensity observed in the region 490–480 cm^{-1} to the $\nu(\text{Cu–N})$ vibration.

Nakamoto *et al.*^{8b} have assigned two bands found at 455 cm^{-1} and 290.5 cm^{-1} for Cu(II) acetylacetonate to the $\nu(\text{Cu–O})$ vibrations, since these are isotope sensitive. In the light of these observations, we have assigned a high intensity band in the region 460–450 cm^{-1} to the $\nu(\text{Cu–O})$. The limit of our spectrophotometer does not allow us to go below 400 cm^{-1} .

Magnetic Data

Magnetic susceptibilities of the complexes have been measured on a Gouy balance at room temperature using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant.

The magnetic moments of these complexes fall in the range of 1.80–1.99 B.M. These closely agree with the spin only value for one unpaired electron and suggest that there is no major spin-spin interactions involved in the complexes. However, this cannot exclude the polymeric nature of the complexes because the polymeric complexes with normal magnetic moments are known in the literature⁹.

Electronic Spectra

The electronic spectra of the complexes in Nujol-Mull have been recorded on a Carl-Zeiss DMR-21 uv spectrophotometer. The important λ_{max} are shown in Table I. The electronic spectra of the complexes in solid state exhibit a broad asymmetric band in the region 630–675 nm suggesting that more than one transition are buried underneath the absorption envelope. The regular tetrahedral complexes absorb in the near i.r. region¹⁰, whereas, the symmetrical octahedral complexes absorb around 800 nm¹¹. This band is highly sensitive to the Jahn-Teller distortion and shows a blue shift with increase in the distortion¹². In the present case a distorted octahedral structure with a symmetry lower than octahedral (Oh)¹³ has been suggested.

Taking into consideration the high intensity of the band in the region 380–400 nm, it has been characterised as the ligand-metal charge transfer band.

Electron Spin Resonance

The ESR spectra of the complexes (in powder form) have been recorded on a Varian spectrometer at 77° K using DPPH as reference.

For copper(II) complexes (Cu^{2+} , $1 \rightarrow 3/2$) four lines are to be expected if copper has an octahedral environment¹⁴. It is possible to distinguish between the two ground states, viz., $d_{x^2-y^2}$, d_{z^2} (or d_{xy}) with the help of ESR spectra. The complexes with the ground state¹⁵ $d_{x^2-y^2}$ (or d_{z^2}) give rise to the spectra with

$g_{\perp} > g_{\parallel} \sim 2.04$, whereas complexes with ground state d_{xy} give rise to the spectra having $g_{\perp} > g_{\parallel} = 2.00$. The complexes under present investigation have four line spectra with average $g_{\parallel}(2.271) > g_{\perp}(2.034)$. The absence of a signal corresponding to the $g = 4$ value rules out any Cu-Cu interaction in the complexes. These observations suggest that the complexes may possess tetragonally distorted octahedral configuration.

All these observations suggest that these copper(II) complexes have coordination number six with tetragonally distorted octahedral configuration. The construction of the model for these complexes indicates that the monomeric structure which can force copper for pentacoordinate geometry involves much steric strain as the O-N-O sequence which is in the plane of the complex does not allow the remaining N and O atoms to coordinate to the one and the same metal ion.

The insolubility of the complexes in common organic solvents, nature of the ligands and analytical data favour a polymeric structure for these complexes. The molecular weights could not be determined due to the insolubility of the complexes.

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