



Synthesis and Spectral Studies of Complexes of Cr (III) and Cu (II) Complexes with Hexamethylenedibiguanide [$\text{Hm}(\text{BigH}^+)_2/\text{C}_{10}\text{H}_{24}\text{N}_{10}$]

Dr. (Mrs.) Bina Rani¹ and Dr. R.K Prasad²

¹Department of Chemistry, Magadh Mahila College, Patna University, Patna-800001, Bihar, India

²Department of Chemistry, Patna Science College, Patna University, Patna-800005, Bihar, India

Abstract: Cu(II) complexes of hexamethylenebiguanide and Cr(III) complexes of hexamethylenebiguanide have been prepared and characterized from elemental analysis, electrical conductance measurement, magnetic susceptibility values and studies of UV and infrared spectra. Cr(III) complexes have been suggested to possess octahedral and Cu (II) complexes that resembles with square planar geometry.

Keywords: structural studies, hexamethylenebiguanide, Cr(III) and Cu(II) complexes.

I. INTRODUCTION

In previous communication^{1,2}, we have reported the complex of Ni(II) and Co(III) with hexamethylenebiguanide [$\text{hm}(\text{BigH}^+)_2/\text{C}_{10}\text{H}_{24}\text{N}_{10}$]. The complexes of this ligand with some bivalent metal ions have appeared long back³. In present paper we are reporting the preparation and structural characterization of the complexes formed by Cr(III) and Cu(II) metal ions with the same ligand.

A large number of substituted biguanides have been prepared and their complexes with various transition metal ions have been investigated and reviewed^{4,5}. The donor ability and mode of bonding of the biguanides have been discussed by various workers⁶⁻²⁰. The unusual stability of biguanide complex have been explained on the basis of aromaticity in the chelate ring formed by metal ions⁶.

Hexamethylenebiguanide(I) is structurally similar to ethylenedibiguanide(II) and piperazinedibiguanide (III) whose donor behavior has been investigated earlier²⁰.

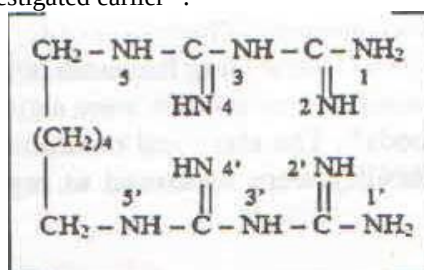


Figure 1

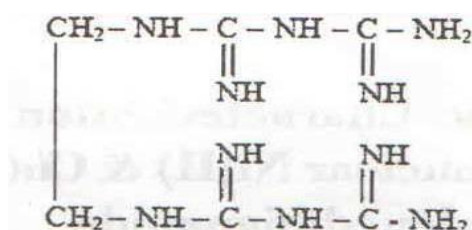


Figure 2

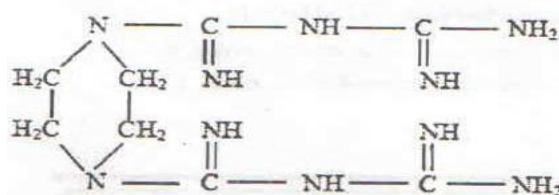


Figure 3

In case of Hexamethylenebiguanide (I) the donor nitrogen atoms are separated apart by twelve atoms whereas in case of ethylenedibiguanide (II) and piperazinedibiguanide (III) by eight atoms. Thus, it is expected that there will be some potential difference in the chelating ability of $\text{hm}(\text{BigH}^+)_2$ from those of ethylenedibiguanide (II) and piperazinedibiguanide (III). Thus keeping this point in view, the complexes of some transition metals with Hexamethylenebiguanide (I) i.e. $\text{hm}(\text{BigH}^+)_2$ have been studied here.

II. EXPERIMENTAL

Materials: Hexamethylenediamine, dicyandiamide and all other chemicals and solvents were commercially available (E. Merck, Fluka and Sisco International) were used and received.

Physical measurement : The results of carbon, hydrogen and nitrogen were obtained from Central Drug Research Institute, Lucknow. The anion and metal ions were estimated by standard methods. The electrical conductance, magnetic susceptibility were measured as reported earlier¹.

The result of UV 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.

Synthesis of the ligand: Hexamethylenebiguanide Acid Sulphate [$\text{hm}(\text{BigH}^+)_2$]. $2\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ was synthesized by the method reported earlier³.

A. Hexamethylenebiguanidiniumcopper(II) hydroxide monohydrate [$\text{Cu}\{\text{hm}(\text{BigH}^+)_2\}(\text{OH})_2 \cdot \text{H}_2\text{O}$]

An aqueous solution of Hexamethylenebiguanide Acid Sulphate (2.8 gm in 60 ml) was made strongly alkali ne by NaOH(4N) and to this was added dropwise an ammoniacal copper(II) sulphate (1.25 gm in 20 ml 1:1 ammonia) when a light rose-violet product was separated gradually. The product was digested on the water bath, filtered and washed till the precipitate was free of sulphate. It was finally washed with alcohol and dried over KOH. The substance slowly becomes crystalline with time.

The micro-analytical data and colour of [$\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_{10})\}(\text{OH})_2 \cdot \text{H}_2\text{O}$] is given below

Complex		Microanalytical data(%):Calculated(found)						X=anions
		colour	Cu	C	H	N	H ₂ O	
[$\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_{10})\}(\text{OH})_2 \cdot \text{H}_2\text{O}$]	Theoretical	Rose violet	15.90	30.04	7.0	35.04	4.50	-
	Obtained		(15.83)	(29.94)	(6.9)	(35.0)	(4.60)	-

B. Hexamethylenebiguanidiniumcopper(II) chloride tetrahydrate [$\text{Cu}\{\text{hm}(\text{BigH}^+)_2\}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$]

Hexamethylenebiguanidiniumcopper(II) chloride was obtained as a rose red crystalline mass by digesting the hexamethylenedibiguanidinium copper(II) hydroxide with ammonium chloride solution on the water bath till the evolution of ammonia has ceased.

Complex		Microanalytical data(%):Calculated(found)						X=anion
		colour	Cu	C	H	N	H ₂ O	
[$\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_{10})\}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$]	Theoretical	Rose Red	12.95	24.46	6.5	28.86	14.68	14.47
	Obtained		(12.92)	(24.13)	(6.0)	(28.51)	(14.08)	(14.20)

C. Hexamethylenebiguanidiniumcopper(II) sulphate tetrahydrate [$\text{Cu}\{\text{hm}(\text{BigH}^+)_2\}\text{SO}_4 \cdot 4\text{H}_2\text{O}$]

The complex sulphate was obtained as above by refluxing the base with ammonium sulphate solution.

Complex		Microanalytical data(%):Calculated(found)						X=anion
		color	Cu	C	H	N	H ₂ O	
[$\text{Cu}(\text{C}_{10}\text{H}_{24}\text{N}_{10})\}\text{SO}_4 \cdot 4\text{H}_2\text{O}$]	Theoretical value	Rose Violet	12.32	23.28	6.2	27.16	13.96	18.63
	Obtained		(12.58)	(23.33)	(5.9)	(27.65)	(13.81)	(18.81)

D. Tris(hexamethylenedibiguanidium)dichromium(III) hydroxide hydrate [$\text{Cr}_2\{\text{hm}(\text{BigH}^+)_2\}_3(\text{OH})_6 \cdot 1.5\text{H}_2\text{O}$]

A solution of hexamethylenebiguanide Acid Sulphate (4 gm in 200 ml water) was made strongly alkaline with (4N) NaOH solution and warmed on a water bath. To this alkaline solution was added dropwise with constant

stirring, a solution of chrome alum (2 gm), taking care that all the chromium combined to give a red solution before any fresh addition was made. The dark red solution soon deposited a red violet flocky mass. After half an hour of digestion, the mixture was cooled in ice with occasional scratching of the sides of the beaker, when the flocky mass changed to a crystalline product. The rose-violet crystals were filtered, washed first with water then with alcohol and finally dried over KOH.

Complex		color	Microanalytical data(%):Calculated(found)					
			Cu	C	H	N	H ₂ O	X=anion
[Cr ₂ (C ₁₀ H ₂₄ N ₁₀) ₃](OH) ₆ .15H ₂ O	Theoretical	Rose Violet	9.58	33.17	7.86	38.71	2.49	-
	Obtained		(9.54)	(33.21)	(7.60)	(38.41)	(2.51)	-

E. Tris(hexamethylenedibiguanidium)dichromium(III) Chloride hydrate

[Cr₂{hm(BigH⁺)₂}₃]Cl₆.4.5H₂O

The hexamethylenedibiguanidium-dichromium (III) chloride hydrate was obtained by digesting the Tris(hexamethylenedibiguanidium) dichromium hydroxide hydrate with ammonium chloride

Complex		color	Microanalytical data(%):Calculated(found)					
			Cu	C	H	N	H ₂ O	X=anion
[Cr ₂ (C ₁₀ H ₂₄ N ₁₀) ₃]Cl ₆ .4.5H ₂ O	Theoretical	Rose Violet	8.32	28.80	6.48	33.60	6.48	17.04
	Obtained		(8.30)	(28.78)	(6.49)	(33.58)	(6.50)	(17.02)

III. RESULTS AND DISCUSSIONS

Hexamethylenedibiguanide sulphate contains ten nitrogen atoms but only two nitrogen atoms of each biguanide fragment having five nitrogen atoms (N₂&N₄) are suitably situated to form six membered chelate ring with metal atoms and both the biguanides fragments coordinate with metal atoms and the ligand behaves as a quadridentate molecules.

The complexes [Cu{hm(BigH⁺)₂}]₂.n H₂O (X=OH; Cl or ½ SO₄²⁻) are paramagnetic and their magnetic moment values occur in the range 1.79-1.86 B.M at room temperature. Trivalent chromium (III) complexes are paramagnetic having magnetic moment values in the range 3.72-3.69 BM indicating oxidation state +3 of chromium. The chelates of bivalent cation [M{hm(BigH⁺)₂}]₂.n H₂O dissolve in hot water but these complexes have poor solubility in cold water. The dinuclear chelate of Cr(III) has extremely low solubility in cold water, but dissolves to some extent in boiling water. The poor solubility of Cr(III) chelates substantiates the binuclear structure of Cr(III) complexes.

The aqueous solutions of complexes are ionic and conduct electricity. The qualitative value of molar conductance of [Cu{hm(BigH⁺)₂}]₂.n H₂O (X= Cl⁻ or ½ SO₄²⁻) in aqueous solution at 30° ± 0.5 occurs in the range of 190-210 ohm⁻¹mol⁻¹cm² which clearly suggested ionic character of the complexes. The Cr(III) complex are also conducting in aqueous medium and qualitative molar electrical conductance value at room temperature is 450 ohm⁻¹mol⁻¹cm² suggesting the ionic nature of [Cr₂{hm(BigH⁺)₂}₃]Cl₆.4.5H₂O. The complexes are insoluble in benzene and chloroform but partially dissolve in ethanol and methanol due to the polar character of solvents and bulky hexamethylene part of chelate ring.

The electronic absorption spectra of copper (II) and chromium (III) complexes show medium absorption bands in the visible region. The low value of λ_{max} indicated the d-d transition in complexes and d-d bands are not enveloped in charge transfer transition or ligand molecule absorption of chelate molecule.

Electronic absorption spectra of chromium (III) complexes show three electronic transition in visible and ultraviolet region located at 490-500, 375-380 and 260 nm (strong) assignable to

A_{2g} → ⁴T_{2g}, ⁴A_{2g} → ⁴T_{2g} and charge transfer transition^{23,24}

The electronic absorption spectra of copper (II) complexes in aqueous medium shows well resolved symmetrical bands at 500 nm and strong absorption near 310 and 270 nm. The symmetrical band at 500 nm is attributed to ²B_{1g} → ²B_{2g} as four coordinated square planar field.

The other transition expected from ²B_{1g} → ²E_g occurs in ultraviolet region and is generally obscured. The electronic absorption band at 310 and 290 cm⁻¹ are attributed to charge transfer transition.

IR spectra: The free ligand and complexes display broad and strong IR band at 3450-3250 cm⁻¹ which attributed for hydrogen bonded H₂O or OH group. The strong and broad IR band located at 3213 cm⁻¹ in free ligand is assigned < (NH₂) and < (OH) vibrations. The free ligand displays < (CH₂) vibrations²⁵⁻²⁷ as weak and sharp

band at 2934 cm^{-1} . The free ligand displays $\nu(\text{CH}_2)$ vibrations as weak and sharp band at 2934 cm^{-1} . The band at 1693 cm^{-1} is attributed to (NH_3^+) vibration whereas 1655 cm^{-1} is assigned to (NH_2) or (NH) vibrations. The (NH) stretch usually occurs in the order of increasing electron cloud at nitrogen atom.

The IR band at 1552 cm^{-1} is also assigned to $\nu(\text{C}=\text{N})$. The IR band at 1469 cm^{-1} is attributed to $\nu(\text{CH}_2)$ and 1390 cm^{-1} due to (NH_2) vibrations. The $\nu(\text{CH}_2)$ and $\nu(\text{C}-\text{N})$ of ligand (1161 cm^{-1}) is not affected in its complexes but observed with reduced intensity. In free ligand the broad and strong IR band at 1070 cm^{-1} attributed to ionic $\text{SO}_4^{2-}(\nu_3)$ vibrations. The IR bands at 1041 cm^{-1} attributed to $\text{SO}_4^{2-}(\nu_1)$ vibration. The ligand also displays a medium and sharp band at 609 cm^{-1} attributed to $\nu_4(\text{SO}_4^{2-})$ vibration.

The IR spectra of complex halide and complex bases of Cu(II) and Cr(III) complexes shows the absence of IR vibrations associated with sulphate group. The complex sulphate $[\text{Cu}\{\text{hm}(\text{BigH}^+)\}_2]\text{SO}_4 \cdot 4\text{H}_2\text{O}$ shows the characteristic of ionic sulphate molecule, sharp broad band at 1112 cm^{-1} and 617 cm^{-1} for copper. The IR spectrum of complexes do not show the presence of coordinated water molecule as (H_2O) is absent near $700\text{--}660\text{ cm}^{-1}$.

The complex bases $[\text{Cu}\{\text{hm}(\text{BigH}^+)\}_2](\text{OH})_2 \cdot \text{H}_2\text{O}$ show a strong band at 1091 cm^{-1} suggesting the presence of $\nu(\text{OH})$ of uncoordinated (OH) molecule. In finger print region of IR spectra of complex show all characteristic of IR vibrations of $(\text{C}=\text{N})$, NH , NH_2 and OH group. The complex $[\text{Cr}_2(\text{C}_{10}\text{H}_{24}\text{N}_{10})_3](\text{OH})_6 \cdot 1.5\text{H}_2\text{O}$ and $[\text{Cr}_2(\text{C}_{10}\text{H}_{24}\text{N}_{10})_3]\text{Cl}_6 \cdot 4.5\text{H}_2\text{O}$ shows the absence of SO_4^{2-} stretching bands indicating removal of SO_4^{2-} by halide or hydroxide group. The base shows band at 1234 cm^{-1} attributed to (OH) band associated with strong hydrogen bonded OH group. In lower region the IR bands observed at 520 cm^{-1} and 420 cm^{-1} in Cr(III) complex are attributed to Cr-N stretches. The band at 474 cm^{-1} and at 447 cm^{-1} attributed due to Cu-N stretching in Cu(II) complexes.

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