Annals of Natural Sciences
Vol. 9(4), December 2023: 17-20
Journal's URL: http://www.crsdindia.com/ans.html
Email: crsdindia@gmail.com

e-ISSN: 2455-667X

Annals
of
Natural Sciences

ORIGINAL ARTICLE

Ligational Behavior of Hydrazine and Dicarboxylic Acids in Mixed-Ligand Complexes of Cu (II)

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ABSTRACT

The purpose of present study was to synthesis of new mixed ligand complexes of Cu (II) with hydrazine and dicarboxylic acids. Hydrazine and its derivatives is good nitrogen donor towards metal ions and a dicarboxylic acid considerd as good oxygen donor and behave as bidentate ligand. The findings showed that the magnetic moment data and ESR spectra suggest that Cu (II) complexes has one unpaired electron indicating para magnetic, low spin and tetragonally distorted configuration.

Key words: *bidentate molecule, derivatives of hydrazine, ligand complexes, magnetic moment*

Received: 24th Oct. 2023, Revised: 12th Nov. 2023, Accepted: 21st Nov. 2023

How to cite this article:
Sajid S (2023): Ligational Behavior of Hydrazine and dicorboxylix acids in mixed-Ligand Complex of Cu (II). Annals of Natural Sciences, Vol. 9[4]: December, 2023: 17-20.

INTRODUCTION

Prior to 1875 only the symmetrically distributed hydrazine, the hydrazo compounds had been known. In 1875 Fischer first time reported the preparation of simple hydrazine and characterized free phenyl hydrazine and salt of nitrogen base. Hydrazine is considered to be one of the simple hydro nitrogen and used as rubber softener and plasticizers. Phenyl hydrazine is preferred for this purpose, and it is said to be plasticize and reduce the viscosity of rubber solution.

After the development of x-ray crystallography and it's successful application in the elucidation of a structure of coordination compounds complexation of transition metal ion with several organic ligands has been the subject of interest for research workers in many diverse discipline, both experimental and the theoretical. A large number of diamine has been examined for the complexing behaviour with several transition and non transition metal ions. The ability of hydrazine to serve as an electron pair donor has already been noted. It is very interesting that hydrazine in coordination with metallic ion appears to act as bidentate molecule compound containing coordinated hydrazine are somewhat limited in number because of the reducing nature of hydrazine compound of noble metal containing coordinated hydrazine are stable only at lower temperature and most generally be prepared under anhydrous conditions. A large number of complexes containing coordinated hydrazine or substituted hydrazine with first row transition metal ions have been reported.

EXPERIMENT

Mixed ligand complexes of transition metal have attracted attention in recent year because they occur in many natural systems. A survey of literature shows that the studies on mixed ligand complexes of transition metal are limited mainly to spectrophotometery and potentiometer [1].

Hydrazine and its derivatives is good donor towards metal ions [2, 3]. Dicarboxyic acids have also been considered as good oxygen donor ligands mixed ligand complexes of (Cu-II) metal with hydrazine and Dicarboxyic acids have been prepared and studied but literature survey reveals that the mixed ligand complexes of transition metal with dicarboxyic acid as secondary ligand have not been studied so far. Comparatively in very few cases their spectral and magnetic studies have known. So it was pressured to synthesis the metal complexes with aliphatic dicarboxyic acids and hydrazine to characterized them by elemental analysis, magnetic data and spectral studies. In previous studies the author [4, 5, 6, 7, 8, 9] has synthesized and characterized some new complexes of first row transition elements. In present communication the complexes of Cu-II with hydrazine (hy), dimethyl hydrazine (Me_2hy) and dicarboxyic acids have been prepared and studied.

The complexes are found to be low spin letragonal distorted in structure. All chemicals used were of anal R grade. Hydrazine (fluka) and dicarboxyic acids were used as supplied while pure dimethylhydrazine was prepared from dimethyl hydrazine hydrochloride as reported earlier [10]. The salt and complexes of Cu-II were synthesized which are assigned to v (M-N) and V (M-O) comparing the spectra of the free acids, their metal salts and hyandMe_2hy. Due to the formation of M-CbondC-O bond is more lengthened and C=O shortened resulting in the shift (C-O) stretching and (C-O) stretching to lower and higher frequencies respectively.

The magnetic moment data (1.9-2.7 B.M.) shows that the Cu-II complexes has one unpaired e^- indicating paramagnetic; low spin complexes and tetragonally distorted or octahedral configuration.

Table 1: Analytical and Magnetic Moment Data of Copper (II) Mixed Ligand Complexes

Compound	Found(Calculated)				Magnetic Moment μ_{eff}(B.M.)
	Metal %	C %	H %	N %	
$Cu(hy)_2C_2O_4$	20.13 (20.72)	14.63 (15.05)	2.26 (2.72)	16.32 (16.61)	1.52
$Cu(hy)_2C_4H_4O_6$	18.65 (18.94)	14.08 (14.45)	3.53 (3.94)	17.02 (17.31)	1.57
$Cu(hy)_2C_4H_4O_4$	19.85 (20.02)	154.62 (15.84)	3.87 (4.03)	17.53 (17.81)	1.45
$Cu(hy)_2C_3H_2O_4$	19.28 (19.66)	12.27 (12.56)	3.17 (3.43)	18.83 (18.95)	1.59
$Cu(Me_2hy)_2C_2O_4$	17.85 (18.34)	20.18 (20.53)	4.42 (4.94)	15.23 (15.71)	1.62
$Cu(Me_2hy)_2C_4H_4O_6$	15.74 (15.97)	22.49 (22.95)	4.69 (5.06)	13.37 (13.83)	1.38
$Cu(Me_2hy)_2C_4H_4O_4$	16.80 (16.99)	24.67 (24.89)	5.35 (5.76)	14.17 (14.69)	1.59
$Cu(Me_2hy)_2C_3H_2O_4$	17.52 (18.22)	23.93 (24.37)	4.88 (5.39)	15.01 (15.42)	1.63

Chemistry of Cu-II ion, one is large extent of distortion due to John Teller effect [11]. As a result an effect the Cu-II complexes are either distorted octahedral [12] or distorted tetrahedral [13]. The electronic spectra of all complexes of Cu-II show one broad strong absorption in the region 16500-18900 cm^{-1}. On this basis all complexes seen to be tetragonaly distorted Cu-II in tetragonal environment three principal absorption bands are expected but only in fewc ases. Their absorption bands have been resolved and are assigned to the transitions.

$^2B_1g \longrightarrow {}^2A_1g$
$^2B_1g \longrightarrow {}^2B_{2g}$
$^2B_1g \longrightarrow {}^2E_g$

The possible energy level sequences may arise which are dependent on tetragonal distortion.

(a) dx^2-y^2	<dxy	<dxz	dyz	<dz^2
(b) dx^{2-y2}	<dxy	<dz^2	<dxz,	dy^2
(c) dx^2-y^2	<dz^2	<dxy	<dxz,	dyz

Case (a) corresponds to a large tetragonal leading to square plan as stereochemistry. As the transition $^2B_1g \longrightarrow {}^2Eg$ is likely to be most intense one [14], and Case (c) to low tetragonal distortion. In all the cases one broad absorption band with a shoulder on lower energy side has been observed the low energy shoulder assigned to transition$^3B_1g \longrightarrow {}^2A_1g$ being equal to the splitting of the ^2Eg term. Because of low intensity of $^2B_1g \longrightarrow {}^2B_2g$, (being equal to 10Dq) this band not observed as separate band in tetragonal compounds since Dq, Dt and Ds cannot be evaluated only the splitting of Eg. (i.e. 4D$_5$+5Dt) has been determined. The ESR spectra of complexes Cu (hy)$_2$ & Cu (Me$_2$hy)$_2$ suggests that Cu-II) ion in-

Table 2: Electronic Spectral Data of Cu (II) Mixed Ligand Complexes (Cm-^{1})

Complexes	$_2B_{1g}-{}^2A_{1g}$	$_2B_{1g}-{}^2E_{1g}$	4Ds + 5Dt
Cu(hy)$_2$C$_2$O$_4$	15000	18700	3700
Cu(hy)$_2$C$_4$H$_4$O$_4$	14300	17400	3100
Cu(hy)$_2$C$_3$H$_2$O$_4$	14000	16900	2900
Cu(hy)$_2$C$_4$H$_4$O$_6$	13800	16500	2700
Cu(Me$_2$hy)$_2$C$_2$O$_4$	15100	18900	3800
Cu(Me$_2$hy)$_2$C$_4$H$_4$O$_4$	14500	17900	3400
Cu(Me$_2$hy)$_2$C$_3$H$_2$O$_4$	14150	17230	3080
Cu(Me$_2$hy)$_2$C$_4$H$_4$O$_6$	13950	16810	2860

a. A regular octahedral stereo chemistry undergoing a dynamic [15] or pseudo rotational [16] type of John Teller distortion.
b. A Occur in cubic hexaminie and pentaammine complexes Cu-II [17].
c. A complex containing grossly misaligned tetragonal axis [18]. The situation(c) is probably most common for the observation of an isotropic ESR-Spectrum. The g-value observed in these complexes is 1.812 & 1.80 respectively which suggest the complex to be (c) category.

ACKNOWLEDGEMENTS

The author is thankful to authorities of G.F. College, Shahjahanpur, for providing laboratory facilities, their valuable suggestion, and encouragement.

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