

EXPLORING THE COMPLEXES OF COBALT (II) AND COPPER (II) WITH 2, 5-DISUBSTITUTED 1, 3, 4-TRIAZOLE LIGANDS

Anusha Mary Joseph

Department of Chemistry, Nirmala College for Women, Coimbatore, Tamil Nadu, India.

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Abstract

New metal complexes of Co (II), and Cu (II) have been synthesized by reacting metal solutions with the ligand 2, 5-substituted 1, 3, 4-triazoles in alcoholic medium. Molecular formulae of the complexes were determined and are further characterized by IR spectroscopy, magnetic susceptibility and molar conductance studies. The ligand acts as a bidentate ligand co-ordinating through the nitrogen atoms present in the ring.

Keywords: Complexes, Ligands, Transition metal complexes, Triazoles.

Introduction:

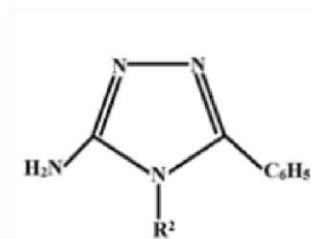
In co-ordination chemistry, a ligand is an ion or molecule that binds to a central metal atom to form a co-ordination complex. Ligands in a complex dictate the reactivity of the central atom, including ligand substitution rates and the reactivity of ligands themselves. Hence ligand selection is a critical consideration in many practical areas and has created a great interest in synthesis and characterization of co-ordination compounds. Triazoles belong to a group of heterocycles that have been reported to possess anti-inflammatory, analgesic, anti-microbial, anti-fungal [1] and many biological activities [2]. The wide range of application of the ligand and its metal complexes made us to prepare some of the new metal complexes.

Experimental Methods All the reagents used are of analar grade.

2.1 Preparation of ligand:

The synthesis of triazoles involves the synthesis of 1, 3,4-oxadiazoles and their conversion into triazoles. The synthesis generally involves three stages. In the first stage semicarbazone was prepared from semicarbazide hydrochloride and sodium acetate crystals. 1-oxa-3, 4-diazoles have been synthesized in the second stage by following the available literature [3]. N-substituted 1, 3,4triazoles were synthesized by refluxing oxadiazoles(from stage 2) in alcohol with the corresponding amino compound or ammonia for 1-2 hrs in the third stage. The reaction mixture was cooled in ice to get the 1-substituted triazoles.

L₁ was prepared by using ammonia, L₂ was prepared by using hydrazine hydrochloride and L₃ was prepared by using hydroxylamine. The structure of the ligand is



Ligands	R2
L1	H
L2	-NH2
L3	-OH

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Hours. The copper complex was prepared by using copper (II)sulphate instead of cobalt(II)chloride. The solvent was then removed by vacuum distillation and then dried.

2.3 Characterization of the complex:

The molecular weight of the complexes was determined by depression of freezing point method (Rast micro method) using camphor as solvent. The metal content of the complexes was determined by complexometric EDTA titration. Magnetic susceptibility measurements were carried out by Guoy balance at room temperature using powdered samples of the complexes. Conductivity measurements were performed on 10^{-3} mol dm^{-3} solutions of the complexes in acetonitrile using a type CM-82 Elico-conductivity bridge with a dip type conductivity cell fitted with a platinum electrodes. The infrared spectra of the solid sample in the range of 4000cm^{-1} - 600cm^{-1} were recorded on PerkinElmer FT IR spectrometer.

III. Results and Discussion:

All the complexes, containing ligands L₁, L₂ and L₃ have been prepared in ethanol. The colour of the complexes varies from light yellow to dark brown. All the complexes are insoluble in ether, acetone and chloroform. All these complexes were characterized by elemental analysis, molar conductance, magnetic and spectroscopic studies.

3.1 Molecular formulae of the complexes:

The observed molecular weights of the complexes, amount of metal present in the complex, most probable molecular formulae of the complexes and their colours are given in Table1. The effective magnetic moment values of the complexes and their conductivity values are given in Table2. The IR spectral data are summarized in Table3. The molecular weight values indicate that the complexes are 1:2 type.

3.2 Magnetic studies of the complexes:

The μ_{eff} values of Co(II) complexes are found to be in the range 4.5 to 5.0 BM while for Cu(II) complexes these values fall within 3.3 to 5.1BM[4]. In the case of Co (II) complexes, the spin only μ_{so} value is 3.88 for

high spin complexes. If the complex is low spin, μ_{so} should be 1.73 BM. Since for most of the Co (II) complexes μ_{obs} lies in the range 4.3 to 5.5 BM, all the Co (II) complexes should be high spin complexes with 3 unpaired electrons.

In the case of Cu (II) complexes, μ_{so} is 1.73 BM with one unpaired electron [5]. Hence the Cu (II) complexes should be paramagnetic but are low spin due to only one unpaired electron. However the observed μ_{obs} values of Cu (II) complexes are abnormally high and lie between 3.5 to 4.6 BM. The high observed spin values indicates spin-exchange interaction between Cu (II) ions.

3.3 Conductivity of the complexes:

A perusal of the conductivity values for the complexes reveals that all the complexes of the triazoles synthesized in this research work have very low conductivity in the range of 10^{-6} mho. This observation suggests that the complex molecule is a neutral molecule with the halide and sulphate ions are held tightly within the coordination sphere along with the triazole ligands.

3.4 IR Spectral studies:

The IR spectral data of the ligand and the complexes are given in table-3. Comparison of the IR spectrum of the free ligand and the complexes reveals that C=N stretching has shifted from 1590cm^{-1} to 1612cm^{-1} . The upward shift in the C=N stretching frequency indicates the formation of coordinate covalent bond involving the nitrogen of azomethine group with the metal atom and hence the triazoles act as bidentate ligands. The new bands appeared for complexes below 450cm^{-1} are due to Cu-N, Co-N bonds as well as metal – halogen and metal-oxygen bands [6-9]. A new band appeared at 3280cm^{-1} for the complexes is due to O-H stretching for water molecules present as water of hydration. The stretching frequencies of all other groups practically remain the same as indicating that they are not involved in complex formation.

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Table – 1 Analytical data of the complexes:

Name of the complex	Molecular weight of the complex Calc. (Th.) g.	Metal content in the complex (g)	Colour of the complex	Probable molecular formulae of the complexes
Co L ₁	479.52 (485.83)	58.56	Pinkish white	[Co(L ₁) ₂ Cl ₂](H ₂ O) ₂
Co L ₂	488.43 (515.83)	58.20	Dirty white	[Co(L ₂) ₂ Cl ₂](H ₂ O) ₂
Co L ₃	514.49 (517.83)	58.16	Brown	[Co(L ₃) ₂ Cl ₂](H ₂ O) ₂
Cu L ₁	524.27 (515.61)	63.13	Pale yellow	[Cu(L ₁) ₂ SO ₄](H ₂ O) ₂
Cu L ₂	542.37 (545.61)	63.38	White	[Cu(L ₂) ₂ SO ₄](H ₂ O) ₂
Cu L ₃	548.24 (547.61)	63.05	Brown	[Cu(L ₃) ₂ SO ₄](H ₂ O) ₂

Table – 2 Magnetic moments and conductivity values of the complexes:

Name of the complex	Magnetic moment $\mu_{eff}=2.839\sqrt{KMT}\times 10^{-2}$	Conductivity values Ω	$\times 10^{-6}$
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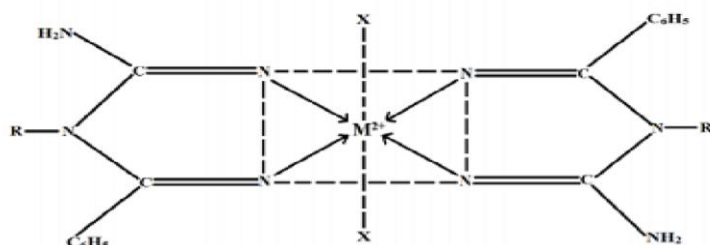
	BM	
Co L ₁	4.83	9.97
CoL ₂	4.84	9.09
Co L ₃	4.85	7.77
Cu L ₁	3.33	5.53
Cu L ₂	5.14	3.27
CuL ₃	4.69	2.48

Table-3 IR spectral data on free ligands and complexes:

S.No.	Group	$\gamma(\text{cm}^{-1})$ for free ligand	$\gamma(\text{cm}^{-1})$ for complexes
1.	Azomethine -C=N	1590	1610
2.	N-H stretching -NH ₂	3460	3460
3.	Aromatic =C-H Asymmetric st.	3060	3064
	Symmetric st.	2992	2992
4.	O-H stretching (water of crystallisation)	-	3284
5.	M-N, M-X, M-O	-	Below 400

Conclusion:

Complexes of 2,5-substituted-1,3,4-triazoles have been synthesized and characterized by magnetic studies, conductivity studies, IR studies and their probable molecular formulae was determined. Based on the above results the structure of the complex may be concluded as follows:



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