

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.⁸

Hexamethylenedibiguanide acid sulphate $[C_{10}H_{24}N_{10}] \cdot 2H_2SO_4 \cdot H_2O$

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:

$SO_4 = 38.20\%$; $N = 27.89\%$; $H_2O = 3.15\%$

$[C_{10}H_{24}N_{10}] \cdot 2H_2SO_4 \cdot H_2O$ requires;

$SO_4 = 38.55\%$; $N = 28.11\%$; $H_2O = 3.61\%$

Preparation of the complex:

Dihydroxo manganese (IV) hexamethylenedibiguanidinium hydroxide⁸:

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 vacuum 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 $70^\circ C$.

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

$[Mn(C_{10}H_{24}N_{10})_2(OH)_2](OH)_2 \cdot 2H_2O$ 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 $[Mn(C_{10}H_{24}N_{10})_2(OH)_2](OH)_2 \cdot 2H_2O$ is obtained. The



diffuse reflectance spectra of Mn^{IV} complex display three absorption⁹ bands at 515 nm, 539 nm and 602 nm which may be attributed to ${}^4A_{2g} \longrightarrow {}^4T_{1g}$, ${}^4A_{2g} \longrightarrow {}^4T_{1g}$ and ${}^4A_{2g} \longrightarrow {}^4T_{2g}$ transitions in octahedral field. A strong band at 295 nm is attributed to the charge transfer transition.

IR SPECTRA¹⁰

The ligand hexamethylene dibiguanide sulphate $\left[Hm \left(BigH^+ \right)_2 \right] SO_4 \cdot H_2O$ contains =NH, -NH, -NH³⁺ and SO_4^{2-} groups. The various modes of IR vibrations of =NH, -NH, -NH³⁺ and SO_4^{2-} groups display IR bands in 3685 to 626 cm^{-1} region. The N-H stretching in -NH³⁺ group is obtained in the range from 3685 to 3365 cm^{-1} . Further the peaks 3019.8 cm^{-1} and 2400.01 cm^{-1} are due to N-H stretching in -NH⁺ group. The C=N stretching is observed at 1650.8 cm^{-1} and C-N stretching is observed in the range 1068.9 to 928.9 cm^{-1} . The sulphate group displays a strong band at 1216.2 cm^{-1} due to ν_3 vibration of SO_4^{2-} and a weak band at 626.9 cm^{-1} due to ν_4 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 -NH₂, -NH⁺ and $\nu(-O-H)$ at 3170 cm^{-1} and 3019.68 cm^{-1} . The $\nu(C=N)$ and $\delta(-NH_2)$ are observed at 1652 cm^{-1} .

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.
- [3] R.K. Prasad, (Mrs) Bina Rani, Divya Singh and Dhananjai Singh, AIJRSTEM, Issue 8, Vol. 2, pp108-111, 2014.
- [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, Spectrosc, Relat Phenom., **406**, 124, 1974.
 - k) S. N. Nandi and D. Banerjee; Z. Anorg. Allg. Chem., **406**, 124, 1974.
 - l) 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.