

ISSN: 2350-0328

International Journal of Advanced Research in Science, Engineering and Technology

Vol. 3, Issue 5 , May 2016

# Structural and Magnetic Aspects of the Complex of Mn<sup>IV</sup> with Hexamethylene dibiguanide (C<sub>10</sub>H<sub>24</sub>N<sub>10</sub>)

Divya Singh, Bina Rani, Sanober Jahan, R.K. Prasad

Department of Chemistry, Magadh Mahila College, Patna University, Patna-800001, Bihar, India Department of Chemistry, Patna Science College, Patna University, Patna-800005, Bihar, India

**ABSTRACT**: Complex of  $Mn^{IV}$  with hexamethylene dibiguanide  $\left[Hm\left(BigH^{+}\right)_{2}\right]$  of composition  $\left[Mn\left(C_{10}H_{24}N_{10}\right)_{2}\left(OH\right)_{2}\right]\left(OH\right)_{2}\Box H_{2}O$  have been prepared and characterized from the studies of electronic absorption spectra, infrared vibrations and magnetic susceptibility measurements. These studies suggest an octahedral geometry for  $Mn^{IV}$  complex.

KEYWORDS: Manganese (IV), Hexamethylene dibiguanide

## I. INTRODUCTION

Hexamethylene dibiguanide sulphate  $\left[ \text{Hm} \left( \text{BigH}^{+} \right)_{2} \right] \text{SO}_{4} \square \text{H}_{2} \text{O}$  behaves as a quadridentate ligand and its complexes with various metal ions are known<sup>1</sup>.

$$\begin{bmatrix} (4) \\ CH_2 - NH - C - NH - C - NH_3^+ \\ & \| & (3) & \| & (1) \\ (5)NH & (2)NH \end{bmatrix}$$

$$(CH_2)_4 \\ \begin{bmatrix} (5) NH & (2)NH \\ (4) & \| & (3) & \| & (1) \\ CH_2 - NH - C - NH - C - NH_3^+ \end{bmatrix}$$
SO 4. H 2O



The ligand has been found to coordinate with N(2) and N(4) of both the biguanide constituent to form two six membered chelate rings with the metal ion. The complexes of a number of biguanides with different metal ions have been studied extensively.<sup>2,3,4</sup>

A number of Mn<sup>IV</sup> complexes have been prepared. Reddish brown coloured crystals of dihydroxo(ethylenedibiguanide)manganese (IV) hydroxide dehydrate have been also reported<sup>5</sup>. The magnetic moment of dihydroxomanganese (IV) biguanide complexes has found to be in the range 2.0-2.83 B.M. at 30°C which is much

lower than the theoretical value of 3.87 B.M. for manganese (IV).<sup>6.7</sup> The low magnetic moment of the Mn<sup>IV</sup> indicates that there may be metal-metal interactions.



## ISSN: 2350-0328

## International Journal of Advanced Research in Science, Engineering and Technology

## Vol. 3, Issue 5 , May 2016

To study chelating behaviour of quadridentate biguanide, we have prepared and characterized the complex of  $Mn^{IV}$  with hexamethylene dibiguanide.

## II. MATERIALS AND METHODS

Materials: Hexamethylene diamine, Dicyandiamide and all other required chemicals and solvents were commercially available and were used as received.

Preparation of the ligand: The ligand was prepared by the reported method.<sup>8</sup>

# Hexamethylenedibiguanide acid sulphate $\begin{bmatrix} C_{10}H_{24}N_{10}\end{bmatrix} 2H_2SO_4 \Box H_2O$

Hexamethylene diamine (12g; 72% solution), dicyandiamide (16g) and water (100 ml) were refluxed for half an hour. All aqueous solution of copper sulphate (10g) was added to the mixture in small portions at a time and the mixture refluxed for a total period of 3 hours. The rose-violet crystals, that separated, were filtered, dissolved in  $H_2SO_4$  (dil.)

and decomposed with  $H_2S$ . The filtrate from CuS was concentrated (50 ml) on the water bath, cooled and treated with alcohol (150 ml). The colourless crystals of the hexamethylenedibiguanide acid sulphate were filtered and purified by recrystallization from hot water, yield: 16-18g.

FOUND:

 $SO_4 = 38.20\%; N = 27.89\%; H_2O = 3.15\%$  $[C_{10}H_{24}N_{10}]$   $DH_2SO_4$   $H_2Orequires;$ 

 $SO_4 = 38.55\%$ ; N = 28.11%; H<sub>2</sub>O = 3.61%

Preparation of the complex:

## Dihydroxo manganese (IV) hexamethylenedibiguanidinium hydroxide<sup>8</sup>:

Hexamethylenedibiguanide sulphate (5g) was dissolved in water (70 ml) containing sodium hydroxide (4g). The solution was cooled and then treated with a strong solution of potassium permanganate (0.4g in 30 ml water). The permanganate was first reduced to green manganate and in course of 20 minutes, dark red crystals of the manganese complex separated out. After cooling for another half hour, the compound was filtered through a sintered glass Gooch crucible and washed with cold water. The product was dried in vaccum over  $CaCl_2$ . The substance forms dark red crystals, insoluble in water. It oxidizes ferrous to ferric ion and liberates iodine from KI in acid solution. The substance decomposes on heating at 70°c.

Found: O (active) = 3.54%; Mn= 12.20%; N = 31.35%

$$\left[\mathsf{Mn}\left(\mathsf{C}_{10}\mathsf{H}_{24}\mathsf{N}_{10}\right)_{2}\left(\mathsf{OH}\right)_{2}\right]\!\left(\mathsf{OH}\right)_{2}\Box\mathsf{2}\mathsf{H}_{2}\mathsf{O}\,\mathsf{requires};$$

O (active) = 3.61%; Mn = 12.45%; N = 31.74%

## **III. RESULTS AND DISCUSSIONS**

#### ELECTRONIC SPECTRA

When an aqueous solution of potassium permanganate is added to a strongly basic solution of hexamethylene dibiguanide sulphate dark red crystals of the complex  $\left[ Mn (C_{10}H_{24}N_{10})_2 (OH)_2 \right] (OH)_2 \square 2H_2O$  is obtained. The



## ISSN: 2350-0328 ced Research in Science,

# International Journal of Advanced Research in Science, Engineering and Technology

## Vol. 3, Issue 5 , May 2016

diffuse reflectance spectra of Mn<sup>IV</sup> complex display three absorption<sup>9</sup> bands at 515 nm, 539 nm and 602 nm which may be attributed to  ${}^{4}A_{2g} \longrightarrow {}^{4}T_{1g}$ ,  ${}^{4}A_{2g} \longrightarrow {}^{4}T_{1g}$  and  ${}^{4}A_{2g} \longrightarrow {}^{4}T_{2g}$  transitions in octahedral field. A strong band at 295 nm is attributed to the charge transfer transition.

## IR SPECTRA<sup>10</sup>

The ligand hexamethylene dibiguanide sulphate  $\left[ \text{Hm} \left( \text{BigH}^+ \right)_2 \right] \text{SO}_4 \Box \text{H}_2 \text{O}$  contains = NH, - NH, - NH<sup>3+</sup> and  $\text{SO}_4^{2-}$  groups. The various modes of IR vibrations of = NH, - NH, - NH<sup>3+</sup> and  $\text{SO}_4^{2-}$  groups display IR bands in 3685 to 626 cm<sup>-1</sup> region. The N-H stretching in -NH<sup>3+</sup> group is obtained in the range from 3685 to 3365cm<sup>-1</sup>. Further the peaks 3019.8 cm<sup>-1</sup> and 2400.01 cm<sup>-1</sup> are due to N-H stretching in -NH<sup>+</sup> group. The C=N stretching is observed at 1650.8 cm<sup>-1</sup> and C-N stretching is observed in the range1068.9 to 928.9 cm<sup>-1</sup>. The sulphate group displays a strong band at 1216.2 cm<sup>-1</sup> due to v<sub>3</sub> vibration of  $\text{SO}_4^{2-}$  and a weak band at 626.9 cm<sup>-1</sup> due to v<sub>4</sub> vibration

## of $SO_4^{2-}$ .

The N-H stretching vibration decreases on the formation of complex with metal ions. The IR spectra of complex dihydroxomanganese (IV) hexamethylene dibiguanidium hydroxide shows vibrations of  $-NH_2$  a  $-NH^+$  and v

(-O - H) at 3170 cm<sup>-1</sup> and 3019.68 cm<sup>-1</sup>. The v (C=N) and  $\delta$  (-NH<sub>2</sub>) are observed at 1652 cm<sup>-1</sup>.

The I.R. spectrum was not recorded in far I.R. region hence the  $\nu$  (Mn – N) vibrations were not observed in the complex.

#### **IV. CONCLUSION**

From the spectral studies (I.R. and Electronic absorption) and physico-chemical properties of the complex the probable structure of the complex must be octahedral.

#### V. ACKNOWLEDGEMENT

We are thankful to the teachers and staffs of the Department of chemistry, Magadh Mahila College, Patna University, Patna for their help and cooperation throughout this experiment. We are also thankful to SAIF CDRI Lucknow and STIC Cochin for doing the IR and UV spectral measurements.

#### REFERENCES

- [1] R.K. Prasad, (Mrs) Bina Rani and Divya Singh, AIJRSTEM, Issue 9, Vol. 1, pp77-80, 2015.
- [2] Ray R. K. Prasad, (Mrs) Bina Rani and Dhananjai Singh, J. Indian Chem. Soc., 83, 718, 2006.
  - R.K.Prasad, (Mrs) Bina Rani, Divya Singh and Dhananjai Singh, AIJRSTEM, Issue 8, Vol. 2, pp108-111, 2014.
- [3] R.K.Prasad, (Mrs) Bina Rani, Divya
  [4] P. Ray, Chem. Rev., 61, 313, 1961.
  - a) S. P. Ghosh, R. K. Prasad and (Mrs) Bina Rani, J. Indian Chem. Soc., 80, 912, 914 ; 2003.
  - b) S. P. Ghosh, R. K. Prasad, J. Indian Chem. Soc., 64, 765, 1987,
  - c) S. P. Ghosh, H. M. Ghosh, J. Indian Chem. Soc., 33, 899, 1956,.
  - d) P. Ray and N. R. Sengupta, J. Indian Chem. Soc., 36, 201, 1959.
  - e) S. P. Ghosh and A. I. P. Sinha, J. Indian Chem. Soc., 38, 179, 1961, J. Inorg. Nucl. Chem., 41, 330, 1964.
  - f) T. R. Bera and J. Konar, J. Indian Chem. Soc., 74, 528, 1997.
  - g) S. Ghosh, C. C. Mukhopadhyay, G. S. De and A. K. Ghosh, J. Indian Chem. Soc., 75, 219, 1998.
  - h) Tannistha Roy Barman and G. N. Mukherjee, J. Chem. Sci., **118**, 411, 2006.
  - i) A. Syamal, Chem. Educ. 4, 33, 1987; 5, 26, 1988.
  - j) W. E. Swartz. Jr. and R. A. Afanzo, J. Electron, Spectrose, Relat Phenom., 406, 124, 1974.
  - k) S. N. Nandi and D. Banerjee; Z. Anorg. Allg. Chem., 406, 124, 1974.
  - 1) T. C. Creitz, R. GSell and D. L. Wampler, J. Chem. Soc., Chem. Soc., Chem. Comun. 1371, 1969.
  - m) D. Sen, J. Chem. Soc. (D), 52, 174, 1975.
- [5] Metal and Non-Metal Biguanide Complexes, R.K. Ray and G.B. Kauffman.



ISSN: 2350-0328 International Journal of Advanced Research in Science, **Engineering and Technology** 

## Vol. 3, Issue 5 , May 2016

- [6] P.Ray, Chem Rev., 61, 313, 1961.
- [7] A.Shyamal, J. Sci. Ind. Res., 37, 661, 1958.
  [8] R. L. Dutta, J. Indian Chem., 37, 32, 1960.
- [9] R.S. Banerjee and S. Basu, J. Inorg. Nucl. Chem., 27, 359, 1965.
- [10] K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compound", John Wiley, New York, 1988.