



Synthesis And Spectral Studies of isomeric Copper(II) Complex Salts With Phenylbiguanide [$\text{PhBigH}^+/\text{C}_8\text{H}_{11}\text{N}_5$]

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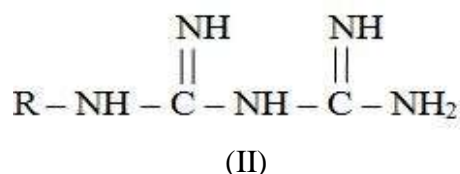
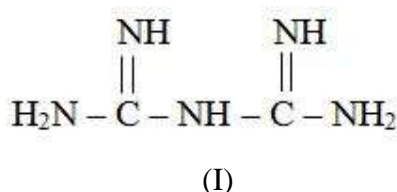
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Abstract: Isomeric cis trans bis(phenylbiguanidinium)copper(II) salts of composition $[\text{Cu}(\text{PhBigH}^+)_2]\text{X}_2 \cdot n\text{H}_2\text{O}$ where $\text{PhBigH}^+ = \text{C}_8\text{H}_{12}\text{N}_5$, $\text{X} = \text{OH}^-, \text{Cl}^-, \text{Br}^-$ or I^- and $n = 1, 2$ or 6 have been isolated and characterized from the studies of their colour, magnetic susceptibilities, infrared vibrations and electronic absorption spectra. The cis variety is isolated at lower temperature and in moderately alkaline medium ($\text{pH} \sim 10-12$) which is transformed to stable trans form by boiling in neutral aqueous medium.

Keyword: Phenylbiguanide, Magnetic susceptibilities and Absorption spectra

I. Introduction

The isomeric authentic cis trans oriented copper(II) complexes with biguanide and substituted biguanides have not appeared in literature so far, though considerably huge bulk of copper(II) complexes with biguanide(I), substituted biguanide(II) and with related ligands have been reported so far¹⁻³. In present communication, we report the preparation and characterization of isomeric cis - trans complex salts of copper(II) with phenyl biguanide(II where $\text{R} = \text{C}_6\text{H}_5^-$) in stable form.



II. Materials and Methods

Materials: Aniline ($\text{C}_6\text{H}_5\text{NH}_2$), Cyanoguanidine (dicyandiamide) and all other chemicals and solvents were commercially available (E. Merck, Fluka and Sisco International) and were used as received.

Physical Measurements: The results of C, H and N were obtained from Central Drug Research Institute, Lucknow. The anions and metal ions were estimated by standard methods⁴. The electrical conductance, magnetic susceptibility were measured as reported earlier¹.

The result of U-V spectra were recorded on VARIAN MODEL 2390 UV-VIS-NIR spectrophotometer and the IR spectra were recorded on JASCO FT/IR – 5300 spectrophotometer in KBr disc at Department of Chemistry (CISC), Banaras Hindu University, Varanasi – 221005.

(A) Synthesis of ligand

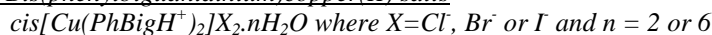
Phenylbiguanide hydrochloride ($\text{C}_8\text{H}_{12}\text{N}_5\text{Cl}$), m.p. $244 - 256^\circ\text{C}$ was prepared by refluxing aniline hydrochloride and dicyandiamide in aqueous medium and crystallized the product with ethanol⁵.

I. cis – Bis(Phenylbiguanidinium) Copper(II) hydroxide hydrate $\text{cis}[\text{Cu}(\text{PhBigH}^+)_2](\text{OH})_2 \cdot \text{H}_2\text{O}$

About one millimole of AR Copper(II) Sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was dissolved in 50ml hot water and treated with 2 millimole of hot aqueous solution of Phenylbiguanide hydrochloride ($\text{C}_8\text{H}_{12}\text{N}_5\text{Cl}$). The resulting solution was slowly treated with concentrated KOH solution with constant stirring, when light rose

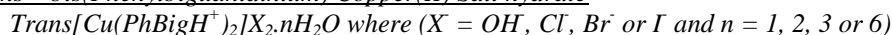
coloured complex base separated as voluminous precipitate. The precipitate was filtered on a buchner funnel. This was washed thoroughly with cold water, ethanol and finally dried in air.

II. *Cis-Bis(phenylbiguanidinium)copper(II) salts*



The complex salts $Cu(PhBigH^+)_2]X_2.nH_2O$ where $X = Cl, Br$ or I and $n = 2$ or 6 were obtained by neutralizing freshly prepared complex base with appropriate haloacids in cold water (pH ~ 5-6). The cold solution on evaporation in air gave light rose red precipitate.

III. *Trans – bis(Phenylbiguanidinium) Copper(II) Salt hydrate*



When cis complex base was suspended in water and refluxed for 1 hour on steam bath gave deep rose red precipitate gradually. It was filtered with water and dried in air.

III. Result and discussion

The elemental analysis of complexes correspond to the formulae given in Table – I.

Table – 1. Microanalytical data of the metal complexes

Sl	Complex	Colour	Microanalytical data(%) : Calculated (found)					
			M	C	H	N	H ₂ O	X ⁻ = anions
1.	Cis [Cu(PhBigH ⁺) ₂](OH) ₂ .H ₂ O	Cis- light rose	13.55 (13.48)	40.89 (40.96)	5.54 (5.56)	29.82 (29.93)	3.83 (3.86)	-
	Trans [Cu(PhBigH ⁺) ₂](OH) ₂ .H ₂ O	Trans- Rose Red	13.55 (13.50)	40.89 (41.00)	5.54 (5.52)	29.82 (29.96)	3.83 (3.79)	
2.	Cis [Cu(PhBigH ⁺) ₂]Cl ₂ .6H ₂ O	Cis – light pink	10.66 (10.70)	32.18 (32.21)	5.69 (5.72)	23.50 (23.75)	18.10 (18.04)	11.90 (11.86)
	Trans [Cu(PhBigH ⁺) ₂]Cl ₂ .6H ₂ O	Trans – rose red	11.70 (11.75)	35.39 (35.41)	5.16 (5.16)	25.80 (27.83)	9.95 (9.60)	13.08 (13.72)
3.	Cis [Cu(PhBigH ⁺) ₂]Br ₂ .2H ₂ O	Cis-Light pink	10.28 (10.29)	35.39 (35.40)	4.24 (4.26)	22.80 (22.89)	5.87 (5.88)	26.08 (26.30)
	Trans [Cu(PhBigH ⁺) ₂]Br ₂ .2H ₂ O	trans- rose red	10.28 (10.27)	35.39 (35.42)	4.24 (4.27)	22.80 (22.86)	5.87 (5.89)	26.08 (26.31)
4.	Cis [Cu(PhBigH ⁺) ₂]I ₂ .2H ₂ O	Cis- pink	8.98 (9.00)	27.14 (27.19)	3.67 (3.68)	19.77 (19.87)	5.09 (5.11)	35.88 (35.98)
	Trans [Cu(PhBigH ⁺) ₂]I ₂ .2H ₂ O	trans- brick red	8.98 (9.01)	27.14 (27.18)	3.67 (3.66)	19.77 (19.89)	5.09 (5.10)	35.88 (35.99)

Similar to biguanide and ethylenediamine, phenylbiguanide also coordinates as chelate molecule and forms bis chelates with bivalent metal ions⁵, The complex salts and base of copper(II) with phenylbiguanide have been obtained in two colour modifications and they have been assigned as cis and trans isomers. The analytical results of complex bases and salts show that they contain water of crystallization. The aqueous solutions of complex base (both isomers) are conducting and the qualitative value of equivalent conductance at 30 °C was found to be (≈ 120) indicating the base to be ionic. The cis variety of complex base and salts in solution gradually change their colour to deep rose red which is trans form. Thus the recrystallisation as well as preparation of cis complex salt was always preferred below 35 °C. The complex salts or bases of cis isomer when boiled at 100 °C for one to two hours or standing them for several days, qualitative conversion to trans isomer occurs. The change in stereochemistry of cis and trans isomer was accompanied by retention of water of crystallisation. The cis chloride is [Cu(PhBigH⁺)₂]Cl₂.6H₂O where as trans form contains three water molecules. The retaining of different quantity of H₂O molecule is probably due to different crystal symmetry and aggregate formation. The complex salts, however loses all water molecule associated with the complex molecule on slow heating. The loss of water molecule on slow heating is accompanied without change in colour lustre as well as morphology of the molecule. This suggests that water molecule are not bonded to central copper(II) rather these are attached as water of crystallization or bonded with hydrogen bonding separately with N-H nitrogen of coordinated biguanide. The quantitative value of equivalent conductance of complexes in very dilute solution is

in the range of 90-110 $\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$. This value supports ionic nature of anions and the complex species are probably mononuclear. The solubility of the complex salt in polar and nonpolar solvents like methanol, ethanol, acetone, chloroform, benzene and dioxane were examined. The complex salts do not dissolve in chloroform and benzene. The insolubility of complex salts or base in nonpolar medium indicate that complex species are ionic in nature. The Jahn Teller distortion present in copper(II) atom (d^9 system) prohibits the formation of regular octahedral complexes for Cu(II). The biguanides and almost all substituted biguanides form square planar complexes with phenylbiguanide (II where $R = C_6H_5$) and other substituted biguanide (II) have similar donor sites and are capable of forming planar isomeric bis chelates with bivalent copper(II) and nickel(II)^{2,3,5}. In substituted biguanides(II) the substituents R enables the coordinated biguanide to arrange in cis and trans position and provides the probability of isolation of cis and trans planar bis chelate (fig III) for Cu(II). The trans isomers have been isolated in stable form and the formation is irreversible. Probably the steric reason of phenyl group causes the higher stability of trans isomer in comparison to cis isomer.

Electronic Spectra

The complexes of Phenylbiguanide show one broad band near 510-540 nm attributed to ${}^2B_{1g} \longrightarrow {}^2B_{2g}$ transition^{6,7}. The strong absorption band about 280 nm in almost all copper (II) complex salts are attributed to charge transfer transition. As the d-d transition is broad, therefore no distinct difference in electronic band position could be noticed between cis and trans isomers. However the electronic transition of cis isomer has remarkably high ϵ_{max} value than the trans which is the usual feature to distinguish cis isomer from the trans one⁸.

IR Spectra

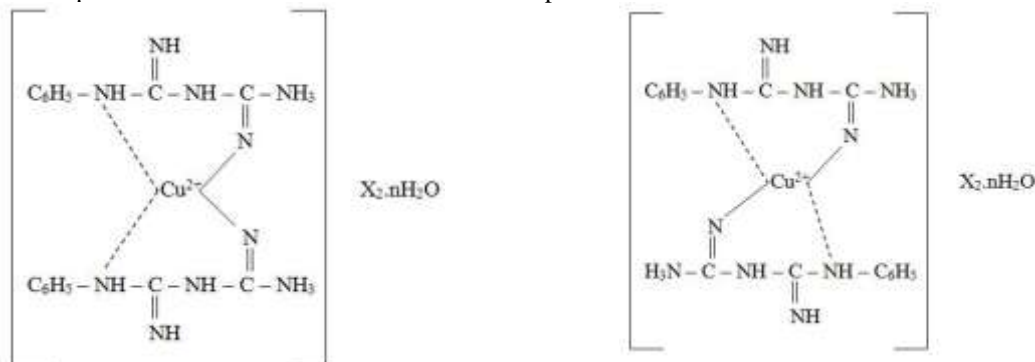
The I.R. spectrum of ligand and their complexes display sharp ν (NH_2) and ν (H-OH) vibration at 3460 cm^{-1} to 3328 cm^{-1} and 3180 cm^{-1} – 3240 cm^{-1} . The absence of large broadness of ν (NH_2) and ν (H-OH) vibration indicated separate hydrogen bonding⁹.

The $\nu(\text{C}=\text{N})$ of biguanide molecule at 1645 cm^{-1} in free phenylbiguanide hydrochloride ($\text{PhBigH}^+\text{Cl}^-$). The $\nu(\text{C}=\text{N})$ frequency in trans isomers is greater than cis isomers. The phenyl ring $\nu(\text{C}=\text{C})$ band is not affected in its complexes. The (NH_2) bending band of free ligand observed at 1531 cm^{-1} is not affected appreciably indicating that terminal NH_2 is not involved in coordination rather it is present as $-\text{NH}_3^+\text{Cl}^-$ in free ligand. The δ (NH) of ligand observed at 1491 cm^{-1} and the band is shifted to higher frequency in complexes indicating the coordination of NH nitrogen in all the complexes. Due to chelate ring formation the $\nu(\text{C}-\text{N})$, $\nu(\text{N}-\text{C})$, $\nu(\text{C}_6\text{H}_5-\text{C})$ and $\delta(\text{NH})$, rocking NH_2 and various deformation and out of plane phenyl ring vibrations are affected appreciably and observed at different positions depending upon the nature of anions. In case of cis complexes the shift of $\nu(\text{C}=\text{NH})$ and $\delta(-\text{NH})$ band is much lower than the trans isomer^{9,10}. The $\delta(\text{NH})$ of cis complexes appears as medium band at lower wave number while in trans complexes, it is raised to higher frequencies.

The I.R. spectrum was not recorded in far I.R. region hence the $\nu(\text{Cu}-\text{N})$ vibration not observed in all complex salts. But in case of cis bromide a medium band located at 410 cm^{-1} and trans bromide at 420 cm^{-1} are tentative assignment of (Cu-N) stretching band¹². In case of cis iodide complex salt a medium band located at 430 cm^{-1} and trans salt 434 cm^{-1} assignable to the (Cu-N) stretching band. The major difference in I.R. vibrations of cis from the trans isomers are sharpness of $\nu(\text{C}=\text{N})$, $\nu(\text{NH})$ and $\delta(\text{NH})$ vibrations. The trans displays sharp band while these vibrations are relatively broad in cis form.

IV. Conclusion

The spectral studies (I.R. and electronic absorption) and physic-chemical properties of complexes confirm that the complexes are planar and have cis-trans attachment in complexes as shown below:-



Cis-bis (Phenylbiguanidinium) Copper(II) halide hydrate (X = Cl⁻, Br⁻, I⁻ and also OH⁻)

Trans-bis (Phenylbiguanidinium) Copper(II) halide hydrate (X = Cl⁻, Br⁻, I⁻ and also OH⁻)

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