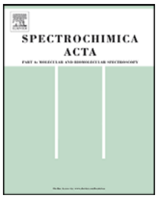
Spectrochimica Acta Part A 72 (2009) 591–596

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa



Template synthesis and physico-chemical characterization of 14-membered tetraimine macrocyclic complexes, [MLX_2] [M = Co(II), Ni(II), Cu(II) and Zn(II)]. DNA binding study on [$CoLCl_2$] complex

Farha Firdaus[a,*], Kaneez Fatma[a], Mohammad Azam[a], Shahper N. Khan[b], Asad U. Khan[b], Mohammad Shakir[a]

[a] *Division of Inorganic Chemistry, Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India*
[b] *Interdisciplinary Biotechnology Unit, Aligarh Muslim University, Aligarh 202002, India*

ARTICLE INFO

Article history:
Received 4 August 2008
Received in revised form 29 October 2008
Accepted 30 October 2008

Keywords:
DNA binding studies
Schiff-base
Spectral studies
Template synthesis
Thermal behavior
Tetradentate macrocyclic complexes

ABSTRACT

The template condensation reaction between glyoxal and 1,8-diaminonaphthalene resulted a few novel mononuclear 14-membered tetraimine macrocyclic complexes of the type, [MLX_2] [M = Co(II), Ni(II), Cu(II) and Zn(II), for X = Cl or NO_3]. The stoichiometry and the nature of the complexes have been deduced from the results of elemental analyses and conductance data. The formation of macrocyclic framework has been inferred from the appearance of imine υ(C=N) and υ(M—N) band in IR spectra and the resonance signals observed in ^{1}H and ^{13}C-NMR spectra. However, the overall geometry of the complexes has been assigned on the positions of bands in electronic spectra and magnetic moment data. The distortion in Cu(II) complexes has been deduced on EPR data. The thermal behavior of these complexes has been studied by TGA analysis. Absorption and circular dichroism studies on the complex proved a significant binding to calf thymus DNA.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The interest in exploring metal ion complexes with macrocyclic ligands has been continually increasing owing to their recognition as models for metalloproteins and antibiotics [1,2]. The macrocyclic Schiff bases have been widely studied due to their selective chelation to certain metal ions depending on the number, type and position of their donor atoms, the ionic radius of metal ion and coordinating properties of counterions [3–5]. The peculiar chemical, structural, spectroscopic and magnetic properties of Schiff base macrocycles and supramolecular structures involving trivalent lanthanide ions with their $4f^n$ configuration make them useful for development of photonic light-converting devices and sensors [6,7], contrast agents in magnetic resonance imaging [8,9], potential radiopharmaceuticals [10], sensitizers for photodynamic therapy and biomedical diagnostics [11,12] and artificial nucleases for hydrolytic cleavage or transesterification of the DNA and RNA phosphate diester backbone [13,14].

Ideally the macrocyclic complexes are formed by adding the required metal ion to a preformed macrocycle. However, the direct synthesis of macrocycles often results in low yield of the desired product with the domination of competing polymerization or other linear side reactions. Many synthetic routes to macrocyclic ligand involve the use of the metal ion template to orient the reacting groups of linear substrates in the desired conformation for the ring closure. The favorable enthalpy for the formation of metal-ligand bonds overcomes the unfavorable entropy of the ordering of the multidentate ligand around metal ion thus promotes the cyclization reaction [1,5,15]. In spite of 1,8-diaminonaphthalene having bidentate nucleophilic centers limited studies have been reported in the field of macrocyclic synthesis [16,17]. Macrocycles, especially the one containing aromatic moieties, are known to form charge transfer complexes with a variety of guests. These macrocycles were used to study complexation of diverse guests to provide new insight into non-covalent binding interactions, chiefly cation π-interactions, which involve the stabilization of a positive charge by the face of an aromatic ring [18]. The effective method for the synthesis of Schiff base macrocyclic complexes which involve the condensation reaction between suitable dicarbonyl compounds and primary diamines carried out in presence of appropriate metal ions as templates in directing the steric course of the reaction. Herein, we report the [2 + 2] template condensation reaction between 1,8-diaminonaphthalene and glyoxal resulting 14-membered Schiff base tetraazamacrocyclic complexes, [MLX_2]

---

* Corresponding author. Tel.: +91 9411415128.
E-mail address: farha_firdaus@yahoo.co.in (F. Firdaus).

1386-1425/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2008.10.054

[M = Co(II), Ni(II), Cu(II) and Zn(II)] and the DNA binding properties of [$CoLCl_2$] complex.

2. Experimental

2.1. Materials and methods

The metal salts $MX_2{\cdot}6H_2O$ (M = Co(II) and Ni(II): X = Cl^- and NO_3^-), $Cu(NO_3)_2{\cdot}3H_2O$, $CuCl_2{\cdot}2H_2O$, $ZnCl_2$ and $Zn(NO_3)_2{\cdot}6H_2O$ (all E. Merck) were commercially available pure samples. The chemicals 1,8-diaminonaphthalene and glyoxal (Aldrich) were used as received. Methanol (AR) was used as solvent. Highly polymerized calf-thymus DNA sodium salt (7% Na content) was purchased from Sigma. Other chemicals were of reagent grade and used without further purification. Calf thymus DNA was dissolved to 0.5% w/w, (12.5 mM DNA/phosphate) in 0.1 M sodium phosphate buffer (pH 7.40) at 310 K for 24 h with occasional stirring to ensure formation of homogeneous solution. The purity of the DNA solution was checked from the absorbance ratio A_{260}/A_{280}. Since the absorption ratio lies in the range $1.8 < A_{260}/A_{280} < 1.9$, therefore no further deproteinization of DNA was needed. The stock solution of complex **1a** with 5 mg/ml concentration was also prepared.

2.2. Synthesis of the complexes

*Synthesis of dichloro/dinitrato[2,4,9,11-dinaphthyl-1,5,8,12-tetraaza-5,7,12,14-tetraene cyclo tetradecan] metal(II), [MLX_2]; [M = Co(II) (**1a**), Ni(II) (**1b**), Cu(II) (**1c**) and Zn(II) (**1d**) for X = Cl; Co(II) (**2a**), Ni(II) (**2b**), Cu(II) (**2c**) and Zn(II) (**2d**) for X = NO_3]*

A methanolic (~25 ml) solution of metal salts (0.01 mol) was added to a magnetically stirred solution of 1,8-diaminonaphthalene (0.02 mol, 3.16 g) and glyoxal (0.02 mol, 2.29 g) in methanol (~25 ml) at room temperature. The reaction mixture was stirred for several hours, leading to precipitation of a solid product. The product was filtered off, washed with methanol and dried in vacuum.

2.3. Determination of binding constant of the DNA–complex **1a**

Knowing the stoichiometry (n), the association constant can be determined by the following equations. The overall association constant (K) for the following type of reaction:

$$n\text{DNA} + \text{Complex}\,\mathbf{1a} \leftrightarrow \text{Complex}\,\mathbf{1a} + \text{DNA}$$

is given by

$$K = \frac{[\text{Complex}\,\mathbf{1a}\text{–}(\text{DNA})_n]}{[\text{DNA}]^n \times [\text{Complex}\,\mathbf{1a}]}$$

If the initial concentration of DNA (a) and the concentration of complex at 50% of the total change of the monitoring parameter (b) are known, the association constant [19] for this reaction can be determined from the following equation:

$$K = \frac{(a/2)}{[(a/2)^n \times b]} \qquad (1)$$

Using Eq. (1), the binding parameter was found to be $K = 5.56 \times 10^4\ M^{-1}$. The value of the binding constant suggests a good binding affinity between the DNA and the complex **1a**.

2.4. Physical measurement

The results of elemental analyses were recorded on PerkinElmer 2400 CHN elemental analyzer, ESI-mass spectra was obtained by electrospray ionization method on a Micromass Quattro II Triple

Table 1
Elemental analysis, m/z values, color, yield, molar conductance and melting point values of the complexes.

Compounds	m/z found (calcd.)	Color	Yield (%)	M	Anal. found (calcd.)				Λ_m ($mol^{-1}\ cm^2\ ohm^{-1}$)	M.P. (°C)
					Cl	C	H	N		
[CoLCl2] **1a**	490.20 (490.25)	Black	60	12.00 (12.02)	14.39 (14.46)	58.75 (58.79)	3.12 (3.28)	11.50 (3.28)	24.0	235 °C
[$CoL(NO_3)_2$] **2a**	543.01 (543.36)	Black	57	10.57 (10.84)	–	53.02 (53.05)	2.71 (2.96)	15.39 (15.46)	15.6	238 °C
[$NiLCl_2$] **1b**	490.00 (490.02)	Black	60	11.73 (11.97)	14.41 (14.46)	58.60 (58.82)	3.08 (3.29)	11.40 (11.43)	12.2	242 °C
[$NiL(NO_3)_2$] **2b**	543.01 (543.11)	Dark brown	62	10.65 (10.80)	–	53.02 (53.07)	2.82 (2.96)	15.38 (15.47)	14.4	250 °C
[$CuLCl_2$] **lc**	494.78 (494.86)	Black	59	12.62 (12.84)	14.21 (14.32)	58.20 (58.25)	3.22 (3.25)	11.12 (14.32)	18.0	245 °C
[$CuL(NO_3)_2$] **2c**	547.72 (547.97)	Black	58	11.18 (11.59)	–	52.49 (52.60)	2.59 (2.94)	15.13 (15.33)	25.0	243 °C
[$ZnLCl_2$] **1d**	496.52 (496.70)	Dark brown	55	13.08 (13.16)	14.20 (14.27)	58.01 (58.03)	3.16 (3.24)	11.15 (14.27)	20.4	230 °C
[$ZnL(NO_3)_2$] **2c**	549.52 (549.80)	Black	64	11.72 (11.89)	–	52.01 (52.43)	2.69 (2.98)	15.02 (2.98)	18.0	235 °C

Download English Version:

https://daneshyari.com/en/article/1237987

Download Persian Version:

https://daneshyari.com/article/1237987

Daneshyari.com