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Dimeric Square Planar Complexes of Cu(II) with Aroyl Hydrazones

N. S. BIRADAR and B. R. HAVINALE
Department of Chemistry, Karnatak University, Dharwar-580003, INDIA

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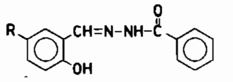
Cu(II) complexes with aroyl hydrazones have been prepared in ethanol medium and characterised by elemental analysis. They have 1:1 stoichiometry. I. R. results show that the hydrazones exist in the enol form in the complexes. These Cu(II) complexes show subnormal magnetic moments and the electronic spectra agree with the square planar configruation. In view of the magnetic and electronic spectral evidence, the dimeric square planar configuration is suggested in which Cu–Cu interaction exists.

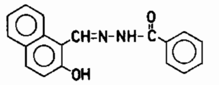
Introduction

The hydrazides have been successfully tried for the complexation and they have been shown to coordinate through C=O and the terminal NH_2 groups.[1–6] The hydrazones containing C=O and C=N coordinating sites are the reaction products of hydrazides and aldehydes or ketones.[7] The *ortho*–hydroxy aldehydes or ketones yield the bases containing an active –OH group in addition to the C=O and C=N coordinating groups. The previous examples[8–11] show that these bases display monovalent bidentate behaviour. However, a few complexes with salicylhydrazone and isopropyl salicylhydrazone are recorded in the literature in which the –OH group remains inert to the complex formation.[5] All this information stands as a testimony for the versatility of the hydrazones as chelating agents. However, the work on the complexes of divalent metal ions with hydrazones is limited.[12–15]

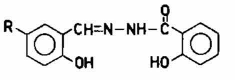
The present work describes the synthesis, spectral and magnetic properties of Cu(II) complexes with the following hydrazones.



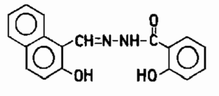
I II III
R=H R=CH$_3$ R=Cl



IV



V VI VII
R=H R=CH$_3$ R=Cl



VIII

The stereochemistry of the complexes has also been discussed in the paper.

Experimental

Materials and Methods

Ethylbenzoate, methylsalicylate and hydrazine hydrate used for preparing the hydrazides were of reagent grade.

Copper acetate was an analytical reagent. Benzoyl hydrazide and *o*-hydroxy-benzoylhydrazide were prepared according to the standard method.[16] The substituted aldehydes were prepared according to Duff's method.[17]

The hydrazones were prepared by the reaction of benzoyl hydrazide or *o*-hydroxy-benzoylhydrazide ($0.1M$) with the corresponding aldehyde ($0.1M$) in ethanol. The hydrazones were recrystallised from ethanol.

Preparation of Complexes

To an ethanolic solution ($0.1M$) of hydrazide and aldehyde, an aqueous copper acetate solution ($0.1M$) was added. The reaction mixture was heated for a while on water bath and the complex precipitated was filtered and washed free from the ligand with ethanol and finally with ether and dried under vacuum over P_2O_5.

Elemental Analysis

The copper in the complexes was estimated volumetrically by standard method[18] and the nitrogen by the Dumas method. Carbon and hydrogen were determined by microanalytical methods. The results of the elemental analysis are shown in Table I.

Physical Measurements

The conductance measurements were done on an ELICO CM-82 conductivity bridge with a cell having a cell constant of 0.829 cm^{-1}. The magnetic measurements were made on a Gouy balance at room temperature using $Hg[Co(SCN)_4]$ as a calibrant. The electronic spectra of the complexes were recorded on a Beckmann DB spectrophotometer in the 350–2000 nm region. The I. R. spectra of the ligands and the complexes in nujol mull were recorded on a Beckmann

TABLE I. Elemental Analysis, Magnetic Moment and Electronic Spectral Data for Cu(II) Complexes of Hydrazones.

S. No.	Ligand No.	Complex No.	Empirical formula	%Cu	%N	%C	%H	μ_{eff} (298°K), B.M.	Electronic Spectra λ_{max} (nm)
1.	I	IX	$(C_{14}H_{10}N_2O_2)Cu$	21.56 (21.08)[a]	8.68 (9.29)	56.63 (55.72)	3.17 (3.31)	1.31	385, 650
2.	II	X	$(C_{15}H_{12}N_2O_2)Cu$	19.52 (20.14)	9.01 (8.88)	56.02 (56.93)	3.73 (3.80)	1.25	395, 630
3.	III	XI	$(C_{14}H_9N_2O_2Cl)Cu$	18.72 (18.92)	8.82 (8.34)	52.38 (50.00)	2.57 (2.67)	1.20	395, 650
4.	IV	XII	$(C_{18}H_{12}N_2O_2)Cu$	17.52 (18.08)	8.48 (7.97)	62.53 (61.45)	3.38 (3.41)	1.44	410, 630[b]
5.	V	XIII	$(C_{14}H_{10}N_2O_3)Cu$	20.95 (20.01)	9.19 (8.82)	53.15 (52.91)	3.35 (3.15)	1.60	390, 630
6.	VI	XIV	$(C_{15}H_{12}N_2O_3)Cu$	20.26 (19.17)	8.96 (8.45)	54.80 (54.30)	4.02 (3.61)	1.56	390, 630
7.	VII	XV	$(C_{14}H_9N_2O_3Cl)Cu$	19.16 (18.05)	7.87 (7.96)	47.76 (47.73)	2.60 (2.56)	1.47	390, 675
8.	VIII	XVI	$(C_{18}H_{12}N_2O_3)Cu$	17.87 (17.29)	8.05 (7.62)	58.41 (58.78)	3.84 (3.26)	1.64	410, 620

[a] Values in parentheses are the calculated values. [b] Electronic spectra in Nujol.

IR-20 spectrophotometer in the 4000–650 cm^{-1} region.

Results and Discussion

The complexes are green in colour, insoluble in common organic solvents. To some extent they are soluble in DMF and DMSO. The results of the elemental analysis (Table I) show that the complexes have 1:1 stoichiometry.

Conductance

The molar conductance in DMSO at the concentration ~ $10^{-3}M$ is too small to measure. Hence the complexes are non-electrolytes.

Magnetic Properties

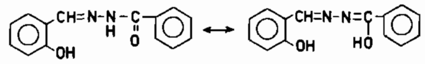
The magnetic moments measured at room temperature are listed in Table I. They are in the range of 1.20 to 1.64 B. M. This value is lower than the spin-only value expected for Cu(II) complexes.[19] It has been well established that the magnetic moments for the mononuclear complexes having no major interaction between two copper moieties[19] are in the range of 1.75 to 2.20 B. M. The subnormal magnetic moments observed in the case of Cu(II) tridentate Schiff base complexes are accounted for by assuming dimeric structure in the solid state and considerable interaction between two Cu(II) systems due to spin exchange phenomena.[20,21] The low magnetic moments observed for these complexes may be due to the significant spin exchange between two Cu(II) ions. This may be accounted for by assuming a dimeric structure for these complexes.

Electronic Spectra

The complexes of Cu(II) show several bands. Amongst them significant bands have been taken for discussion. These Cu(II) complexes show a band in the range 620–675 nm which is the characteristic copper band. Copper(II) is a d^9 ion and hence the Jahn–Teller effect is operative.[22] For an octahedral complex the expected $^2E_g \rightarrow {}^2T_{2g}$ band is around 800 nm.[22] This shows a considerable blue shift as the Jahn–Teller distortion leads to a square planar structure.[23] The band in the region 385–410 nm is the subject of much controversy and in a number of complexes it has been recognised as the characteristic band representing the Cu–Cu linkage.[24,25] Keeping all these observations in view and taking into consideration the observed subnormal magnetic moments, we can suggest that these Cu(II) complexes may have a dimeric square planar structure in which two copper entities are linked through oxygen. The high intensity of the 385–410 nm band may be due to the ligand–metal charge transfer which may in the binuclear complexes overlap in the blue region. Hence, Cu(II) complexes may be regarded as binuclear complexes.

Infrared Spectra

The important infrared frequencies along with their assignments are listed in Table II. The hydrazones under present discussion exhibit *keto–enol* tautomerism and as such they exist in one of the two forms in the complexes:[26]



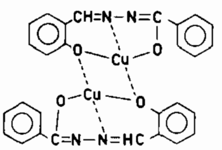
If in the complexes the ligands exist in the *keto* form, one can expect the NH and C=O stretching vibrations in the spectra, whereas both of these stretching frequencies will remain absent if the ligands are in the *enol* form in the complexes.

In these complexes, the NH stretch[27] of the ligand around 3200 cm^{-1} is not observed. The high intensity band due to the C=O stretch[28,29] in the region 1670–1650 cm^{-1} is not observed in the complexes. The broad weak band due to the intramolecular H-bonded OH[30] has vanished in the complexes IX–XII, whereas it is retained in the complexes XIII–XVI. In complexes XIII–XVI this may be due to the OH intramolecularly hydrogen-bonded to the nitrogen of the free C=N group. The band due to the phenolic C–O[30] around 1280 cm^{-1} shows a considerable high frequency shift in the complexes and appears in the region 1350–1305 cm^{-1}. The C=N stretch[29] of the ligand in the region 1625–1610 cm^{-1} is observed in the 1612–1600 cm^{-1} region suggesting that the coordination bond is formed between the nitrogen of the azomethine group and the Cu(II) moiety. An intense band observed in the region 1640–1630 cm^{-1} may be assigned to ν (C=N) due to the *enolic* form of the ligand.

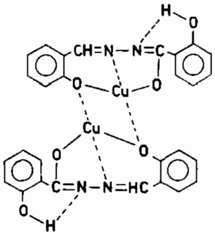
All these pieces of evidence suggest that in the complexes of Cu(II) the aroyl hydrazones exist in the *enol* form and exhibit bivalent tridentate behaviour.

The analytical results show that the complexes have 1:1 stoichiometry and the electronic spectral results suggest a square planar configuration. The subnormal magnetic moment values obtained for these complexes indicate significant spin exchange between two copper ions. Infrared results show that the aroyl hydrazones exist in the *enol* form.

All these facts taken together with the common square planar configuration known in the Cu(II) complexes prompt us to propose the following structures for these complexes.



IX - XII



XIII - XVI

Acknowledgements

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TABLE II. Important Infrared Frequencies (in cm^{-1}) of Cu(II) Complexes of Aroyl Hydrazones and Their Assignments.[a]

S. No.	Ligand No.	Complex No.	ν(C=N) free	ν(C=N) bonded	ν(C=C)	ν(C–O)
1.	I	IX	1640	1612	1563 1495	1315
2.	II	X	1635	1600	1562 1495	1317
3.	III	XI	1632	1605	1550 1495	1350
4.	IV	XII	1630	1605	1562 1500	1305
5.	V	XIII	1635	1608	1565 1515	1320
6.	VI	XIV	1635	1610	1560 1510	1340
7.	VII	XV	1632	1605	1560 1520	1308
8.	VIII	XVI	1638	1610	1512 1490	1310

[a] In the ligands the following assignments may be made: ν(NH) ~3200 cm^{-1}; ν(Intramolecular H-bonded –OH), 2800–2700 cm^{-1}; ν(C=O), 1670–1650 cm^{-1}; ν(C=N), 1625–1610 cm^{-1} and ν(C–O) ~1280 cm^{-1}.

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