

Synthesis and Characterization of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Complexes With Polydentate 14-Membered Macrocyclic Ligand

Najla H. Taher
Department of Chemistry
College of Education for Girls
University of Mosul

Akram A. Mohammed
Department of Chemistry
College of Education
University of Mosul

Received
12 / 05 / 2010

Accepted
03 / 11 / 2010

الخلاصة

يعطي التفاعل التكثيفي [2+2] بين السميكاربازيد وبنزويل اسيتون (بنسبة مولارية 1:1) في المحلول المائي عند درجة حرارة المختبر ليكابد قاعدة شيف حلقي رباعي اليمين (L): 5، 12-ثنائي مثيل - 9، 14 - ثنائي فنيل - 1، 3، 4، 8، 10، 11-هكسا ازا سايكلو تيترا ديكان-2، 9-ثنائي ون . حضرت المعقدات الحلقية ذات الصيغة العامة $[ML]Cl_2$ [حيث ان $M =$ كوبلت، نيكل، نحاس، خارصين او كادميوم ثنائية موجبة] من تفاعل الليكاند الحلقي (L) مع كلوريدات الفلزات (بنسبة مولارية 1:1) في الايثانول وشخصت هذه المعقدات من خلال التحليل الدقيق للفلز، أطياف الأشعة تحت الحمراء، الطيف الالكتروني، القياسات المغناطيسية وقياسات التوصيلية المولارية . أظهرت قياسات الأشعة تحت الحمراء ارتباط ايون الفلز مع الليكاند من خلال ذرات نتروجين اليمين وان لهذه المعقدات شكل مربع مستوي كما دلت قياسات التوصيلية الكهربائية لهذه المعقدات بانها اليكترولينية بنسبة 1 : 2.

ABSTRACT

The condensation reaction of [2+2] semicarbazide with benzoylacetone in a 1:1 molar ratio in aqueous solution at room temperature resulted in the formation of a novel Schiff base tetraimine macrocyclic ligand (L): 5,12-dimethyl-7, 14-diphenyl-1, 3, 4, 8, 10, 11-hexaazacyclotetradecane-2,9-dione. Macrocyclic complexes of the type, $[ML]Cl_2$ [M= Co(II), Ni(II), Cu(II), Zn(II) 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 spectra, magnetic susceptibility and conductivity measurements. IR spectra confirm coordination of imine nitrogens to the central metal ion. A square planar geometry has been suggested for all the complexes. The molar conductance values of the complexes show that they are 1:2 electrolytes.

INTRODUCTION

Synthetic macrocyclic complexes of transition metals have attracted much attention as promising objects in coordination and supramolecular chemistry⁽¹⁾. The chemistry of metal macrocycles is extensive because of their close relationship to molecules of biological significance⁽²⁻⁶⁾. The importance of these complexes is due to the role they play as models for protein metal binding sites in biological systems, as synthetic ionophores⁽⁷⁾, electrocatalysts in fuel cells⁽⁸⁾, MRI contrast agents^(9,10), luminescent sensors⁽¹¹⁾, anticancer drugs⁽¹²⁾ and radioimmunotherapeutic agents⁽¹³⁾. These extensive applications have been worth investigating for the design of new macrocyclic ligands for biological and industrial applications. Coordination compounds containing macrocyclic ligands have been studied in recent decades owing to their wide applications in biological and sensor fields^(14,15).

Over the past decades great attention has been devoted to the design and synthesis of Schiff bases with enhanced ability to selectively encapsulate the given metal ion⁽¹⁶⁾. A large number of macrocycles and their complexes with metal ion have been synthesized and characterized⁽¹⁷⁻¹⁹⁾. A literature search reveals that a large number of hexaazamacrocyclic metal complexes have been prepared and characterized⁽¹⁸⁻²⁰⁾. Also hexaazamacrocyclic has long been an extremely useful and versatile macrocyclic ligand in coordination, bioinorganic chemistry^(20,21), and they are known to give several mononuclear complexes, in spite of the large size of the cavity formed by the macrocyclic backbones, as well as to stabilize various anions in their protonated forms⁽¹⁸⁾. Because of the wide range of medicinal applications of semicarbazide and its ability to coordinate with metal ions⁽²²⁾, therefore it is highly desirable to synthesize and characterize macrocyclic complexes with semicarbazide. Here we report, the synthesis and characterization of hexaazamacrocyclic complexes $[ML]Cl_2$ obtained from the reaction of the macrocyclic ligand (L) with the metals chlorides (Fig.1).

EXPERIMENTAL

1. Chemicals:

All chemicals used in the present work including $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2$, $CdCl_2$, semicarbazide and benzoylacetone are Analytical Reagent (A.R) grade used without further purification.

2. Synthesis of the macrocyclic ligand (L)⁽³⁴⁾:

Aqueous solution of semicarbazide (2.23 g, 0.02 mol.) in distilled water (100 mL) and benzoylacetone (3.25 g, 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 brown solid was precipitated out, which was filtered, washed with distilled water and dried in air.

3. Synthesis of the macrocyclic complexes [ML]Cl₂:

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

A warm ethanolic suspension (50 mL) of the ligand (4.02 g, 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 off, washed with ethanol and then dried in air.

4. Analytical and physical measurements:

Metal contents have been determined by applying gravimetric methods⁽²³⁾ after the decomposition of the complexes by acid digestion with concentrated nitric acid. Melting points were determined by using electrothermal 9300 digital apparatus. Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring set LF-42 using 0.001 M of the complexes in dimethylformamide (DMF) solutions at room temperature. IR spectra were recorded on a Bruker tensor 27 spectrophotometer in the 400-4000 cm⁻¹ range using KBr disc. Electronic spectra were recorded on a Shimadzu 1601 spectrophotometer in DMF at 25°C for 0.001 M solution of the compounds using a 1 cm quartz cell. Magnetic susceptibilities of the complexes have been measured by Bruker B.M.6. using Faraday method.

RESULTS AND DISCUSSION

The prepared complexes are brown 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 (135-168) ohm⁻¹cm².mol⁻¹ (Table 1) indicating a 1:2 electrolytic nature of these complexes⁽²⁴⁾.

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

Compound	Colour	Yield %	m.p C ^o	% Metal		Λ_M ohm ⁻¹ cm ² mol ⁻¹
				*Cal.	Found	
L	Brown	61	141-143	-----	-----	-----
[Co(L)]Cl ₂	Dark Brown	67	232	11.07	10.73	141
[Ni(L)]Cl ₂	Dark Brown	55	207	11.04	11.82	168
[Cu(L)]Cl ₂	Dark Brown	69	254	11.84	12.51	135
[Zn(L)]Cl ₂	Brown	51	211	12.14	11.99	160
[Cd(L)]Cl ₂	Dark Brown	66	222	19.20	20.08	164

* Cal. = calculated

IR spectra:

The characteristic infrared frequencies of the complexes are summarized in Table (2). The absence of an absorption at 3261 cm^{-1} in the IR spectrum of the ligand shows that the amino groups of semicarbazide are absent, and the absence of a strong band at 1601 cm^{-1} shows the absence of ketonic groups of benzoylacetone. It confirms the elimination of water molecules and as a result, cyclization takes place through the formation of a macrocyclic ligand (tetraaminemacrocyclic).

A band observed at 3299 cm^{-1} assigned to $\nu(\text{N-H})$ of secondary amino group in the ligand. New bands appeared in the spectrum of the free ligand within the regions 1669 , 1417 , 1221 and 748 cm^{-1} , assignable to amide I $\nu(\text{C=O})$, amide II [$\nu(\text{C=N}) + \delta(\text{N-H})$], amide III [$\delta(\text{N-H})$] and IV [$\phi(\text{C=O})$] bands⁽²⁵⁾, respectively. It provides a strong evidence for the presence of a closed cyclic product. In the complexes spectra, the bands appear in the regions (1684 - 1659), (1415 - 1409), (1242 - 1238) and (767 - 763) cm^{-1} , assignable to amide I, II, III, and IV, respectively.

In the IR spectrum of the free ligand, a band appears at 1586 cm^{-1} , corresponding the $\nu(\text{C=N})$ group. The IR spectra of these complexes show an absorption in the (1548 - 1515) range attributed to the imine, $\nu(\text{C=N})$. this absorption band is showing a shift to the lower side in the complexes, suggesting coordination through the nitrogen of the $\nu(\text{C=N})$ group⁽²⁶⁾.

A new broad band located at (586 - 568) cm^{-1} region in the IR spectra of all complexes could be assigned to the chloride ion (Table 2). The positions of this band suggested the ionic nature and the non-involvement of this group in coordination⁽²⁷⁾, and therefore remained outside the coordination sphere. This observation were in good agreement with the conductance values of all the complexes and which have been supported the given formula for this complexes. Finally, the M-N bands are not observed in the IR complexes spectra since they are hidden under the broad bands of chloride ion.

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

Compound	$\nu(\text{N-H})$	$\nu(\text{C=N})$	Amide I	Amide II	Amide III	Amide IV	Ionic Cl
L	3299	1586	1669	1417	1221	748	-----
[Co(L)]Cl ₂	3324	1538	1659	1412	1238	763	569
[Ni(L)]Cl ₂	3333	1548	1680	1409	1238	764	586
[Cu(L)]Cl ₂	3315	1515	1684	1411	1242	766	573
[Zn(L)]Cl ₂	3331	1538	1681	1415	1239	767	579
[Cd(L)]Cl ₂	3332	1526	1681	1409	1239	766	568

Electronic spectra and the magnetic moments:

The electronic spectra of the macrocyclic ligand and its complexes were recorded in DMF at room temperature and are given in Table 3. The aromatic bands of the ligand at 48543 and 40650 cm^{-1} are attributed to benzene $\pi \rightarrow \pi^*$ transitions. The band around 33112 cm^{-1} is due to the $n \rightarrow \pi^*$ transition of the non-bonding electrons present on the nitrogen of the imine groups in the ligand. In the spectra of the complexes, the $n \rightarrow \pi^*$ transition is shifted to higher energy (blue shift), however, this transition is shifted to lower energy (red shift) in the cadmium spectrum (Table 3). This shift in the spectra of the complexes 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⁽²⁸⁾. The absorption at 20833 cm^{-1} for the free ligand could be assigned to a charge transfer transition. Although the square planar complexes of Co(II) are not very common, the electronic spectrum of Co(II) complex exhibits a band at 22026 cm^{-1} in DMF solution. This is attributable to ${}^2A_{1g} \rightarrow {}^2E'_g$ transition in square planar geometry⁽²⁹⁾. The magnetic moment of Co(II) complex was found to be 2.05 B.M. supports the square planar geometry around the Co(II) ion⁽³⁰⁾. The electronic spectrum of the Ni(II) complex shows a band at 21645 cm^{-1} , which is attributed to the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition⁽³¹⁾, suggesting square planar geometry for the nickel ion. The diamagnetism of the Ni(II) complex indicates an essentially square planar environment about Ni(II), which is in agreement with the electronic spectrum of the [NiL]Cl₂ compound⁽³²⁾. The Cu(II) complex shows a d-d absorption band at 22421 cm^{-1} , corresponding to the ${}^2B_{1g} \rightarrow {}^2E_g$ transition. The absence of band below 10000 cm^{-1} excludes the possibility of tetrahedral geometry⁽³¹⁾. A value of 1.66 B.M. for Cu(II) ion has been observed, which is well within the expected region found for square planar copper(II) complex⁽³²⁾. Finally, taking into account the spectra of Zn(II) and Cd(II) complexes and other physiochemical evidences (Table 1,2, and 3), four-coordinated square planar geometry is suggested for Zn(II) and Cd(II) complexes^(31,33,35).

Table (3): The electronic spectra and magnetic moments of the compounds

Compound	Band (nm)	Absorption region (cm^{-1})	Possible assignments	Magnetic moment (B.M)
L	206	48543	$\pi \rightarrow \pi^*$	-----
	246	40650	$\pi \rightarrow \pi^*$	
	302	33112	$n \rightarrow \pi^*$	
[Co(L)]Cl ₂	204	49019	$\pi \rightarrow \pi^*$	2.05
	242	41322	$\pi \rightarrow \pi^*$	
	278	35971	$n \rightarrow \pi^*$	
	340	29911	Charge transfer	
	454	22026	${}^2A_{1g} \rightarrow {}^2E'_g$	

[Ni(L)]Cl ₂	208	48076	$\pi \rightarrow \pi^*$	Diamagnetic
	238	42016	$\pi \rightarrow \pi^*$	
	278	35971	$n \rightarrow \pi^*$	
	462	21645	$^1A_{1g} \rightarrow ^1A_{2g}$	
[Cu(L)]Cl ₂	208	48076	$\pi \rightarrow \pi^*$	1.66
	280	35714	$n \rightarrow \pi^*$	
	446	22421	$^2B_{1g} \rightarrow ^2E_g$	
[Zn(L)]Cl ₂	204	49019	$\pi \rightarrow \pi^*$	Diamagnetic
	240	41666	$\pi \rightarrow \pi^*$	
	280	35714	$n \rightarrow \pi^*$	
	454	22026	Charge transfer	
[Cd(L)]Cl ₂	204	49019	$\pi \rightarrow \pi^*$	Diamagnetic
	246	40650	$\pi \rightarrow \pi^*$	
	338	29585	$n \rightarrow \pi^*$	
	456	21929	Charge transfer	

CONCLUSIONS

From the above discussion, and from the data given in Tables 1,2 and 3, it is concluded that the macrocyclic ligand acts as tetradentate donor coordinated through the nitrogen atoms of C=N groups. All the complexes are found to be mononuclear. A square planar geometry is proposed for all of them and the chloride anions which stay outside the coordination sphere of the complex as counter ions. The tentative structure suggested for the complexes is shown in Figure 1.

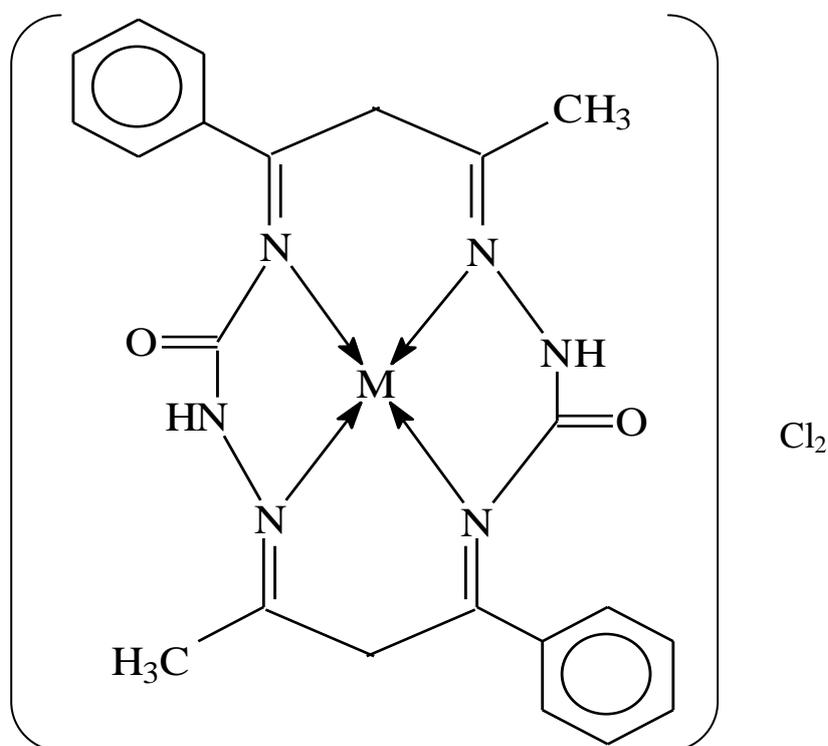


Fig. 1: The suggested structure of the [ML]Cl₂ complexes
M= Co(II), Ni(II), Cu(II), Zn(II) or Cd(II)

REFERENCES

- 1) Tarafdar M.T.H., Saravanan N. and Crouse K.A., *Trans. Met. Chem.*, 26: 613 (2001).
- 2) Konig B., Gallmeier H.C. and Klinke R.R., *Chem. Commun.*, 2390 (2001).
- 3) Singh D.P., Kumar R., Malik V. and Tyagi P.J., *J. Enzyme Inhib. Med., Chem.*, 22: 177 (2007).
- 4) Chandra S. and Sangeetika, *Spectrochim. Acta*, 60A: 2153 (2004).
- 5) Kim Y.S., Song R., Lee C.O., and Sohn Y.S., *Bioorg. Med. Chem. Lett.*, 14: 2889 (2004).
- 6) Hunter T.M., Paisey S.J. and Park H.S., *J. Inorg. Biochem.*, 98: 713 (2004).
- 7) Zinic M. and Skaric V., *J. Org. Chem.*, 53: 2582 (1988).
- 8) Behret H., Clauberg W. and Sandstede G.J., *J. Electroanal. Chem.*, 74: 393(1976).
- 9) Hovland R., Gloyard C., Aasen A. J. and Klaveness J., *J. Chem. Soc., Perkin Trans.*, 2: 929 (2001).
- 10) Pope S.J.A., Kenwright A.M., Boote V.A. and Faulkner S., *J. Chem. Soc., Perkin Trans.*, 3780 (2003).
- 11) Beeby A., Bushby L.M., Malleo D., and Willams J.A.G., *J. Chem. Soc., Perkin Trans*, 4854 (2002).
- 12) Jeony J.H., Chun M.W. and Chung W.K., *Korean J. Med. Chem.*, 6: 47 (1996).
- 13) Cox J.P.L., Jankowski K.J., Katakya R., Parker D., Beeley N.R.A., Boyce B.A., Daton M.A.W., Millar K., Millican A.T., Horrison A. and Walker C., *J. Chem. Soc. Chem.*, 12: 797 (1989).
- 14) Laullo S.J. and Witvrouw M., *Ind. J. Chem.*, 39B: 842 (2000).
- 15) Zhang H.C., Huang W.S. and Pu L., *J. Org. Chem.*, 66: 481 (2001).
- 16) Bligh S.W.A., Choi N., Evagorou E.G., McPartlin M. and White K.N., *J. Chem. Soc., Dalton Trans*, 3169 (2001).
- 17) Amato M.E., Ballistreri F.P., Pappalardo A., Tomaselli G.A. and Toscano R.M., *Molecules*, 15: 1442 (2010).
- 18) Niasari M.S., *Polyhedron*, 28(12): 2321 (2009).
- 19) Zangrando E., Kulisic N., Ravalico F., Bratsos I., Jedner S., Casanova M. and Alessio E., *Inorg. Chim. Acta*, 362 (3): 820 (2009).

- 20) Nunez C., Bastida R., Macias A., Lodeiro C. and Valencia L., *Inorg. Chim. Acta*, 362 (10): 3454 (2009).
- 21) Niasari M.S. and Najafian H., *Polyhedron*, 22 (18): 2633 (2003).
- 22) Clarkson S. G. and Basolo F., *Inorg. Chem.*, 12: 1528 (1993).
- 23) Vogel A.I., "A Text-Book of Quantitative Inorganic Analysis". 3rd. Ed., Longman, New York (1972) pp: 493,497,526,529,533.
- 24) Geary W.J., *Coord. Chem. Rev.*, 7: 81 (1971).
- 25) Shakir M. and Varkey S.P., *Polyhedron*, 14: 1117 (1995).
- 26) Abd-Elzaher M.M., *J. Chin. Chem. Soc.*, 48: 153 (2001).
- 27) Bellamy L.J., "The Infrared Spectra of Complex Molecules". 3rd. Ed., Methuen, London (1966).
- 28) Williams D.H. and Fleming I., "Spectroscopic Methods in Organic Chemistry". 4th Ed., McGraw-Hill, London (1989).
- 29) Iskander M.F., Ei-Syed L. and Ismail K.Z., *Trans. Met. Chem.*, 4: 225 (1979).
- 30) Carlin R.L., "Transition Metal Chemistry". Vol. I., MerceL Dekker, (1995).
- 31) Lever A.B.P., "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam (1984).
- 32) Duta R.L. and Syamal A., "Elements of Magneto-Chemistry". 2nd. Ed., Elsevier, New Delhi (1992).
- 33) Radovanovic B.C.S. and Andjelkovic S.S., "Analytical Laboratory" (1997).
- 34) Chandra S. and Pundir M., *Spectrochim. Acta A*, 69:1 (2008).
- 35) Raman N., Kulandaisamy A., Jeyasubramanian K., *Synth. React. Inorg. Met.–Org. Nano-Met. Chem.*, 34(1):17 (2004).