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Template Synthesis of 16-membered Octaazamacrocyclic Complexes of Zn(II) Ions

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ABSTRACT

Template condensation of metal ion with hydrazine, 2,4-Pentanedione and acetaldehyde in a 1:4:2:2 molar ratio resulted in the formation of 16-membered octaazamacrocyclic complexes: dichloro/nitro[2,5,8,10,13,16-hexamethyl-3,4,6,7,11,12,14,15-octaazacyclohexadecane - 2, 7, 10, 15-tetraene)Zn(II). The formula of the complex was derived and found to be of the type [$ZnLX_2$] where X=Cl or NO_3. The geometry of the complexes has been characterized by elemental analysis IR measurements. An octahedral geometry is suggested for the complexes.

Keywords: Octaazamacrocyclic ligand, template synthesis, Zn(II)

Introduction

Transition metal macrocyclic complexes have received much attention because of their close relationship of biological significance(1-3). Complexation with Zn(II) metal center usually results in complexes with 4-coordination number and tetrahedral geometry. This is due to the fact that Zn is a late transition metal with full of valance electrons which means that a stable 18-electron complex can be formed through 4- coordination number with its ligands. Due to this reason 5-coordinate Zn Complex is considered unusual and expected to be unstable. They synthesized by template reactions. A great attention has been devoted in the past decade to design and synthesize Schiff bases with enhanced ability to selectively encapsulate the given metal ion [4-5].

Due to the growing interest in Polyazamacrocyclic ligands and their transition metal complexes[6-11] the synthesis and spectroscopic characterisation of Zn(II) octaazamacrocyclic complexes [$ZnLX_2$] with 16-membered macrocyclic ligand are represented in this paper.

Experimental

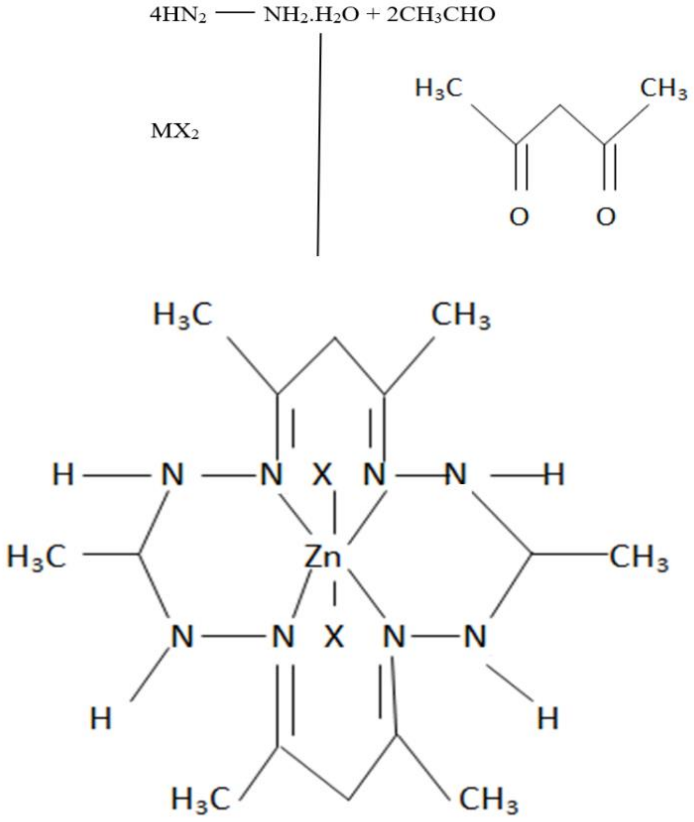
All the chemical used were of analytical grade and procured from Sigma-Aldrich (USA) and Fluka (USA). The metal salts were purchased from E.merck (Germany) and were used as received.

Synthesis of Complex

The methanolic solution (˜ 25 ml) of hydrazine hydrate (0.04 moles) a methanolic solution (˜25ml) of acetaldehyde (0.02 moles) were mixed together under constant stirring for 8 hrs. A methanolic solution (˜25ml) of the metal salt (0.01 mole) was added to this mixture followed by the addition of 2,4- pentanedione (0.02 moles). After regular stirring a solid product is formed, which was filtered, washed several times methanol and dried under vaccum over P_4O_{10}.

Physical Measurement

The C & H contents were determined on a Carlo-Erba 1106 elemental analyser (C.D.R.I Lucknow, India). The N content of the complexes was determined using the Kjeldahl method[12] . The metal contents were determined by volumetric analysis.[13] molar conductance values were measured on systronics conductometer model-303 at 298K in acentonitrile. The magnetic susceptibility values were measured at room temperature on a Gouy balance using $CuSO_4.5H_2O$ as the calibrant. Correction for dimagnetism were realised using Pascal Constants[14]. The chemical shifts are given in ppm relative to tetra methylsilane. The IR spectra was recorded as KBr pellets on a Beckman-20 spectrometer.The electronics spectra were recorded in acetonitrite on a Shimadzu 160A.



Result and Discussion

Octaazamacrocyclic complexes [$ZnLX_2$] (X=Cl or NO_3) have been synthesized by the template condensation of hydrazine acetaldehyde and 2,4-pentanedione in a 4:2:2 molar ratio as shown in fig 1. Both complexes are stable to atmosphere and completely soluble in water. Based on elemental analysis Table (1) complexes were assigned the composition (ZnLX2). The complexes were non-electrolytic in nature[15]. The complexes are diamagnetic in nature.

Table-1

Compound	colour	YIELD	M.P (0°c)	Molar Conductance $m^2 ohm^{-1} mol^{-1}$	Found (Cal) % Zn C H N Cl O
[$ZnLCl_2$] $C_{14}H_{28}N_8ZnCl_2$	Yellowish white	40	230	29	14.58 37.78 6.26 25.18 15.93 - 14.63 37.83 6.30 25.22 15.99
[$ZnL(NO_3)_2$ $C_{14}H_{28}N_{10}O_6Zn$	Yellowish white	42	250	26	13.01 33.75 5.59 28.11 - 19.25 13.07 33.80 5.63 28.16 19.31

I.R. Spectra

In the complexes a band of 1580 and 1615 cm-1 region had appeared which may be assigned to the imine V (C=N) stretching vibration. The coordination of chloro and nitrate groups has been ascertained by bands in the 235-255 and 255-310 cm^{-1} region which may reasonably be assigned [23, 25] to ν (M-O) of the ONO2 group and ν (m-cl)

Table-2

Compound	ν(N-H)	ν(C-H)	νC=N)	ν(C-N)	ν(N-N)	ν(m-cl)	ν(m-o)
[$ZnLCl_2$]	3248	2915	1580	1195	950	310	-
[$ZnL(NO_3)_2$]	3230	2895	1615	1180	965	-	250

^{1}HNMR spectra

A sharp signal at 2:45-2:50 ppm corresponding to imine methyl protons[26] has appeared on ^{1}HNMR spectra of the Zn(II) complexes. A singlet observed in the region 2.20-2.30 ppm to methylene protons of the 2,4-pentanedione. Doublet in the 1.80-1.82 ppm range due to methyl protons of the acetaldehyde moiety. A multiplet in 1.50-1.53 ppm region may be assigned of the aldehyde moiety.

Table-3

^{1}H NMR spectroscopic data of Zn Complexes.

Compound	CH_3-C$\equiv$N	C-CH_2-C	-CH_3	N-CH-N	-NH
$ZnLCl_2$	2.45(s)	2.30(s)	1.80(d)	1.50(m)	6.30(m)
ZnL(NO_3)2	2.50(s)	2.20(s)	1.82(d)	1.53(m)	6.28(m)

s=singlet, d=doublet, m= multipate

Reference:

1. Koning B., Gallmeier H.C and Klinke R.R., Chem. Commun 2390(2001)
2. Sibert J.W. Cory A.H and Cory J.G., Chem. Commun. 154(2002)
3. Bernhardt P.V. and Sharpe P.C., Inorg. Chem. 394123(2000)
4. Anniebligh S.W, Choi N., Evagorou E.G., Mepartlin M. and white K.N.J. chem. Soc., Dalton Trans, 4131(1999)
5. Adams h., Bastida R., Fenton D.E., macias A., Spey S.E and Valenica L., J. Chem. Soc Dalton Trans, 4131(1999)
6. H.C. rai and B.Sahoo, J.Indian chem. Soc. 53,646 (1976)
7. D.P. Singh, R.Kumar, V. Mallik,P.Tyagi, J.Inorg. Biochem 96,393 (2003)
8. Z.H.A El-Wahab, J. coord. Chem 43,231(2009)
9. C.B. Singh and B. Sahoo, J Inorg, Nuel Chem 36,126 (1974)
10. Sulekh Chandr, Monika Tyagi and Swati agarwal, J. Serb. Chem. Soc. 75(7)935(2010)
11. H.C. Rai, C.B. Singh and B. Sahoo, Indian J. Chem. 14A,504(1976)
12. I.L. Finar, Organic chemistry, 6th ed. Longman group Ltd. London 1974. P4
13. A.I. Voggel, Quantitative Inorganic analysis, ELBS, London, 1962, P.536
14. R.S Drago, Physical Methods in chemistry, W.B. Saunders Co. London. 1977, P.413
15. Geary W.J., use of conductivity measurements in organic solvents for the characterization of coordination componds. Coorf chem. Rev 7, 81(1971)