

STUDY OF DIFFERENT pH IN MIX NITROGEN – SULPHUR DONOR MACROCYCLIC LIGAND

Prem Nath Chanchal
Research scholar,
Dept. of Chemistry
J. P. University, Chapra

ABSTRACT

The principal health hazards are caused by lead, mercury, arsenic, chromium, cadmium, antimony and their compounds. That is why, from an environmental point of view, there is strong need to determine these ions in chemical and biological samples. Ionophore based membrane electrodes are well-established analytical tools, routinely used for the measurement of wide variety of ions directly in complex biological and environmental samples. In this respect, macrocycles have been used as suitable neutral carriers for constructing ion-selective electrodes for heavy and toxic metals. The environmental and health effects of metal ion pollution are important and complex problems. Almost every metal or metallic compound encountered in manufacturing industry pose some type of ecological hazard. Macrocycles have been in use for several decades as synthetic dyes. There are however many other uses for them. Macrocycles play a vital role in biological systems as well. Haeme, the active site in the haemoglobin (the protein in blood that transports oxygen) is a iron containing porphyrin. Chlorophyll, the green photosynthetic pigment found in plants, contains a chlorin ring (a macrocycle) with magnesium at its centre. Vitamin B₁₂ also contains a macrocycle, called corrin.

Key Words: - Ionophore, macrocycles, Chlorophyll, haeme etc.

INTRODUCTION

Macrocyclic compounds find useful applications in removing heavy metals from aqueous solution for water purification.

as molecular switches and linear motors for constructing artificial nanoscale machinery (rotaxanes).

as chemical sensors in mimicry of cellular receptors

as molecular recognition agents.

as recognition agent for peptides.

as organic light emitting diodes.

The chemistry of macrocyclic ligands has been a fascinating area of current research interest to the chemists all over the world. The continued interest and quest in designing new macrocyclic ligands stem mainly from their use as models for protein-metal binding sites in biological systems, as models for metalloenzymes, as sequestering reagents for specific metal ions, as models to study the magnetic exchange phenomena, as chemical sensors and batteries, as therapeutic reagents for the treatment of metal intoxication, as medical imaging agents, as catalysts, and in biomedical and fuel cell applications.

The synthesis of macrocycles was unsuccessful and wasteful endeavour for many because of the low yields, the many side products of the reaction, and the large volume of the solvents that were required to give sufficient dilution to minimize polymerization and encourage cyclization.⁴⁶ Phthalocyanine and its derivatives bear a strong structural resemblance to natural porphyrin systems.

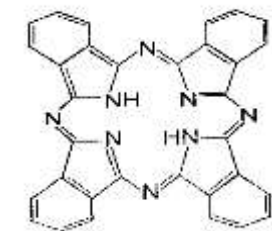


Fig.

The extensive metal-ion chemistry of phthalocyanine ligands is both interesting and varied. For example, specific phthalocyanines have been shown to behave as semiconductors, as catalysts for a variety of chemical transformations, and have been involved in model studies for a number of biochemical systems. All these properties favour the use of these compounds as pigments and dyes. Recognition of the importance of complexes containing macrocyclic ligands has led to considerable effort being invested in developing reliable and inexpensive synthetic routes for these compounds. These macrocycles which contain varying combinations of aza (N), oxa (O), phospho (P) and thia (S) ligating atoms can be tailored to accommodate specific metal ions by the fine tuning of ligand design features, such as the macrocyclic hole size, nature of the ligand donors, donor set, donor array, ligand conjugation, ligand substitution, number and size of the chelate rings, ligand flexibility

and nature of the ligand backbone. The different type of macrocyclic ligands are particularly exciting because of the importance in generating new areas of fundamental chemistry and many opportunities of applied chemistry. The majority of macrocycles represent creative and focused efforts to design molecules which will have particular uses. The metal ion may direct the condensation preferentially to cyclic rather than polymeric products, "the kinetic template effect" or stabilize the macrocycles once formed, "the thermodynamic template effect".

This chapter deals with the preparation of the ligand 1,7,10,16-tetraaza-4,13-dithia-2,6,11,15-tetraoxocyclooctadecane and the methods for physico-chemical analysis of the ligand and its coordination compounds with Co(II), Ni(II) and Cu(II) ions prepared in acidic, alkaline and neutral media. These methods include the estimation of the elements, molar conductance and magnetic moment measurements, I.R. and u.v. spectral analysis.

PROCEDURE :

White crystals of 1,7,10,16-tetraaza-4,13-dithia-2,6,11,15-tetraoxocyclooctadecane were separated. The crystals were filtered out, recrystallised in ethanol, washed with cold distilled water and then dried over anhydrous CaCl₂. The m.p. of the ligand was recorded to be 128.4C. The yield of the ligand was very poor (~10%). From microanalytical data and molar mass determination, the molecular formula of the ligand was found to be C₁₂H₂₀N₄S₂O₄, which is in confirmity with the structure of the ligand. 0.01 mole of ethane-1,2-diamine was dissolved in minimum volume of ethanol and the solution was heated for a few minutes. To this hot solution, an ethanolic solution of 0.01 mol of 3thiapentane-1,5-dioic acid was added slowly with contant stirring. The mixture solution was then refluxed for about one hour in a round bottom flask on a water bath using air condenser. The solution was then cooled and allowed to stand overnight.

METHODS :

The estimation of metals (Co, Ni and Cu) in the coordination compounds was carried out by standard methods. The coordination compounds were first decomposed with a view to bring the metals in their proper ionic form in solution and then they were quantitatively analysed.

As described in the estimation of cobalt, weighed amount of coordination compound of nickel was decomposed and brought into ionic solution as chloride. Nickel was precipitated as Nickel dimethyl glyoximate in slightly ammoniacal solution. The precipitate was quantitatively transferred

to previously weighed sintered glass crucible. The precipitate, dried at 100-120⁰ C, was then weighed as $[\text{Ni}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2]$. A known mass of the coordination compound was ignited for a few minutes and then treated with a few drops of conc. HNO_3 acid by which the residual carbon was oxidized to CO , and the oxide of cobalt was converted to nitrate. The product was heated to expel nitric acid. Finally, excess of conc. H_2SO_4 was added to convert the nitrate into sulphate and then heated between 450-500⁰ C and weighed as CoSO_4 . The weighed amount of copper complex was decomposed in a pyrex beaker by repeated evaporation with HNO_2 acid and HClO_4 until a clear solution was obtained. The solution was then boiled with HCl and the volume was reduced to 10 to 15 ml. The clear solution was diluted with water and then copper was determined iodometrically.

MEASUREMENT

The cell constant was determined at room temperature 30⁰C using N/10 and N/100 KCl solution. Pure DMF and conductivity water were used as solvents.

Electrical conductivity of solution of complexes were measured by conductivity meter bridge manufactured by Wiss Tachen Werch Stathen type-LBR at room temperature in dimethyl formamide (DMF).

The pole pieces were fixed at a distance of 1.8 cm and all measurements were made with 5 ampere current.

The centre of the maximum field between the pole pieces were determined by a topographical survey with the tube containing a column of paramagnetic substance like ferrous ammonium sulphate. The tube containing the specimen for measurement was always suspended between the poles in such a way that its lower end coincide with the centre. The bottom of the suspension tube was, therefore, always in the region of maximum field even under oscillation during weighing. The field was found to be practically negligible at 11.6 cm above this point. The specimen tube was, therefore, always filled upto height of about 11.6 cm. Filling up of the specimen tube requires some skill. Generally the substance was well powdered in a agate mortar. A small amount of the substance was then introduced into the tube and rammed with a properly fitting glass rod. In this way the required length was filled in uniformly.

RESULT AND DISCUSSION

In low spin square planar coordination compounds of Ni(II), two transitions. The electronic spectra of several octahedral, square planar and tetrahedral coordination compounds of Ni(II) have been reported. Low spin square planar coordination compounds of Ni(II) should give two d-d transition bands but these occur at high energy in the charge transfer region and have not been satisfactorily explained.

I.R. SPECTRA

Comparison of the IR. spectra of the ligand and its Coordination compound with Ni(II) in acidic, neutral and alkaline media reveals the following facts

- (i) The medium intensity band at 3320 cm^{-1} in the spectrum of the ligand of vibration of 2° amine group shifts towards lower frequency side by 30 to 50 cm^{-1} in the spectra of complexes. This indicates the Coordination of the ligand to the metal ion through the nitrogen atom group in all the coordination compounds of Ni (II).
- (ii) The weak and sharp band at 1540 cm^{-1} (amide II band) in the spectrum of ligand shifts towards lower frequency side by 10 to 20 cm^{-1} in the spectrum of coordination compounds. This further supports the coordination of the ligand to the metal ion through the nitrogen atom. The appearance of a new band in far infrared region in the spectra of coordination compounds at 530 cm^{-1} supports the participation of nitrogen atoms group in coordination to the metal ion.
- (iii) The amide I band at 1650 cm^{-1} in the spectrum of the ligand remains unchanged in position as well as intensity in the spectrum of the coordination compounds indicating the non-participation of oxygen atoms of group in coordination to the metal ion.
- (iv) There is a broad band at $3350\text{-}3600\text{ cm}^{-1}$ in the spectrum of $(\text{Ni}(\text{C}_{12}\text{H}_{20}\text{N}_4\text{S}_2\text{O}_4)(\text{H}_2\text{O})_2)\text{Cl}_2$, which was absent in the spectrum of the ligand. This band may be assigned to mode of vibration due to the coordinated water This is further supported by the appearance of a new band at 840 cm^{-1} in the spectrum of the coordination compound, which is characteristic of the wagging mode of vibration of the coordinated water molecule.

- (v) Two new infra-red spectral bands appear at 3375 and 3415 cm^{-1} in the spectrum of $[\text{Ni}(\text{C}_{12}\text{H}_{20}\text{N}_4\text{S}_2\text{O}_4)(\text{NH}_3)_2]\text{Cl}$, which may be reasonably assigned of 3415 of coordinated ammonia molecules.
- (vi) The band at 3500 cm^{-1} in the spectrum of $(\text{Ni}(\text{C}_{12}\text{H}_{20}\text{N}_4\text{S}_2\text{O}_4)\text{Cl}_2]$ may be assigned mode of vibration. This confirms the presence of chlorine atom in the coordination sphere. On the basis of the microanalytical data, magnetic moment and molar conductance values, uv-vis, and I.R. spectral study. following structures have been proposed for the coordination compounds of Ni(II) prepared with 1,7 10, 16-letraaza-4, 13-dithia- 2,6,11 15-tetraoxocyclooctadecane as the ligand in acidic (pH = 6). neutral (pH = 7.0) and alkaline (pH = 10) media.

SUMMARY AND CONCLUSION

The magnetic moment values of coordination compounds give useful information about their geometry Magnetic moment values for the coordination compounds of Co(II) in the range of 4.88 to 5.0 B.M. (Table - 1) suggest their octahedral geometry. The molar conductance values of coordination compounds justify their formulation.

The magnetic moment values of coordination compounds of Cu(II) observed in the range of 1.90 to 2.00 B.M. (Table-5.5). indicate distorted octahedral geometry of coordination compounds.

Table

Magnetic Moment Values (obs.) of the coordination compounds of Cu(II)

Sl. No.	Coordination Compound	Magnetic Moments (obs.)	Magnetic Behaviour
1.	$[\text{Cu}(\text{C}_{12}\text{H}_{20}\text{N}_4\text{S}_2\text{O}_4)\text{Cl}_2]$	1.90 B.M.	Paramagnetic
2.	$[\text{Cu}(\text{C}_{12}\text{H}_{20}\text{N}_4\text{S}_2\text{O}_4)\text{Cl}_2]\text{Cl}_2$	2.00 B.M.	Paramagnetic
3.	$[\text{Cu}(\text{C}_{12}\text{H}_{20}\text{N}_4\text{S}_2\text{O}_4)\text{Cl}_2](\text{NH}_3)]\text{Cl}_2$	1.95 B.M.	Paramagnetic

The comparison of I.R. spectra of the ligand (Table-3) and its coordination compounds with Co(II), Ni(II) and Cu(II) give information about the nature of metal-ligand linkages in coordination compounds.

REFERENCES

1. R. Vaum, N. D. Heindel, H. D. Burns, J. Emrich J. Pharm. Sdi., 71 1223 (1962)
2. E Van Caomelbecke, A. Derbin, P. Hambright, Rachel Garcia, Anass Doukkali, Saoiabi Ahmed, K. Ohkubo, S. Fukuzumi, K. M. Kadish Inorg. Chem, 44, 3789 (2005)
3. D. E. Fenton, H. Okawa Perspectives of Bioinorganic Chemistry: JAI Press, London, 8 (1993)
4. Serdar Karabocek, Nevin Karabocek, Asligul Armutcu Transition Met. Chem. 31 459 (2006)
5. E Kimura Pure and Appl. Chem. 65, 355 (1993).
6. S. Cunha, S. M. Oliveira, Jr M. T Rodrigues, R. M. Bastos, J. Ferrari, C. M. A Oliveira, L. Kato, H. B. Napolitano, I. Vencato, C. Lariucci J. Mol. Struct., 752. 32 (2005)
7. S. Blain, P. Appriou, H. Chaumeil, H. Handel Anal. Chim. Acta. 232, 331 (1990)
8. Dharampal Singh, Krishan Kumar. Ramesh Kumar, Jitendra Singh J. Serb. Chem. Soc 75(2). 217 (2010)
9. S. Chandra, R. Gupta, N. Gupta, S. S. Bawa Chem 31 147 (2006) Transition Met.
10. S. A. J. Collen, F M. Everatres, F. A. Huf J. Chromatogr. A; 788, 95 (1997)