

Synthesis and Structural Characterization of Cu(II) Complexes of 2-Arylhydrazono-1-Phenylamino Butane-1,3-Dione

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Cu(II) complexes of 2-arylhydrazono-1-phenylamino butane-1,3-dione (AHPABD) having substituents H, 2-NO₂, 3-NO₂, 4-NO₂, 4-CH₃, 3-Cl in the phenyl ring have been prepared and characterised by elemental analysis, IR and electronic spectral studies. The analytical results suggest that complexes are formed in 1:2 (M:L) ratio and are isostructural in which AHPABD acts as bidentate ligand.

INTRODUCTION

Hydrazones comprise an important class of multidentate ligands which are pharmacologically important¹. Hydrazone derivatives have been extensively used for Cu(II) complex formation in the recent past²⁻⁷. The literature survey reveals that no study of 2-arylhydrazono-1-phenylaminobutane-1,3-dione (AHPABD) complexes of Cu(II) has been carried out; hence these need investigation.

EXPERIMENTAL

Substituted anilines, NaNO₂, HCl, aceto-acetanilide, sodium acetate, copper acetate used were of AR grade. All the ligands synthesised were characterised by m.p., IR, UV-visible spectroscopy. The AHPABD was synthesised by the diazotisation of aniline derivatives followed by coupling with a compound having active methylene group *i.e.* 1-phenylamino butane-1,3-dione. By this method following series of hydrazone compounds have been synthesised:

1. 2-Phenyl hydrazono.
2. 2-(2'-Nitro) phenyl hydrazono.
3. 2-(3'-Nitro) phenyl hydrazono.
4. 2-(4'-Nitro) phenyl hydrazono.
5. 2-(4'-Methyl) phenyl hydrazono.
6. 2-(3'-Chloro) phenyl hydrazono.
7. 2-(4'-Bromo) phenyl hydrazono.
8. 1-Phenyl amino butane 1, 3 Dione.

These hydrazone compounds were utilized in the synthesis of Cu(II) complexes. The methanolic solution of the ligand 2×10^{-3} M was added to the metal salt solution 1×10^{-3} M in the methanol (1 : 2 M : L ratio). The reaction mixture

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was refluxed for about 2 h and the solution was cooled and solvent volume reduced which on standing gave crystals which were filtered, washed with water and dried. The Cu(II) complexes of substituted AHPABD were also obtained by one more method. In this method ethanolic solution of ligand was added (2 : 1) to a Cu(II) salt solution in water followed by the addition of 5.0 mL of NH_3 and solution refluxed for 2 h and then cooled. The complex so precipitated was washed with water and dried. C, H and N analyses of copper complexes were performed by the microanalytical section of D.R.D.E. Gwalior, using Carlo-ERBA elemental analyser. IR spectra of the ligand of the complexes were recorded on Perkin-Elmer-883 spectrophotometer in the range $4000\text{--}200\text{ cm}^{-1}$. Samples were prepared in Nujol and KBr. Ethanolic solution of the complexes was used for obtaining electronic spectra. Spectra of ligands of Cu(II) complexes were recorded on SPECORD UV-visible spectrophotometer.

RESULTS AND DISCUSSION

Cu(II) complexes of substituted AHPABD were subjected to elemental analysis. The observed values of C, H, N are in close agreement with the values calculated on the basis of molecular formula. The analytical results also indicate that complexes are formed in 1 : 2 (M : L) ratio (Table-1).

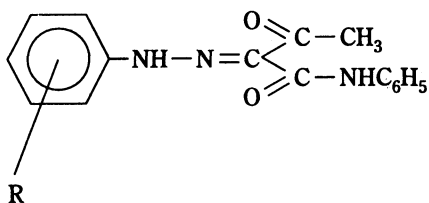
TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE COPPER(II) CHELATES

S.No	R	Complexes/ (Colour)	m.p. ($^{\circ}\text{C}$)	Analysis % Found (Calcd)		
				C	H	N
1.	H	$\text{Cu}(\text{C}_{16}\text{H}_{14}\text{N}_3\text{O}_2)_2$ (Coffee)	209	61.58 (61.12)	4.17 (4.26)	13.40 (13.02)
2.	2- NO_2	$\text{Cu}(\text{C}_{16}\text{H}_{13}\text{N}_4\text{O}_4)_2$ (Algae green)	203	53.81 (53.28)	3.64 (3.42)	11.70 (11.52)
3.	4- CH_3	$\text{Cu}(\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}_2)_2$ (Coffee brown)	199	58.94 (58.78)	3.99 (4.02)	12.89 (12.92)
4.	3- Cl	$\text{Cu}(\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_2\text{Cl})_2$ (Coffee)	207	55.45 (55.46)	3.75 (4.00)	12.12 (12.32)
5.	4- Br	$\text{Cu}(\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_2\text{Br})_2$ (Brown)	210	49.26 (46.68)	3.33 (3.98)	10.27 (11.27)

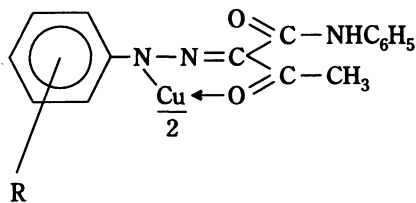
The IR absorption bands show that spectra of the complexes have similar features indicating that all the complexes are isostructural. Structure of ligand indicates that it can function as a bidentate ligand—one hydrazono nitrogen and one oxygen of ketonic group as possible bonding sites. The IR spectra of the ligand show an absorption band in the range $1660\text{--}1640\text{ cm}^{-1}$ which can be assigned to $\nu(\text{C}=\text{O})$ stretching frequency. As is evident from the structure (I), the ligand has two $>\text{C}=\text{O}$ groups of both the carbonyl frequencies, which are much lower than the normal near 1720 cm^{-1} ; the reason for this is that one carbonyl group is hydrogen bonded with the H of the $>\text{N}\text{--}\text{H}$ group. The other reason is that $>\text{C}=\text{O}$ group is in conjunction with $>\text{C}=\text{N}\text{--}$ group which leads to delocalisation of electrons⁸. The lowering of frequencies by $50\text{--}70\text{ cm}^{-1}$ of this band in the spectra of the complexes suggests that $>\text{C}=\text{O}$ group is involved in

chelation. The two bands (due to $>C=C<$ stretching of phenyl ring and $>C=N-$ of the azomethane) are observed in the same region ($1600-1580\text{ cm}^{-1}$) for both the ligands and complexes, excluding the possibility of coordination of nitrogen of azomethane group ($>C=N-$).

The absorption band in the region ($3400-3100\text{ cm}^{-1}$) which could have given the idea regarding the involvement of $>NH$ in the coordination could not be made in the IR spectra of ligand and in the complexes. But from the structure of the ligand it is clear that if coordination is taking place through the nitrogen of the hydrazono group ($-NH-$) six-membered chelate ring will be formed, but if nitrogen of the $>C=N-$ group will be involved then five-membered ring will be formed. As it is known that six-membered chelates ring is more stable than five-membered ring, the possibility of $-NH-$ in coordination is more in which a labile proton is lost. Thus possible structure of the complexes on the basis of IR is as structure (II):



Structure-I



Structure-II

where $R=H, 2-NO_2, 3-NO_2, 4-NO_2, 4-CH_3, 3-Cl, 4-Br$.

Generally high intensity bands⁹ observed in the electronic spectra above $25000-20000\text{ cm}^{-1}$. These are due to either intra-ligand transition or due to metal to ligand or ligand to metal charge transfer process. The bands in the region $425-360\text{ nm}$ and $265-230\text{ nm}$ are due to internal ligand transition arising from the $Ph-N-N=C$, $Ph-NH-C=O$ and $CH_3-C=N$.

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