

Synthesis and Spectroscopic Characterization of mixed ligand cobalt complexes with Biguanide and Nitrogen donor ligands

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Abstract – Biguanide are versatile nitrogen rich organic compounds with broad applications in medicinal chemistry, coordination chemistry and catalysis. The parent biguanide molecule, C₂N₅H₇, acts as a nitrogen donor bidentate ligand, featuring two units that enable strong chelation with metal ions, leading to the formation of stable complexes. Their ability to coordinate transition metals has facilitated the design of metal-biguanide complexes with remarkable biological and catalytic properties. These complexes display diverse coordination modes influenced by steric and electronic factors, resulting in distinct physiochemical and magnetic behaviours. Spectroscopic and crystallographic investigations reveal rich structural variations, while computational studies offer insight into electronic configurations and reactivity patterns. Metal biguanide systems have been examined for antimicrobial, anticancer and catalytic roles highlighting their importance in contemporary chemistry. This work outlines the synthesis and characterization of biguanide based metal complexes, underlining their relevance in material science and medicinal research.

Key Words: Biguanide, Copper complex, elemental analysis UV-Vis spectra, IR spectra, .

1.INTRODUCTION

Biguanide exists primarily as open-chain systems, although certain cyclic biguanide derivatives are also used in medicinal chemistry, where they often display enhanced biological activity. Owing to their electron rich nature, biguanides are highly basic and are typically employed in their monoprotonated form in the pharmaceutical applications. The first synthesis of biguanide was reported by Rathke in 1879, who prepared it by reacting cyanamide with guanidine. Subsequently, in 1929, Slotta and Tschesche discovered the hypoglycemic activity of the biguanide derivative metformin in animal studies[1]. Biguanide and its derivatives have since found extensive use in medicine because of their diverse pharmacological profiles[2]. A prominent example is metformin, the most widely prescribed oral hypoglycemic agent for managing type 2 diabetes. Another is proguanil, an antimalarial drug. Phenyl aminopropyl biguanide is also employed as both a disinfectant and an anti malarial agent[3][4][5]. Structurally, biguanide is formed by the condensation of two guanidine molecule with the elimination of an ammonia molecule. It acts as a bidentate ligand and coordinates to the central metal ion, here Co (III) through its imino and amino nitrogen atoms.

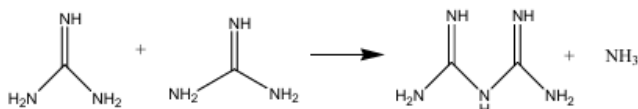


Fig.1. Condensation reaction to form Biguanide

2. MATERIALS & METHOD

Dicyandiamide, Ammonium Chloride, benzylamine , Copper sulphate and all other chemicals used were obtained from commercial sources and employed without further purification.

Physical measurements: Elemental analysis for C, H, S and N were carried out at SAIF, Cochin using a CHNS analyzer (Elementar Vario EL III). UV-Vis-NIR Spectra were recorded on a 5000 UV-Vis-NIR Spectrophotometer, and IR spectra were recorded on an FT-IR spectrophotometer at SAIF, Cochin. The ligand and the corresponding complexes were prepared according to the reported literature methods [6].

Synthesis of Biguanide sulphate [7]:

Biguanide sulphate was prepared by modifying the method reported by Smolka and Friedrich. In this procedure, a mixture of ammonium chloride and Dicyandiamide(C₂H₄N₄) in a 2:1 molar ratio was dried in an oven and then ground thoroughly in a mortar and pestle. The resulting mixture was transferred to a Pyrex beaker and heated with a Bunsen burner. During heating, the mixture was continuously stirred with a glass rod, and the temperature was maintained at 155°C for approximately 10 minutes, until it converted into a molten mass. This molten mass was poured into a large volume of water and then treated with Cuprammonium sulphate, immediately yielding a rose red precipitate of copper biguanide sulphate. The precipitate was collected on a Buchner funnel and washed thoroughly with the cold water until the filtrate become colorless. The moist copper biguanide sulfate was then decomposed with a cold 10% H₂SO₄ solution, affording a blue solution that upon standing in the cold, deposited large crystals of biguanide sulphate.

Synthesis of Dibenzylamine bisbiguanidinium Cobalt(III) Sulphate

The Cobalt dibenzylamine dibiguanide sulphate was synthesized by oxidation neutralization of Cobalt hydroxide precursor using dilute sulphuric acid under aerobic conditions . Exactly 1gram of Cobalt (III) dibenzylamine dibiguanide hydroxide was dissolved in 50ml distilled water in a 250 ml Erlenmeyer flask by gentle heating and stirring, forming a clear pink solution. The mixture was cooled to room temperature and aerated vigorously with the aeration flask for 30 minutes to initiate partial auto oxidation. Dilute sulphuric acid was added dropwise over 20 minutes while maintaining aeration and stirring a few drops of 3% H₂O₂ were added to ensure complete oxidation to cobalt as evidenced by the solution turning stable pink . The PH stabilized at 4.5 to 5.5 , avoiding ligand protonation. Stirring continued under air for two hours, the solution was filtered hot to remove traces of unreacted material concentration under vacuum at 45°C. The pink microcrystals were filtered, washed with ice cold water and dried over CaCl₂ in vacuum. Yield was 0.88g.

RESULTS AND CONCLUSION

A. Physio-Chemical Analysis

The synthesis of biguanide afforded a yield of 3gm when 8gm of dicyandiamide and 16gm of ammonium chloride were fused. The ligand is white in color whereas the corresponding complex is pink. The prepared complex is stable in air. The melting point of the ligand is 231-232°C and its molar mass is 235.24 g.mol⁻¹.

Table I

Physio-chemical properties of synthesized ligand and complex

SL.No.	Properties	Ligand value	Complex value
1.	Name	Biguanide sulphate	Dibenzylamine bisbiguanidinium Cobalt sulphate
2.	Color	White crystalline	Pink
3.	Physical state	Crystalline solid	Crystalline solid
4.	Yield	3 gm	0.88 gm
5.	Stability	Stable in Air	Stable in Air
6.	Recrystallization solvent	Distilled water	Ethanol

B. Elemental Analysis

Elemental analysis provides information on the Carbon, Nitrogen, Hydrogen and Oxygen content and was carried out using an Elementar Vario EL III instrument. The metal content was determined by the gravimetric method.

Table II

Elemental content of ligand and complex

SL. No		N	H	O	C	M
1.	Ligand	29.9%	4.3%	31.7%	10.21 %	-
2.	Complex	15.35%	4.41 %		39.47 %	6.46 %

C. FT-IR Spectral Analysis

The FT-IR spectrum of the biguanide ligand was recorded using a Nicolet iS50 FT-IR instrument in the frequency range of 4000-450cm⁻¹. The IR spectral frequency bands of the free biguanide ligands are listed in the Table III

Table III

FT-IR Spectral band positions of synthesized biguanide ligand

WAVENUMBER (in cm ⁻¹)	ASSIGNMENT
3389 cm ⁻¹	NH ₂ amine
929 cm ⁻¹	N-H deform
769 cm ⁻¹	N-H wagging
1069 cm ⁻¹	C-N sym stretching
1626 cm ⁻¹	C=N sym stretching

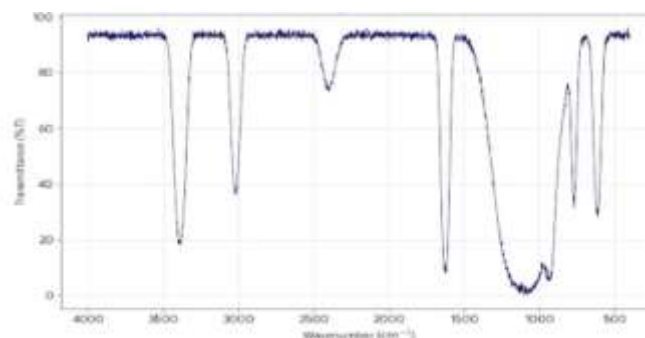


Fig 2: FT-IR Spectra of Biguanide Sulphate

The FT-IR spectrum of Cobalt dibenzylamine dibiguanide sulphate shows prominent peak leveled approximately as 980 cm⁻¹, 1104 cm⁻¹, 1133 cm⁻¹ and 1180 cm⁻¹. The 900 cm⁻¹ to 1200 cm⁻¹ region is a characteristics of SO₄²⁻ vibrations in the coordination compounds. These align with the standard sulphate bands often split due to coordination mode lowering tetrahedral geometry. The table IV below assigns them for metal sulphate complexes.

Table IV

FT-IR Spectra Of synthesized metal complex

Peak (cm ⁻¹)	Vibration mode
980 cm ⁻¹	v ₁ Symmetric SO ₄ ²⁻ stretch
1104 cm ⁻¹	v ₃ Asymmetric stretch
1133 cm ⁻¹	v ₃ Asymmetric stretch
1180 cm ⁻¹	v ₃ Asymmetric stretch

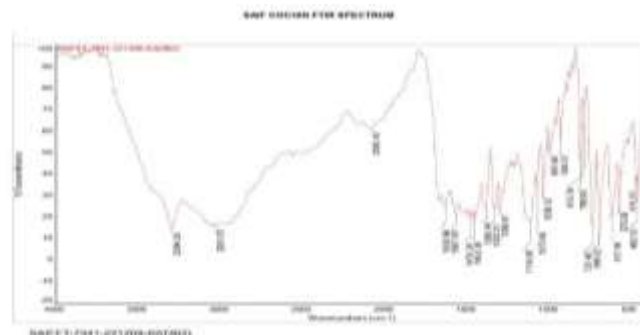


Fig.3: FT-IR Spectra of Metal Complex

D. UV-Vis Spectral Analysis

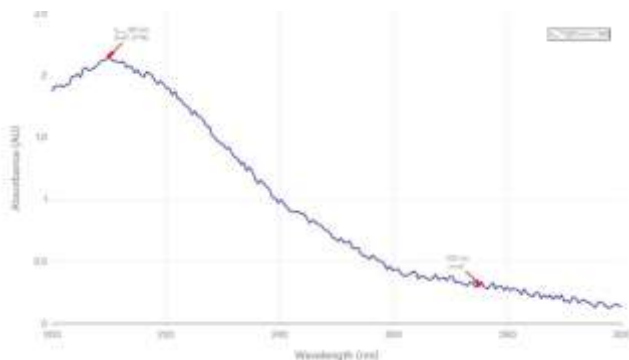


Fig 4: UV-Vis Spectra of Biguanide Sulphate

Biguanide sulphate UV spectrum shows intense $\pi \rightarrow \pi^*$ transition from guanidinium C=N chromophore around 210-230 nm and weaker $n \rightarrow \pi^*$ bands near 270-290 nm due to delocalized lone pairs.

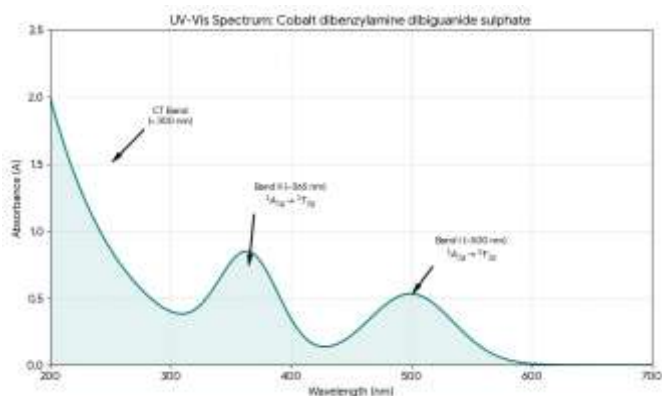


Fig 5: UV-Vis Spectra of Metal Complex

Table V

UV-Vis Spectra of Cobalt dibenzylamine dibiguanide sulphate

Band label	Wavelength	Assignment
CT band	<300 nm	Charge transfer
Band II	~365 nm	$^1A_{1g} \rightarrow ^1T_{2g}$
Band I	~500 nm	$^1A_{1g} \rightarrow ^1T_{1g}$

3. CONCLUSIONS

On the basis of a stoichiometric, spectral studies (IR and UV Spectra) and physiochemical properties. Octahedral structure have been proposed for Cobalt dibenzylamine dibiguanide sulphate Complex. The proposed structure of the Cobalt dibenzylamine dibiguanide sulphate Copper ethylene dibiguanide sulphate is as follows

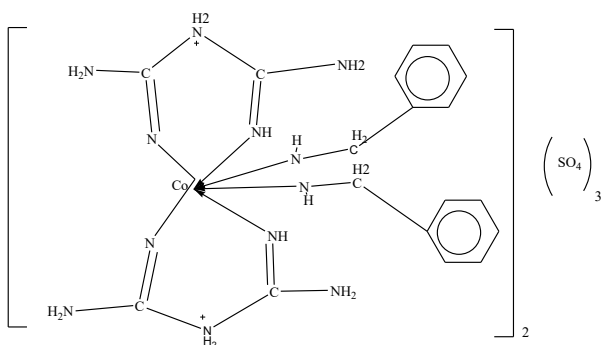


Fig 6: Structure of Cobalt ethylene dibiguanide sulphate

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