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Some novel complexes of Cu(II) and Zn(II) with nitrogen and sulphur containing macrocycles: Synthesis and characterisation

Dr. Sanjay Kumar, Priyanka and Rabindra Singh

Abstract

A novel series of complexes of Cu(II) and Zn(II) with macrocyclic ligands 1,5,8,12-tetraaza-6,7,13,14-dibenzo-2,4,9,11-tetramethyl cyclotetradeca-1,4,8,11-tetraene (L₁) and 1,7,9,15-tetraaza-4,12-dithia-2,6,10,14-tetraoxocyclohexadecane (L₂) have been synthesised by template condensation method and characterised on the basis of elemental analyses, molar mass determination, molar conductance and magnetic susceptibility measurements, IR and UV-Vis spectroscopic investigations. The complexes were found to have molecular formula as [M(L₁)(H₂O)₂]Cl₂ and [M(L₂)(H₂O)₂]Cl₂, where M=Cu(II) and Zn(II). Complexes of Cu(II) were paramagnetic while those of Zn(II) were diamagnetic as expected for a d¹⁰ system. Magnetic moment values and the range of uv spectral bands suggested octahedral geometry for the complexes. The nature of metal-ligand bonds was established by IR spectral investigations. All the complexes were found to have 1:2 electrolytic nature.

Keywords: Macrocycles, template condensation, magnetic susceptibility, spectral investigation

1. Introduction

Macrocycles and metal chelates derived from them have been the domain of research for inorganic and bioinorganic chemists since the last few decades due to their resemblance with naturally occurring macrocycles of biological importance. Metal chelates of macrocyclic ligands are useful as antiviral, antibacterial, antifungal ^[1], anticarcinogenic ^[2] and antifertile ^[3] agents. By modifying the ring-size, nature of donor atoms [N, S, O or P] and the ring substituents, a great variety of macrocyclic ligands and their metal complexes of great importance can be synthesised. Macrocyclic compounds are being used in detecting tumour lesions due to their chelating properties. Metal complexes of macrocyclic ligands are becoming the important components of chelation therapy for removing toxic heavy metals from biological systems. Complexes of macrocyclic ligands with lanthanides find applications as MRI contrast agents ^[4]. Macrocyclic complexes are also used as dyeing agents ^[5], light emitting devices ^[6], DNA binding agents ^[7] and in various pharmacological studies ^[8]. Binuclear non-heme iron, manganese and copper macrocyclic complexes connected by μ-oxo bridges are used extensively as catalysts for C-H bonds oxidation ^[9]. Recent studies suggest that μ-carbido diiron macrocyclic complexes can also be used as catalysts for oxidation ^[10, 11]. μ-carbido ruthenium phthalocyanine is effective catalyst in cyclopropanation of olefins and carbene insertion into the N-H bonds of amines ^[12].

Keeping in view the wide range of applications of macrocyclic compounds and their metal chelates, we report the synthesis and characterisation of some novel complexes of Cu(II) and Zn(II) with nitrogen and sulphur containing macrocyclic ligands.

2. Experimental

2.1 Materials and methods

All chemicals used were of analytical grade purchased from Sigma Aldrich and were used as received without further purification. The microanalysis of C, H and N present in ligands and complexes was done by elemental analyser E U R O E A (Model EA 3000). The magnetic susceptibility of complexes was determined using vibrating sample magnetometer (Model PAR 155). Molar conductance of complexes was measured using digital conductivity meter (HPG System, G-3001). Metals in complexes were estimated by the methods available in literature ^[13].

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The IR spectra of ligands and complexes were recorded within the range of 4000-400 cm^{-1} using Agilent Technologies FT-IR spectrophotometer (Carvy 630). Electronic spectra of metal complexes were recorded on Hitachi 300 spectrophotometer. Molar masses of complexes were determined by cryoscopic method.

2.2 Synthesis of complexes

The complexes were synthesised by the template condensation of the constituents of ligands under the influence of Cu^{2+} and Zn^{2+} ions where by the coordination sphere of metal ions provides proper chemical and steric environment for the condensation rather than polymerisation of the constituents of ligands.

2.2.1 Synthesis of complexes of 1,5,8,12-tetraaza-6,7,13,14-dibenzo-2,4,9,11-tetramethylcyclotetradeca-1,4,8,11-tetraene (L_1) with Cu(II) and Zn(II) ions

0.02 mole of pentane-2,4-dione and 0.02 mole of 1,2-diaminobenzene were dissolved separately in minimum volume of ethanol. The two solutions were mixed and filtered. An aqueous solution of 0.01 mole of copper (II) chloride dihydrate, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ /Zinc(II) acetate dihydrate, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was added slowly to the ethanolic solution containing pentane-2,4-dione and 1,2-diaminobenzene with constant stirring. The mixture was refluxed for about 4 hours on a water bath using water condenser. It was then left for about 24 hours when light blue/white solid precipitated out. The precipitate was filtered, washed with distilled water and then with ethanol. It was further recrystallized from dimethylformamide (DMF). The precipitate was dried at 110°C in an electric oven and its m.p. was recorded. The complexes were found to be insoluble in common organic solvents such as benzene, toluene, methanol, ethanol,

chloroform, carbon tetrachloride and ether. However, they were found to be soluble in DMF and DMSO. The yield was approximately 70%.

2.2.2 Synthesis of the complexes of 1,7,9,15-tetraaza-4, 12-dithia-2,6,10,14-tetraoxocyclohexadecane (L_2) with Cu(II) and Zn(II) ions

0.01 mole of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was dissolved in minimum volume of ethanol and the solution was transferred to a round-bottom flask of 500 ml capacity. To this solution were added 50 ml of ethanolic solution of 0.20 mole of methanediimine and 50 ml of ethanolic solution of 0.20 mole of 3-thiapentane-1,5-dioic acid. The mixture solution was refluxed on a water-bath using a water condenser for about 4 hours. It was then allowed to cool for about 24 hours at room temperature. Light blue/white crystals were separated out which were filtered, washed with water and then with ethanol. The complexes were insoluble in water and common organic solvents such as benzene, toluene, methanol, ethanol, carbon tetrachloride, chloroform and ether. However, they were found soluble in DMF and DMSO. The precipitate was dried at 110°C in an electric oven and its m.p. was recorded. The yield was approximately 60%.

3. Results and Discussion

3.1 Microanalytical data

From microanalytical data (Table-1), the stoichiometries of the newly synthesised complexes were established. The experimental molar masses proved beyond doubt the monomeric nature of complexes. The microanalytical data and the observed molar masses of complexes were in good agreement with the proposed molecular formula (Table-1) of respective complexes.

Table 1: Microanalytical data related to complexes

Sl. No.	Complex Compound	Colour	M.P.	Molar mass found (Calculated)	% Found (% Calculated)					
					C	H	N	S	Cl	M
1.	$[\text{Cu}(\text{L}_1)(\text{H}_2\text{O})_2]\text{Cl}_2$	Light Blue	228°C	515.32 (514.54)	51.27 (51.30)	5.32 (5.44)	10.76 (10.88)	—	13.76 (13.80)	12.42 (12.35)
2.	$\text{Cu}(\text{L}_2)(\text{H}_2\text{O})_2\text{Cl}_2$	Light Blue	241°C	491.26 (490.54)	24.53 (24.46)	4.11 (4.08)	11.35 (11.42)	13.14 (13.05)	14.56 (14.47)	13.16 (13.51)
3.	$[\text{Zn}(\text{L}_1)(\text{H}_2\text{O})_2]\text{Cl}_2$	White	246°C	516.52 (516.38)	51.26 (51.13)	5.38 (5.42)	10.75 (10.84)	—	13.86 (13.75)	12.24 (12.22)
4.	$[\text{Zn}(\text{L}_2)(\text{H}_2\text{O})_2]\text{Cl}_2$	White	243°C	493.22 (492.38)	24.45 (24.37)	4.12 (4.06)	11.46 (11.37)	13.12 (12.99)	14.66 (14.42)	13.54 (13.83)

M = Cu(II), Zn (II)

$\text{L}_1 = 1, 5, 8, 12$ -tetraaza-6, 7, 13, 14-dibenzo-2, 4, 9, 11-tetramethylcyclotetradeca-1, 4, 8, 11-tetraene.

$\text{L}_2 = 1, 7, 9, 15$ -tetraaza-4, 12-dithia-2, 6, 10, 14-tetraoxocyclohexadecane

3.2 Molar Conductance

The molar conductance of metal complexes were measured in 10^{-3}M DMF solution at room temperature. The molar conductance values of complexes were found in the range of 165-175 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ indicating their 1:2 electrolytic nature [14]. The electrolytic nature of complexes is due to the presence of two chloride ions outside the coordination sphere. The presence of chloride ions outside the coordination sphere was further confirmed by the addition of AgNO_3 solution to the solution of metal complexes in DMF leading to the formation of two moles of white precipitate of AgCl per mole of the complex. Thus, all the complexes have been reasonably

formulated as given in Table-1.

3.3 Magnetic Susceptibility

Cu(II) complexes exhibit magnetic moment values in the range of 1.90-1.92 BM indicating octahedral environment of ligands around Cu(II) ion. The higher values over 1.73 BM corresponding to one unpaired electron in Cu(II) ion may be due to contribution from first order Zeeman effect. The magnetic moment values of Zn(II) complexes were not measured as they were expected to be diamagnetic corresponding to a d^{10} system.

3.4 Electronic spectra

The electronic spectra of Cu(II) complexes exhibited a broad and unsymmetrical band in the range of 15400-16200 cm^{-1} . This band may be reasonably assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition. The broadness of the band may be due to John-Teller distortion. Consequently, Cu(II) complexes have been

assigned distorted octahedral geometry. The electronic spectra of Zn(II) complexes were not recorded as Zn(II), a d^{10} system, was not expected to give d-d transition bands.

3.5 Infrared Spectra

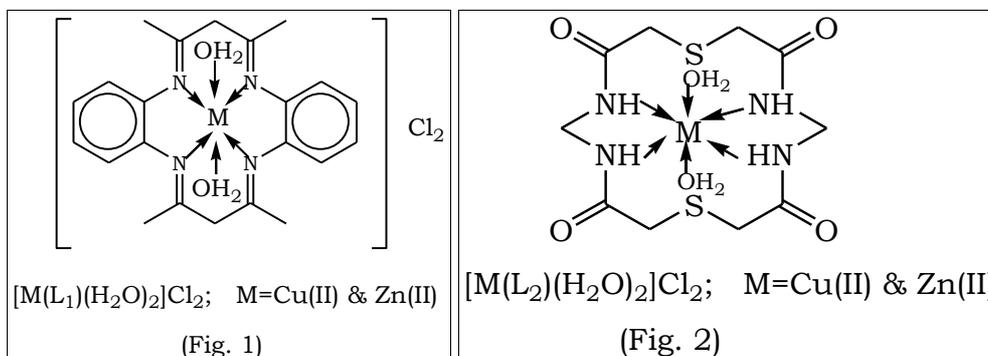
Comparison of infrared spectra of ligands L_1 and L_2 and corresponding complexes of Cu(II) and Zn(II) revealed the following facts:

1. The medium intensity band at 1680 cm^{-1} in the I.R. spectrum of the ligand L_1 due to ν_{C-N} (azomethine) mode of vibration was red shifted by $10\text{-}20\text{ cm}^{-1}$ in $[\text{Cu}(L_1)(\text{H}_2\text{O})_2]\text{Cl}_2$ and $[\text{Zn}(L_1)(\text{H}_2\text{O})_2]\text{Cl}_2$ indicating the participation of azomethine nitrogen in coordination to the metal ions.
2. A broad band appeared in infrared spectra of all the complexes in the range $3420\text{-}3600\text{ cm}^{-1}$, which was absent in the infrared spectra of ligands L_1 and L_2 , may be reasonably assigned to ν_{OH} mode of vibrations due to coordinated water molecule.
3. The infrared bands in the region $220\text{-}250\text{ cm}^{-1}$ in all the complexes may be assigned to ν_{M-O} mode of vibrations [15]. This fact further supported the coordination of water molecules to metal ions in all the synthesised complexes.

4. The appearance of new bands in infrared spectra of complexes in the region $280\text{-}295\text{ cm}^{-1}$ may be due to ν_{M-N} mode of vibrations [16].
5. The amide band I and amide band II at 1680 cm^{-1} and 1506 cm^{-1} respectively in the infrared spectrum of L_2 got shifted towards lower frequency region by $15\text{-}20\text{ cm}^{-1}$ in $[\text{Cu}(L_2)(\text{H}_2\text{O})_2]\text{Cl}_2$ and $[\text{Zn}(L_2)(\text{H}_2\text{O})_2]\text{Cl}_2$ indicating the coordination of the ligand L_2 to metal ions through nitrogen atoms.
6. The band at 710 cm^{-1} due to ν_{C-S} mode of vibration in the spectrum of ligand L_2 remained unaffected in position and intensity indicating the non-participation of the sulphur atom of the ligand L_2 in the coordination to the metal ions.

The infrared spectral studies of ligands and corresponding complexes establish the nature of metal-ligand bonding in newly synthesised complexes.

On the basis of elemental analyses, molar mass determination, conductance and magnetic moment measurements, infrared and electronic spectroscopic investigations, distorted octahedral geometry for Cu(II) complexes and octahedral geometry for Zn(II) complexes have been established.



4. Conclusion

The newly synthesised metal complexes have been characterised on the basis of elemental analysis, molar mass determination, magnetic susceptibility and molar conductance measurements, infrared and electronic spectroscopic investigations. The copper (II) complexes have been found to have distorted octahedral geometry while those of Zn (II) have octahedral geometry. All the complexes have 1:2 electrolytic nature. The Cu(II) complexes are paramagnetic whereas Zn(II) complexes are diamagnetic as expected of a d^{10} system.

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