

Synthesis and Characterization of Some 16- Membered Tetraimine Macrocylic Complexes

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Abstract

[2+2] Condensation of thiosemicarbazide with 2,5-hexanedione in a 1:1 molar ratio in aqueous solution at room temperature resulted in the formation of a novel Schiff base tetraimine macrocylic ligand, (L): 5,8, 13, 16 – tetramethyl – dione -3, 10 – dithia – 1, 2, 4, 9, 11, 12-hexaaza cyclohexadeca-1,4,9,12-tetraene (fig.1) or may be 5, 8, 13, 16 – tetramethyl – dione -2, 10 – dithia – 1, 3, 4, 9, 11, 12-hexaaza cyclohexadeca-1,4,9,12-tetraene (fig.2). Macrocylic complexes of the type, $[MLCl_2]$ $[M=Co(II), Ni(II), Cu(II), Zn(II) \text{ or } Cd(II)]$ have been prepared by reacting metal (II) chlorides with the ligand (L) in 1:1 molar ratio in ethanol. The prepared complexes were characterized by metal content analyses, IR, electronic spectroscopy, magnetic susceptibility and conductivity measurements. IR spectra confirm coordination of imine nitrogens to the central metal ion. An octahedral geometry has been suggested for all the complexes. The molar conductance values of the complexes show that they are non-electrolytes.

Introduction

Macrocylic complexes have attracted interests of both inorganic and bioinorganic chemists in recent years [1-4], because they offer a wide variety of donor atoms, ionic charges, coordination numbers, and geometry of the resultant complexes [5-7]. Understanding of metal ion chemistry of macrocylic ligands has important implications for a range of chemical and biochemical applications [8-10]. Hexaazamacrocycle has long been an extremely useful and versatile macrocylic ligand in coordination, bioinorganic chemistry [11-12]. Because of the wide range of medicinal applications of thiosemicarbazide and its ability to coordinate with metal ions [13], therefore it is highly desirable to synthesize and characterize macrocylic complexes with thiosemicarbazide. Here we report, the synthesis and characterization of hexaazamacrocylic complexes $[MLCl_2]$ obtained from the reaction of the macrocylic ligand (L) with the metals chlorides (Fig.1) or (Fig.2).

Experimental

Materials :

All chemicals used in the present work such as thiosemicarbazide, 2,5-hexanedione and metals chlorides were of Analytical Reagent (A.R) grade (B.D.H and Fluka).

a-Synthesis of the macrocylic ligand (L) :

Aqueous solution of thiosemicarbazide (0.02 mol.) in distilled water (100 mL) and 2,5-hexanedione (0.02 mol.) were mixed in 1:1 molar ratio with constant stirring for 2 hours. The mixture was cooled down to 5°C and kept undisturbed for 24 hours. A creamish white solid was precipitated out, which was filtered, washed with distilled water and dried in air.

b-Synthesis of the macrocylic complexes:

These complexes were synthesized by the same general method as follows :

A warm ethanolic suspension (50 mL) of the ligand (0.01 mol.), and hot ethanolic solution (50 mL), of the corresponding metal salts (0.01 mol.) were mixed together with constant stirring. The mixture was refluxed for 6 hours. The products were precipitated which were filtered, washed with ethanol and then dried in air.

Analysis and physical measurements

Metal contents were determined according to the standard procedure [14]. Melting points were determined by using Electrothermal 9300 digital melting points apparatus. Molar conductivities of the complexes have been measured using an electrolytic conductivity measuring set LF-42 on 0.001M dimethylformamide (DMF) solutions at room temperature, IR spectra were recorded on a Bruker (tensor 27) spectrophotometer in the 4000-400 cm^{-1} range using KBr disc. Electronic spectra were recorded on a Shimadzu 1601 spectrophotometer in DMF solvent at 25°C for 0.001M solution of the compounds using a 1cm quartz cell. Magnetic susceptibility measurements of the complexes in the solid state were determined using Faraday's method at room temperature using a Bruker BM6 apparatus.

Results and discussion

The prepared complexes are coloured solids, stable in air at room temperature. The analytical data of the synthesized complexes are listed in Table 1. Molar conductances of the complexes in DMF are in the range (5-31)

$ohm^{-1}cm^2mol^{-1}$ (Table 1) indicating a non-electrolytic nature of these complexes [15].

Table (1) : The physical and analytical properties of the complexes

Compound	Colour	Yield %	m.p C ⁰	% Metal		ΛM $ohm^{-1} cm^2 mol^{-1}$
				(Found)	Calculated	
L	Creamish white	61	242
$[Co(L)Cl_2]$	Dark Brown	65	258	11.98	12.59	31
$[Ni(L)Cl_2]$	Olive	62	255	12.04	12.55	8
$[Cu(L)Cl_2]$	Beige	78	260	12.69	13.44	25
$[Zn(L)Cl_2]$	Milky Yellow	57	247	14.09	13.78	5
$[Cd(L)Cl_2]$	Yellow	77	250	21.32	12.55	12

IR spectra :

The characteristic infrared frequencies of the complexes are summarized in Table 2. The absence of an absorption at 3300 cm^{-1} in the IR spectrum of the ligand shows that the amino groups of thiosemicarbazide are absent, and the absence of a strong band at 1713 cm^{-1} shows the absence of ketonic groups of 2,5-hexanedione. It confirms the elimination of water molecules and, as a result, cyclization takes place the formation of a macrocyclic ligand (tetraaminemacrocyclic). A band observed at 3195 cm^{-1} assigned to ν (N-H) of secondary amino group in the ligand. New bands appeared in the spectrum of the free ligand within the regions 1586, 1419, 1255 and 792 cm^{-1} assignable to thioamide I [\square (N-H) + ν (C=N)], thioamide II [ν (C=S) + ν (C=N) + ν (C-N)], thioamide III [ν (C-N) + \square (N-H)] and thioamide IV [ν (C=S)] bands, [16-17] respectively.

It provides a strong evidence for the presence of a closed cyclic product. In the complexes spectra, the bands appear in the regions (1570-1513), (1438-1415), (1279-1212) and (790 - 685) cm^{-1} assignable to thioamide I, II, III, and IV, respectively. In the IR spectrum of the free ligand, a band appears at 1650 cm^{-1} , corresponding the ν (C=N) group. The IR spectra of these complexes show an absorption in the (1607 - 1591) cm^{-1} range attributed to the imine, ν (C=N). This absorption band is showing a shift to the lower side in the complexes, suggesting coordination through the nitrogen of the ν (C=N) group [18-19]. Further proof of the coordination to the nitrogen atom is provided by the appearance of the bands (M-N) in the 466 - 434 cm^{-1} region in the IR spectra of the complexes. The M-Cl bands do not appear due to instrument limitation.

Table (2) : Important IR spectral bands (cm^{-1})

Compound	ν (N-H)	ν (C=N)	Thio amide I	Thio amide II	Thio amide III	Thio amide IV	ν (M-N)
L	3195	1650	1586	1419	1255	792	-----
[Co(L)Cl ₂]	3179	1598	1513	1431	1250	685	466
[Ni(L)Cl ₂]	3050	1606	1570	1438	1235	790	434
[Cu(L)Cl ₂]	1369	1607	1532	1432	1279	769	434
[Zn(L)Cl ₂]	3204	1591	1531	1415	1212	783	463
[Cd(L)Cl ₂]	3179	1602	1568	1438	1245	774	458

Electronic spectra and the magnetic moments :

The electronic spectrum of the macrocyclic ligand (L) and its complexes were recorded in DMF (Table 3). A band was observed at 32894 cm^{-1} in the spectrum of the ligand, which is attributed to $n \rightarrow \square^*$ transition in the C=N chromophore [20]. This band shows a blue shift in the spectra of the complexes (Table 3) due to the polarization in the C=N bond caused by the metal-ligand electron interaction during bond formation, indicating the involvement of (C=N) group in metal complexation. However, the absorption maxima of the metal complexes bear close resemblance with that of the free ligand, which indicates that no structural alteration of the ligand occurred during complexation. The electronic spectrum of the Co(II) complex exhibits absorptions in the regions 10183, 15015, 16447 and 35211 cm^{-1} . These bands may be assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$, ${}^4T_{1g} \rightarrow {}^4A_{2g}(\nu_2)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ transitions, respectively. The fourth band is attributed to $n \rightarrow \square^*$ transition (blue shift). The positions of these bands suggest an octahedral environment around the Co(II) ion [21-22]. The magnetic moment value for the Co(II) complex at room temperature was found to be at 4.9 B.M, indicating six-coordinated complex [23]. The electronic spectrum of the Ni(II) complex is consistent with the formation of an octahedral geometry with the appearance of three bands

at 10162, 16556 and 34482 cm^{-1} . These bands refer to the ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(\nu_1)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(\nu_2)$ transitions, respectively [21]. The third band at 34482 cm^{-1} is assigned to $n \rightarrow \square^*$ transition (blue shift). The ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$ transition may be overlapped by the ligand absorption band, therefore it can not be observed. The octahedral geometry of Ni(II) ion in the complex is confirmed by the measured magnetic moment value, 2.92 B.M. [23]. Unfortunately, some of the expected weak d-d transitions in the visible region for the Cu(II) complex cannot be detected even with concentrated solution, may be due to their very low intensity or lost in the low energy tail of the ligand absorption band. The electronic spectrum of the Cu(II) complex displays a band at 34722 cm^{-1} assigned to $n \rightarrow \square^*$ (blue shift). The Cu(II) complex shows magnetic moment at 1.99 B.M., corresponding to one unpaired electron [23]. The absorption spectra of Zn(II) and Cd(II) complexes show no bands due to d-d transitions. This phenomenon is natural as there is no possibility of transition due to non availability of empty d-orbital. The electronic spectra of these complexes, show bands at 34965 and 36495 cm^{-1} , which attributed to $n \rightarrow \square^*$ transition for the Zn(II) and Cd(II) complexes, respectively. Zn(II) and Cd(II) complexes are diamagnetic as expected for d^{10} configuration.

Table (3) : Magnetic moments and electronic spectral data (cm^{-1})

Compound	\square_{eff} B.M.	d-d transitions and $n \rightarrow \pi^*$ bands (cm^{-1})
L	-----	32894
[Co(L)Cl ₂]	4.90	10183, 15015, 16447, 35211
[Ni(L)Cl ₂]	2.92	10162, 16556, 34482
[Cu(L)Cl ₂]	1.99	34722
[Zn(L)Cl ₂]	Diamagnetic	34965
[Cd(L)Cl ₂]	Diamagnetic	36495

Conclusions

The present study revealed an octahedral geometry around Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes, in which the macrocyclic ligand acts as

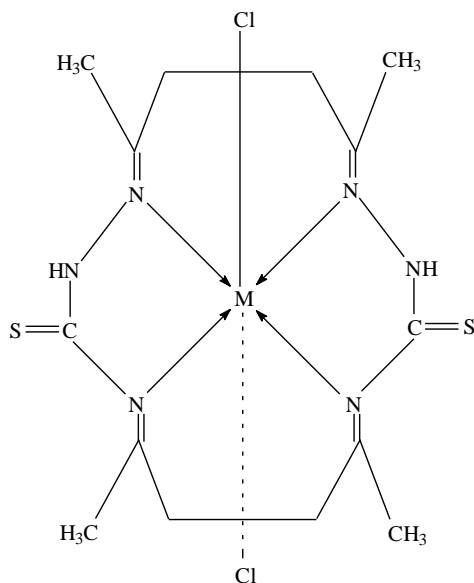


Fig.1: The Proposed Structure of the Macrocyclic Complexes [M(L)Cl₂]

tetradentate donor coordinated through the nitrogen atoms of $\nu(\text{C}=\text{N})$ groups.

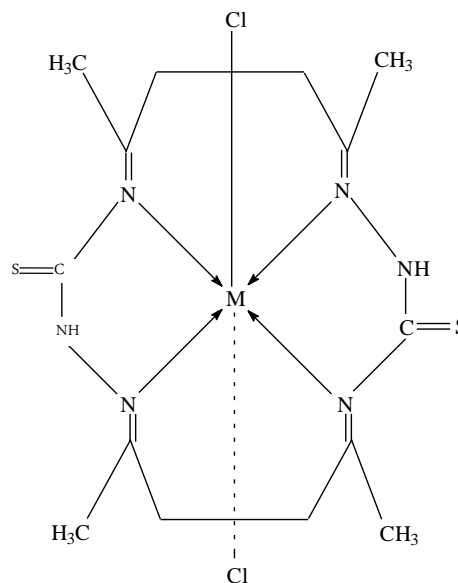


Fig.2: The Proposed Structure of the Macrocyclic Complexes [M(L)Cl₂]

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تحضير وتشخيص لبعض المعقدات الحلقية (مكونة من ١٦ ذرة) رباعية اليمين

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الملخص

يعطي التفاعل التكتيفي [2+2] بين الثايوسيميكاربازيد و ٢، ٥-هكسان ثنائي -ون- (بنسبة مولارية ١: ١) في المحلول المائي عند درجة حرارة المختبر ليكاند قاعدة شيف حلقي رباعي اليمين (L) : ٥، ٨، ١٣، ١٦-رباعي مثيل-ثنائي اون-٣، ١٠-ثنائي ثايا-١، ٢، ٤، ٩، ١١، ١٢-هكسا ازا سايكلووهكساديك-١، ٤، ٩، ١٢-رباعي ين (شكل ١) او قد يكون ٥، ٨، ١٣، ١٦-رباعي مثيل-ثنائي اون-٢، ١٠-ثنائي ثايا-١، ٣، ٤، ٩، ١١، ١٢-هكسا ازا سايكلووهكساديك-١، ٤، ٩، ١٢-رباعي ين (شكل ٢). حضرت المعقدات الحلقية ذات الصيغة العامة [MLCl]₂ [حيث ان M = كوبلت ، نيكل ، نحاس ، خارصين او كادميوم ثنائية موجبة] من تفاعل الليكاند الحلقي (L) مع كلوريدات الفلزات (بنسبة مولارية ١: ١) في الايثانول وشخصت هذه المعقدات من خلال التحليل الدقيق للفلز، اطياف الاشعة تحت الحمراء، الطيف الالكتروني ، القياسات المغناطيسية وقياسات التوصيلية المولارية. اظهرت قياسات الاشعة تحت الحمراء ارتباط ايون الفلز مع الليكاند من خلال ذرات نتروجين اليمين وان لهذه المعقدات شكل ثماني السطوح كما دلت قياسات التوصيلية الكهربائية لهذه المعقدات بانها غير موصلة.