

COORDINATION BEHAVIOR OF MIXED NITROGEN – SULPHUR DONOR MACROCYCLIC LIGAND AT DIFFERENT P^H

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ABSTRACT

The macrocycles and their complexes have attracted the interest of both inorganic and bioinorganic chemists in recent years and have been the domain of the research work in view of their wide range of applications. Macrocyclic complexes have also received special attention because of their mixed soft-hard donor character, versatile co-ordination behaviour and pharmacological properties, i.e. toxicity against bacterial growth. Antibiotics are vital molecules used for the treatment of bacterial infections in both human and animals but due to their regular use resistance against them has increased substantially and is posing an ever increasing therapeutic problem. Transition metal macrocyclic complexes have received great attention due to their biological activities, including antiviral, anticarcinogenic, antifertile, antibacterial and antifungal¹. Macrocyclic metal complexes of lanthanides, e.g., Gd (III), are used as MRI contrast agents.

Key Words :- macrocyclic, antibiotics, anticarcinogenic, Gd (III) etc.

INTRODUCTION

Macrocycles have been in use for several decades as synthetic dyes. Phthalocyanine is porphyrin (a nitrogen containing macrocycle) analogue, which is arguably the most useful, in use as dyes and pigments since their discovery in 1928, due to their dark blue colour. There are however many other uses for them. Macrocycles play a vital role in biological systems as well. Haeme, the active site in the hemoglobin (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. Macrocycles may be single-ring systems, e.g ., structures or

multiring systems, e.g., the cryptates. The obvious resemblance between a planar metal complex of macrocycles and the prosthetic groups in hemoglobin, chlorophyll and vitamin B₁₂, has stimulated research on the synthesis of macrocycles and on the structures, bonding, and reactions of macrocycle-metal complexes.

Macrocyclic ligands are polydentate ligands containing their donor atoms either incorporated in or, less commonly, attached to a cyclic backbone. As usually defined, macrocyclic ligands contain at least three donor atoms and the macrocyclic ring should consist of a minimum of nine atoms. A very large number of synthetic, as well as many natural macrocycles have now been studied in considerable depth. A major thrust of many of these studies has been to investigate the unusual properties frequently associated with cyclic ligand complexes. In particular, the investigation of spectral, electrochemical, structural, kinetic and thermodynamic aspects of macrocyclic complexes have all received considerable attention. The macrocyclic complexes of metal ions are synthesized by the reaction of the required metal ion with the preformed macrocyclic ligands, but there are potential disadvantages in this method. The synthesis of macrocycle in the free form often results in a low yield of the desired product with side reactions where polymerization is predominating. In order to circumvent this problem, the ring-closure step in the synthesis may be introduced to restrict rotation in the open-chain precursors thereby facilitating cyclization. One effective method for the synthesis of macrocyclic complexes involves an in situ approach where in the presence of a metal ion in the cyclization reaction markedly increases the yield of the cyclic product. The chemistry of macrocyclic ligands has been a fascinating area of current research interest to the chemists all over the world.

The porphyrin ring of the iron containing haem proteins and the related chlorin complex of magnesium in chlorophyll, together with the corrin ring of vitamin B₁₂ have all been studied for many years.

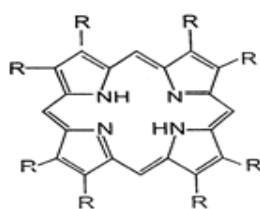


Fig.

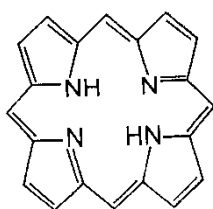


Fig.

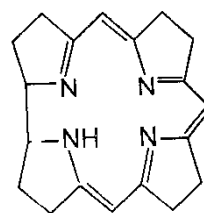


Fig.

PREPARATION OF THE LIGAND AND METHODS FOR PHYSICO-CHEMICAL ANALYSIS

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.

Preparation of the ligand :

The ligand 1, 7, 10, 16-tetraaza-4, 13-dithia-2, 6, 11, 15 tetraoxocyclooctadecane was prepared by the condensation of ethane-1,2-diamine and 3-thiapentane-1,5-dioic acid (1 : 1 molar ratio).

PROCEDURE :

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 constant 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. 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 CaCl_2 . 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 $\text{C}_{12}\text{H}_{20}\text{N}_4\text{S}_2\text{O}_4$, which is in confirmity with the structure of the ligand.

ANALYTICAL 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.

COBALT :

A known mass of the coordination compound was ignited for a few minutes and then treated with a few drops of conc. HNO₃ acid by which the residual carbon was oxidized to CO₂ and the oxide of cobalt was converted to nitrate. The product was heated to expel nitric acid. Finally, excess of conc. H₂SO₄ was added to convert the nitrate into sulphate and then heated between 450-500⁰ C and weighed as CoSO₄.

NICKEL :

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 [Ni(C₄H₇N₂O₂)₂].

COPPER :

The weighed amount of copper complex was decomposed in a pyrex beaker by repeated evaporation with HNO₂ acid and HClO₄ 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.

CONDUCTIVITY MEASUREMENT

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

U. V .- Visible Spectro Photometric Measurement :

The electronic absorption spectra of the complexes were recorded with Hitachi-320 spectrophotometer.

I. R Spectra :

The infrared spectra of the complexes and ligands were recorded as nujol mull on Perkin Elemer spectrophotometer. Nujol gives characteristic sharp peaks at 2960 cm^{-1} to 2800 cm^{-1} and 1460 cm^{-1} to 1380 cm^{-1} and a small peak at about 700 cm^{-1} . The I.R. bands of complexes taken in nujoi mull range has been excluded for the nujol mull while recording the I.R. spectra of complexes.

MAGNETIC SUSCEPTIBILITIES

Magnetic susceptibility of the complexes were determined by Gouy's method. These were provided with ground glass stoppers to which was attached a glass hook for suspension. Thus the length of the suspension could be adjusted. 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.

DETERMINATION OF MAXIMUM FIELD STRENGTH

The field was determined by using a number of standard substances like copper sulphate or ferrous ammonium sulphate. Accurate values of their mass susceptibilities are known.

RESULT AND DISCUSSION

Low spin square planar coordination compounds of Ni(I) should give two d-d transition bands but these occur at high energy n the charge transfer region and have ot been satisfactory explained. 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(I) have been reported.

SUMMARY AND CONCLUSION

The molar conductance values of coordination compounds justify their formulation as given in Table – 1.

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.

Table - 1

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

Sl. No.	Coordination Compound	Magnetic Moments (obs.)	Magnetic Behaviour
1.	[Co(C ₁₂ H ₂₀ N ₄ S ₂ O ₄)Cl ₂]	4.96 B.M.	Paramagnetic
2.	[Co(C ₁₂ H ₂₀ N ₄ S ₂ O ₄)Cl ₂]Cl ₂	4.88 B.M.	Paramagnetic
3.	[Co(C ₁₂ H ₂₀ N ₄ S ₂ O ₄)Cl ₂](NH ₃)Cl ₂	5.00 B.M.	Paramagnetic

The magnetic moment values of coordination compounds of Ni(II) fall in the range of 2.92 to 3.10 B.M. (Table – 2) indicating octahedral geometry for the coordination compounds.

Table - 2

Magnetic Moment Values (μ_{obs}) of coordination compounds of Ni(II)

Sl. No.	Coordination Compound	Magnetic Moments (obs.)	Magnetic Behaviour
1.	[Ni(C ₁₂ H ₂₀ N ₄ S ₂ O ₄)Cl ₂]	3.10 B.M.	Paramagnetic
2.	[Ni(C ₁₂ H ₂₀ N ₄ S ₂ O ₄)Cl ₂]Cl ₂	2.92 B.M.	Paramagnetic
3.	[Ni(C ₁₂ H ₂₀ N ₄ S ₂ O ₄)Cl ₂](NH ₃)Cl ₂	2.98 B.M.	Paramagnetic

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.

REFERENCES

1. P.M. Reddy, Y P HO, K. Shankar R. Rohini, V. Ravinder Eur. J. Med, Chem. 10, 1 (2009)
2. P M Reddy. A. V v S Prasad, R. Rohini V. Ravinder Spectrochim. Acta, 68A, 1000 (2007)
3. P M. Reddy, A.V.V.S Prasad, R Rohini, V Ravinder Spectrochim. Acta. 70A, 704 (2008)
4. M. B. Reddy, K. Shanker, P Usha Rani, R. Rohini, Ch. K. Reddy. V. Ravinder J. Indian Chem. Soc. 84, 971 (2007)
5. P.M. Reddy, A.V V.S Prasad V. Ravinder Transition Met. Chem. 32, 507 (2007)
6. S. Ilhan H. Temel Transition Met. Chem. 32. 1039 (2007)
7. S. Chandra, A. Gautem, M. Tyagi Transition Met. Chem. 32, 1079 (2007)
8. LT Boalc, E Marolla. P Taraldi Polyhedron; 26, 1663 (2007)
9. B. H. M. Mruthyunjayswamy, B.I. Omkar Y Jadegoud J. Braz Chem. Soc. 16, 783 (2005)
10. K. Shanker A. M. Reddy, P Muralidhar R. Rohini, V. Ravinder International Journal of Chem Tech Researrh; 1 777 (2009)
11. Eugeniusz Kubaszewski, Tadeusz Malinski J. Heterocyclic Chem. 29, 1417 (1992)
12. J. Eilmes Polyhedron. 6, 943 (1985)