



Spectral Characterization of the Complex Compounds of Ni (II) and Cu (II) Metal ions with Piperazinedibiguanide

Divya Singh¹, Bina Rani¹ and R.K. Prasad²

¹Department of Chemistry, Magadh Mahila College,
Patna University, Patna-800 001, Bihar, India

²Department of Chemistry, Patna Science College,
Patna University, Patna-800 005, Bihar, India

Abstract: Complexes of Ni(II) and Cu(II) with Piperazinedibiguanide $[C_8H_{18}N_{10}] \cdot 2H_2SO_4 \cdot 1.5H_2O$ of the molecular composition $[NiPip(BigH)_2]X_2 \cdot nH_2O$ and $[CuPip(BigH)_2]X_2 \cdot nH_2O$ have been prepared and characterized from the studies of IR, UV and magnetic measurements. Magnetic studies shows that the complexes of Ni(II) are diamagnetic and of Cu(II) are paramagnetic. The results of spectroscopic analysis and magnetic studies indicate square planar structure for Ni(II) and Cu(II) complexes.

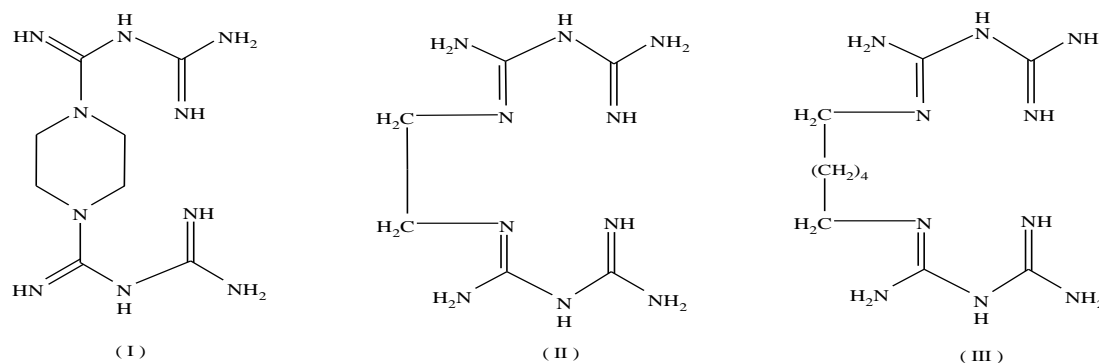
Keywords: Nickel, Copper, Complexes, IR, UV

I. Introduction

Complex compounds of biguanide and substituted biguanide have been studied extensively¹⁻³ as of their high coordination power and medicinal value. Piperazinedibiguanide is a heterocyclic biguanide whose complexes have not been studied much.

Piperazinedibiguanide (I) is structurally similar to ethylenedibiguanide (II) and Hexamethylenedibiguanide (III) whose donor behavior has been investigated thoroughly⁴.

Hexamethylenedibiguanide (III) and ethylenedibiguanide (II) forms stable chelate ring in which these ligands are behaving as quadridentate N – donor ligand (Fig. 1).



Piperazinedibiguanide has been found to act as a quadridentate ligand⁸ it coordinates to the central metal atom like Cu or Ni through four donor N-atoms and thus forms an inner metallic complex of ethylene dibiguanide type. To study the chelating behavior of quadridentate substituted biguanide, we have prepared and characterized the complexes of Cu (II) and Ni (II) with piperazinedibiguanide.

II. Materials and Methods

Materials: Piperazine, Dicyandiamide and all other chemicals required were available commercially and used as such.

Physical Measurements: The results of C, H, S and N were obtained from Central Drug Research Institute, Lucknow. The anions and metal ions were estimated by standard methods⁵⁻⁷. Magnetic properties were measured as reported earlier¹.

The result of U-V spectra were recorded on Carry 5000 UV-VIS-NIR spectrophotometer at SAIF STIC and the IR spectra were recorded on Perkin Elmer at Central Drug Research Institute, Lucknow. And the magnetic measurements (VSM) were done from CIF, IIT Guwahati.

The ligands and the complexes were prepared by the reported method⁸.

Synthesis of Ligand

Piperazinedibiguanide Sulphate $C_8H_{18}N_{10} \cdot 2H_2SO_4 \cdot 1.5H_2O$

Piperazine (4.3g) and dicyandiamide (8.4g) were heated with about 75 ml of water in a conical flask on the water bath for about 3 hours with occasional addition of 5 ml of $CuSO_4$ solution (10g in 30 ml water) at an interval of 20 minutes. To the resulting mixture, a solution of NaOH (2.8g) was added and the heating was continued till the mixture turned red. This was cooled and filtered and the red residue was then decomposed with H_2SO_4 (1:3). The white piperazinebiguanide sulphate separates out, gradually on cooling. This was filtered and washed with cold water until free from copper. The product was then dissolved in ammonia and a little NaOH then the mixture was filtered and acidified with dil. H_2SO_4 (1:1). On cooling, shining white crystals of piperazinedibiguanide sulphate separates out from the solution. These were filtered washed with cold water and dried in air.

Found: N = 29.40%, S = 13.37%

$C_8H_{18}N_{10} \cdot 2H_2SO_4 \cdot 1.5H_2O$ requires:

N = 29.35%, S = 13.41%

Preparation of Complexes

(a) Copper piperazinedibiguanide hydroxide: Piperazinedibiguanide sulphate (4.7g) dissolved in ammonia and a little caustic soda solution (about 20ml of 2N NaOH); was treated with an ammoniacal solution of $CuSO_4$ (1.g) with constant stirring. The precipitate of red violet copper piperazinedibiguanide hydroxide which separated immediately was filtered and washed with cold water till free from sulphate. The product was dried in a dessicator to a constant weight.

Found:

Cu = 15.46%; N = 34.80%; H_2O = 21.97% (by loss at 105°C)

$[CuPip(BigH)_2](OH)_2 \cdot 3H_2O$ requires:

Cu = 15.60%; N = 34.50%; H_2O = 22.10%

The substance forms red violet powder, insoluble in water and alcohol. When heated with solution of ammonium salts it liberates NH_3 . It is readily decomposed by dil. acids.

(b) Copper piperazinedibiguanide chloride: It was obtained as a red violet residue when the complex Cu base was heated with a solution of NH_4Cl on the water bath till the evolution of NH_3 ceased. The product was filtered, washed with cold water and dried in air. The substance is sparingly soluble in hot water and practically insoluble in alcohol.

Found:

Cu = 13.69%; Cl = 15.42%; H_2O = 15.55% (by loss at 105°C)

$[CuPip(BigH)_2]Cl_2 \cdot 4H_2O$ requires:

Cu = 13.70%; Cl = 15.40%; H_2O = 15.60%

Found (anhydrous product):

Cu = 16.39%; Cl = 18.28%

Calc. Cu = 16.34%; Cl = 18.27%

(c) Copper piperazinedibiguanide sulphate: It was obtained as violet compound from the complex base and $(NH_4)_2SO_4$ solution in the same way as the complex chloride. The substance is insoluble in water and alcohol.

Found:

Cu = 12.57%; S = 6.15%; H_2O = 19.29% (by loss at 105°C)

$[CuPip(BigH)_2]SO_4 \cdot 5.5H_2O$ requires:

Cu = 12.40%; S = 6.20%; H_2O = 19.31%

Found (anhydrous product):

Cu = 15.40%; S = 7.72%

Calc. Cu = 15.30%; S = 7.73%

(d) Copper piperazinedibiguanide nitrate: It was prepared from the complex base and a solution of ammonium nitrate as described in the previous case. The substance forms red powder insoluble in water and alcohol.

Found:

Cu = 13.70%; H_2O = 3.88% (by loss at 105°C)

$[\text{CuPip}(\text{BigH})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ requires:

Cu = 13.80%; H_2O = 3.90%

Found (anhydrous product):

Cu = 14.39%

Calc. Cu = 14.39%

(e) Nickel piperazinedibiguanide nickel hydroxide: It was obtained as a buff coloured precipitate by adding an ammoniacal solution of NiSO_4 to that of piperazinedibiguanide sulphate in presence of an excess of caustic soda. The product was filtered, washed well with cold water and dried in a dessicator to a constant weight. When the colour of the substance changes to yellow. The substance is insoluble in water and alcohol and liberates NH_3 from NH_4^+ salt solution.

Found:

Ni = 21.93%; N = 29.40%; H_2O = 16.80% (by loss at 105°C)

$[\text{NiPip}(\text{BigH})_2](\text{OH})_2 \cdot \text{Ni}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ requires:

Ni = 22.17%; N = 26.40%; H_2O = 17%

Found (anhydrous compound):

Ni = 26.52%; N = 31.85%

Calc. Ni = 26.70%; N = 31.80%

(f) Nickel piperazinedibiguanide chloride: It was obtained as insoluble orange yellow product by heating the complex nickel base, described above, with a solution of NH_4Cl on the water bath until the evolution of NH_3 ceased. The product was washed with cold water and dried in air to a constant weight.

Found:

Ni = 11.34%; N = 27.22%; Cl = 13.48; H_2O = 25.88% (by loss at 110°C)

$[\text{NiPip}(\text{BigH})_2]\text{Cl}_2 \cdot 7.5\text{H}_2\text{O}$ requires:

Ni = 11.31%; N = 27.00%; Cl = 13.60; H_2O = 26%

Found (anhydrous compound):

Ni = 15.19%; Cl = 18.49%

Calc. Ni = 15.20%; Cl = 18.50%

(g) Nickel piperazinedibiguanide hydroxide: It was obtained as an insoluble orange coloured product by keeping the complex nickel chloride (1 mol) in contact with a solution of caustic soda (2 moles) for two days and then heating the mixture on the water bath for some time. The product was washed with cold water and dried in a dessicator to a constant weight.

Found:

Ni = 15.70%; N = 37.33%; H_2O = 16.70% (by loss at 105°C)

$[\text{NiPip}(\text{BigH})_2](\text{OH})_2 \cdot 1.5\text{H}_2\text{O}$ requires:

Ni = 15.70%; N = 37.46%; H_2O = 16.80%

Found (anhydrous compound):

Ni = 15.19%; Cl = 18.49%

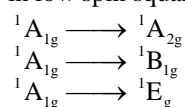
Calc. Ni = 15.20%; Cl = 18.50%

III. Results and Discussions

Piperazinedibiguanide was prepared by condensing piperazine with dicyandiamide. This was found to be act as a quadridentate ligand⁸ it coordinates to the central metal atom like Cu or Ni through four donor N-atoms and thus forms an inner metallic complex of ethylene dibiguanide type⁸.

Electronic spectra

Ni (II) has ^3F ground state term. In excited state three states are spin allowed and three are spin forbidden transition in low spin square planar complexes of d^8 system. The spin allowed transitions are:



The electronic band at ${}^1\text{A}_{1g} \longrightarrow {}^1\text{B}_{1g}$ occurs in visible region. The complexes of piperazinedibiguanide display one broad band around 445 nm attributed to ${}^1\text{A}_{1g} \longrightarrow {}^1\text{B}_{1g}$ transition. The strong absorption band about 295 nm in nickel (II) complex salts are due to charge transfer transition.

The diamagnetic behavior of the complex of Ni (II) with the piperazinedibiguanide and absorption at these wavelengths suggests a square planar structure for nickel (II) piperazinedibiguanide complexes which involves linkage of Ni (II) with the piperazinedibiguanide ligand.

Only this $[\text{NiPip}(\text{BigH})_2](\text{OH})_2 \cdot \text{Ni}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, Ni (II) complex was found to be paramagnetic. The Ni (II) in $[\text{NiPip}(\text{BigH})_2]$ is as usual diamagnetic⁸. The paramagnetism is due to the ionic nickel in $\text{Ni}(\text{OH})_2$.

The Cu (II) complexes show two bands, one at around 270-295 nm which shows charge transfer band and another at around 510-540 nm which shows ${}^2\text{B}_{1g} \longrightarrow {}^2\text{B}_{2g}$ transition.

The paramagnetic behaviour and absorption at these wavelengths suggests a square planar structure for copper (II) piperazinedibiguanide complexes.

Infra Red Spectra^{9,10}

The free ligand shows $-\text{NH}_3^+$, N-H and O-H stretching vibrations as a broad band at 3403.49 cm^{-1} and a medium sharp band at 3019 cm^{-1} owing to the asymmetric stretching of N-H and C-H vibrations. A band at 1632.63 cm^{-1} attributes to C=N stretch, O-H and N-H def. A band at 1404.16 cm^{-1} shows N-C-N and C-H stretching. The bands in the range $1299 - 1214\text{ cm}^{-1}$ show C-N stretch and ring vibrations. The strong and medium band at 1215.76 and 668.74 cm^{-1} may be attributed to C-C-N def., C-H and SO_4^{2-} stretching vibrations.

The band for N-C-N stretch is shown at higher frequencies $1475-1538\text{ cm}^{-1}$ as compared to the free ligand (1404.16 cm^{-1}).

In the complexes the C=N stretching vibrations are seen at lower frequency in the range $1602-1625\text{ cm}^{-1}$. Such lowering of the C=N stretching frequency on complex formation may be attributed to a lowering of the C=N bond order and formation of a metal-nitrogen bond. The coordination of metal atom with the nitrogen atom of the ligand occurs through the imino nitrogen since it forms more stable complex. The stability is due to π -conjugation¹¹.

The intensity of metal nitrogen bond is found to be generally very weak in metal complexes. The IR spectra of complexes are not resolved much in the region $500 - 400\text{ cm}^{-1}$ therefore, the vibrations due to metal-ligand bond could not be assigned.

IV. Conclusion

From the stoichiometry, magnetic measurements, spectral studies (IR & electronic absorption) and physico-chemical properties square planar structures have been proposed for these substituted biguanide complexes.

V. Acknowledgements

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 grateful to Professor L.K. Mishra, Professor (Retd.), Patna Science College, Patna University, Patna for his help in clearing doubts.

We are also thankful to SAIF CDRI Lucknow, SAIF STIC Cochin and IIT Guwahati for doing the elemental analysis, IR, UV spectral and magnetic measurements.

VI. References

1. R. K. Prasad, (Mrs) Bina Rani and Dhananjai Singh, J. Indian Chem. Soc., 83, 718, (2006).
2. R.K.Prasad, (Mrs) Bina Rani, Divya Singh and Dhananjai Singh, AIJRSTEM, 2, 108, (2014).
3. 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).
 - f. J. Inorg. Nucl. Chem., 41, 330, (1964).
 - g. T. R. Bera and J. Konar, J. Indian Chem. Soc., 74, 528, (1997).
 - h. S. Ghosh, C. C. Mukhopadhyay, G. S. De and A. K. Ghosh, J. Indian Chem. Soc., 75, 219, (1998).
 - i. Tannistha Roy Barman and G. N. Mukherjee, J. Chem. Sci., 118, 411, (2006).
 - j. A. Syamal, Chem. Educ. 4, 33, 1987; 5, 26, (1988).
 - k. W. E. Swartz, Jr. and R. A. Afanzo, J. Electron, Spectrosc, Relat Phenom., 406, 124, (1974).
 - l. S. N. Nandi and D. Banerjee; Z. Anorg. Allg. Chem., 406, 124, (1974).
 - m. T. C. Creitz, R. Gsell and D. L. Wampler, J. Chem. Soc., Chem. Soc., Chem. Comun. 1371, (1969).
 - n. D. Sen, J. Chem. Soc. (D), 52, 174, (1975).
4. R.K. Prasad, (Mrs.) Bina Rani and Dhananjai Singh, J. Indian Chem. Soc., 83, 718 (2003).
5. P. Ray and K.Chakravarthy, J. Indian Chem. Soc., 18, 609, (1941).
6. P. Ray and N. N. Ghosh, J. Indian Chem. Soc., 15, 350, (1938).
7. A textbook of Quantitative Inorganic Analysis A.I. Vogel Longman Scientific and Technical copublished by John Wiley & Sons, (5th Edition) 1989.
8. P.Ray and A.K. Choudhary, J. Indian Chem. Soc., 27, 615, (1950).
9. Infrared and Raman Spectra of Inorganic and Coordination Compound, K. Nakamoto, John Wiley, New York, 1988.
10. Infrared Spectra of Complex molecules, Methen and Co. Ltd., L. J. Bellamy, John Wiley and Sons Inc., Ed 1958.
11. Mirela Calinescu, Ticuta Negreanu-Pirjol, Rodica Georgescu and Octavian Calinescu, Cent. Eur. J. Chem., 8(3), 543-549 (2010)