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Synthesis and Characterization of Some Mixed Ligand Complexes of Zn(II) with 4, 4´- Bipyridine: Anti-inflammatory and Analgesic Activities of these Complexes

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Abstract

The mixed ligand complexes of Zn(II) with 4,4-bipyridine and some organic acids or amino acids were prepared in the solid form and characterized by elemental analysis, conductivity, magnetic moment measurement, IR, ^{1}H-NMR, ^{13}C-NMR and FAB^{+} mass studies. To study anti-inflammatory and analgesic activities of these complexes, some Swiss albino mice of 5-7 weeks old were taken. One dose of the test compounds of 10 mg/kg was selected throughout the research work. The anti-inflammatory activity of the test compounds were determined by 'carrageenan induced mice paw edema inhibition' method. The analgesic activity was determined by 'acetic acid induced writhing' methods. These three compounds showed positive effects as anti-inflammatory and analgesic agents. Anti-inflammatory and analgesic activities of the test compounds at 50 mg/kg were quite comparable to those of standard drugs at 10 mg/kg.

Keywords: Zinc; Organic acids; 4, 4'-Bipyridine; Anti-inflammatory; Analgesic activity.

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1. Introduction

The chemistry of metal complexes is now the most active research field of inorganic chemistry. Coordination chemistry stands as landmark in the area of scientific advancement embracing most diverse branches of science, engineering and technology. Organic acids or amino acids bearing N, O and S donors in their side chains, cysteine, cystine and leucine are the most prominent for Zn [1, 2]. However, the importance of Zn for stabilization of protein loops in enzymes, Zn fingers etc., has generated new interest in the field of Zn coordination chemistry [3-9]. Zn complex based units are present in a number of nucleic acid binding and gene regulatory proteins [10-13]. The transcription

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factor III A, (TF III A) contains nine tandem repeats of the amino acid motif and each repeat has two invariant cysteine and two invariant histidines coordinated to Zn (Zn-finger) [14-17]. These complexes have applications in clinical, analytical and industrial in addition to their important roles in catalysis and organic synthesis [18]. Some of metal complexes are used as model molecules for biological oxygen carrier systems, as metal indicators in complexometric titrations and colorimetric reagents and to biochemical research [19].

Pain has been defined as an unpleasant sensory and emotional experience associated with actual or potential tissue damage [20]. The direct and indirect action of chemical mediators, such as arachidonic acid metabolites (prostaglandins and leukotrienes), peptides, serotonin, acetylcholine, cytokines, nitric oxide, among others, which can be produced or released following tissue injury or by exogenous irritants (formalin, acetic acid), are responsible for the multiplicity of events that occur during pain transmission, in both the peripheral and central nervous systems [21].

Inflammation produces in the liberation of endogenous mediators like histamine, serotonin, bradykinin, prostaglandins etc. Prostaglandins are ubiquitous substances that indicate and modulate cell and tissue responses involved in inflammation [22]. Most of the anti-inflammatory drugs now available are potential inhibitors of cyclooxygenase (COX) pathway of arachidonic acid metabolism. Hence, for treating inflammatory diseases analgesic and anti-inflammatory agents are required [23]. Non-steroidal anti-inflammatory drugs (NSAIDs) are the most clinically important medicines [24] but have some adverse effects [25].

2. Experimental

2.1. *Materials*

Diphenic acid (dpa), Phthalic acid (pha), DL-Leucine (leu) and 4, 4-Bipyridine (bpy) were obtained from the Sigma (USA). AR grade zinc chloride, carrageenan reagent and diclofenac sodium were obtained from E Merck. They were used as supplied.

2.2. *Synthesis of metal complexes*

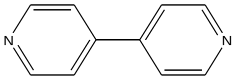
The three complexes K[Zn(bpy)(dpa)]Cl… (1), K[Zn(bpy)(pha)]Cl… (2), K[Zn(bpy)(leu)]Cl… (3) were synthesized by mixing an aqueous solution containing equimolar ratios of bpy (0.001 moles, 0.156 g) and dpa (0.001 moles, 0.212 g), pha (0.001 moles, 0.166g), leu (0.001 moles, 0.101 g), which were added simultaneously and independently to equimolar concentrations of zinc chloride. Stoichiometric ratios of metal and ligands are dissolved in aqueous medium and are refluxed until the complex is precipitated, and if not, the pH of the solution mixture is changed to precipitate the complex. The synthesized complexes were found to be insoluble in the commonly known organic solvents. Consequently, the following physical measurements and analysis were carried out to check the purity and elucidation the structure. All the metal complexes were stable to air and moisture and decompose at very high temperatures (>300^0C).

The complexes of the Zn (II) were obtained as follows:

$$ZnCl_2 + bpy + A\text{-}H \longrightarrow Zn(bpy)(A)$$

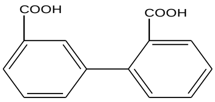
where, bpy = 4,4′-Bipyridine and A = anion of Diphenic acid, Phthalic acid and DL-leucine.

4,4′-Bipyridine = bpy



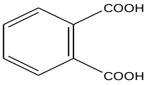
Diphenic acid =

dpa



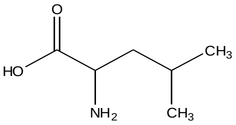
Phthalic acid =

pha



DL-Leucine =

leu



2.3. *Elemental analysis and conductivity data*

Carbon, hydrogen and nitrogen analyses were obtained from the microanalytical Heraeus Carlo Etba 1108 elemental analyser. Chloride analysis was carried out by Mohrs method. The metal contents were estimated from these solutions on an atomic absorption spectrometer, Perkin–Elmer 23380. Conductivity of metal complexes was measured in freshly prepared DMSO solutions and obtained using a Digisun Digital conductivity bridge (model: DI-909) and a dip type cell calibrated with KCl solution.

2.4. *Spectral analysis*

The IR spectra were recorded (as KBr discs) on a Horiba FT-710 Spectrometer in the region 4000–400 cm^{-1}. For ^1H NMR spectra deuterated solutions of complexes 1, 2 and 3 were prepared in 99.8% of $CDCl_3$. The pH of the solution was maintained at 5–6 by adding DCl solution. ^1H-NMR spectra were recorded for the above complexes of concentration 5×10^{-2} mol dm^{-3} at room temperature on a JEOL-JMN 400 NMR Spectrometer. TMS was used as the internal standard. The ^{13}C-NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 using TMS as internal standard with JEOL-JMN 200 MHz high resolution NMR Spectrometer. FAB^+ mass spectra of the complexes were recorded using a JEOL-JMS-D 300 Spectrometer operating at 20 eV or 70 eV (HRMS).

2.5 *Magnetic susceptibilities*

Magnetic susceptibilities of the Zn complexes were recorded at room temperature on a Faraday balance (CAHN-7600) using $Hg[Co(CNS)_4]$ as the standard. Diamagnetic corrections were made by using Pascal's constants [26].

2.6 *Anti-inflammatory and Analgesic activity*

The anti-inflammatory activity [27] of the test compounds were determined using the carrageenan-induced mice paw edema inhibition method employing 1.0% carrageenan solution as the phlogistic agent. The test compounds were administered orally as suspensionsin 3% DMSO, 30 min before the ingection of the phlogistic agents

The analgesic activity of the test samples were studied [28] using acetic acid-induced writhing model in mice. Swiss albino mice of either sex were divided into control, standard and different test groups contains four mice in each.

3. Results and Discussions

Analytical data corresponding to the 1, 2 and 3 complexes are compiled in Table 1. It may be seen from the table that the complexes are in equimolar stoichiometric 1: 1 : 1 ratio. The presence or absence of chloride ions in the above complexes was determined by Mohr's method. No evidence was found for the presence of chloride ions in the coordination sphere of the complexes. The conductivity values (Table 1) in DMSO correspond to ionic as chloride ions, present outside the coordination sphere and electrolytes for the complexes [29].

Table 1. Analytical and physical data of the complexes.

Complex	C found (calcd)	H found (calcd)	N found (calcd)	Metal found (calcd)	Λ_m (ohm^{-1}cm^2 mol^{-1})	μ_{eff} (B.M.) (Temp.K)
[Zn(bpy)(dpa)]	62.61 (62.63)	3.47 (3.50)	6.08 (6.11)	14.13 (14.14)	13	Diamagnetic
[Zn(bpy)(pha)]	53.33 (53.35)	3.33 (3.35)	7.77 (7.79)	18.05 (18.08)	13	Diamagnetic
[Zn(bpy)(leu)]	54.85 (54.87)	5.71 (5.74)	12 (12.02)	18.57 (18.59)	14	Diamagnetic

The IR absorption frequencies for the ligands and their zinc complexes were recorded in the range 4000- 400 cm^{-1}. A strong band (due to carboxylate group) at 3070 cm^{-1} in the spectra of the free ligands is shifted to lower wave number at 3050-3060 cm^{-1} in the complexes studied, showing the coordination of carbonyl oxygen to the metal atom [30]. The coordination of nitrogen to the metal atom is supported by the appearance of a new absorption band at 517-544 cm^{-1}, which may be assigned to υ(Zn-N) vibrations. The infrared spectra of all the zinc complexes did not show the strong band in the region 3105-2740 cm^{-1} due to υ(COOH), indicating the deprotonation of the carboxylate group of the amino acids with zinc metal as expected. In the spectra of the complexes two sharp bands observed at 1585 and 1379 cm^{-1} are assigned to the υasym(COO) and υsym(COO), respectively. Furthermore, the separation between asymmetric and symmetric vibrations is about 270 cm^{-1}, indicating the covalent nature of the metal-oxygen bond.

Table 2. Color, melting point and IR data for Zn(II) complexes.

Comp.	Colour	m.p	IR data
01	White powder	295-297(d)	IR (KBr): υ(OH), 3059; υ(C=O), 1611; υasym(COO), 1552; υsym(COO), 1379; bend(OH), 1145; υ(Zn-N), 517; υ(Zn-O), 409 cm^{-1}
02	White powder	>300	υ(OH), 3068; υ(C=O),1659; υasym(COO), 1585; υsym(COO), 1396; bend(OH), 1138; υ(Zn-N), 574; υ(Zn-O), 532 cm^{-1}
03	White powder	>300	υ(OH), 3299; υ(C=O), 1616; υasym(COO), 1506; υsym(COO), 1364; bend(OH), 1173; υ(Zn-N), 544.31; υ(Zn-O), 413.65 cm^{-1}

The characteristic resonance peaks for the synthesized compounds have been recorded in DMSO-d6. The expected resonances are assigned by their peak multiplicity, intensity patterns and integration. The ^{1}H-NMR spectra of the free ligands showed single resonance at (11.4±0.10) ppm for COOH and however, also present in the metal complexes as they were prepared in aquous medium and completely not purified. A complex multiplet signal in the region (7.20 - 7.82) ppm for the aromatic protons is observed in the ligands and these remained almost at the same position in the spectra of the metal complexes. In the spectrum of 4, 4´-bipyridine, the integral of the aromatic region corresponded to nine protons; five protons of the phenyl ring are observed at 7.6 ppm. Organic acids (diphenic acid, phthalic acid, leucine) protons on the α-carbon of the carboxylic acid moieties appeared at 3.96 – 4.30 ppm. In general, the complexes obtained were found to exhibit no additional resonances and thus reflected the purity of the complexes.

Evidence of the formation of the complexes is also clearly displayed in the ^{13}C- NMR spectra. The ^{13}C- NMR spectra of complexes showed the δ(COO) signal shifted to the downfield region which is lower compared to that of the ligand (174 –176) ppm indicating that the carboxylate anion is bonded to zinc atom upon complexation. The considerable shift in the resonance of the carbon atom attached to nitrogen indicates the involvement of nitrogen atom in coordination. The occurrence of eight resonances in the range of (118.3 – 150.7) ppm in the ^{13}C- NMR spectra of the complexes and ligands is defined as aromatic carbon signals. Though, it is also possible that the shifting of carbon is due to the change in hybridization of nitrogen attached to carboxylate group but in the light of IR, UV and ^{1}H NMR spectral studies it seems more plausible that the shifting in these carbons is due to the involvement of carboxylate oxygen.

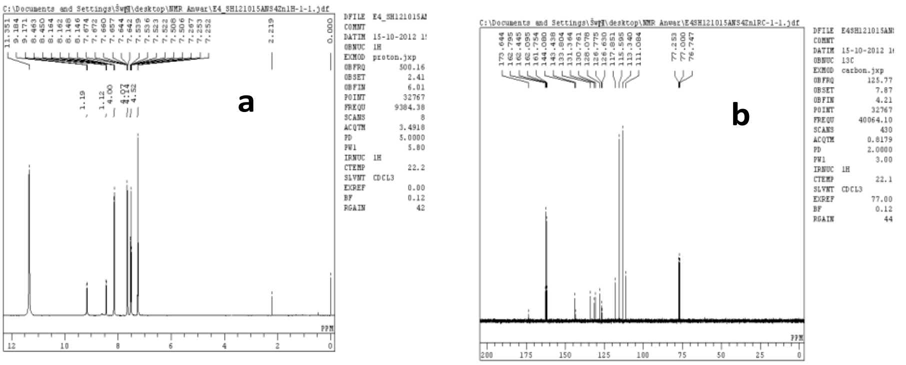


Fig. 1. a) ^{1}H-NMR, and b) ^{13}C-NMR spectra of Zn(bpy)(dpa).

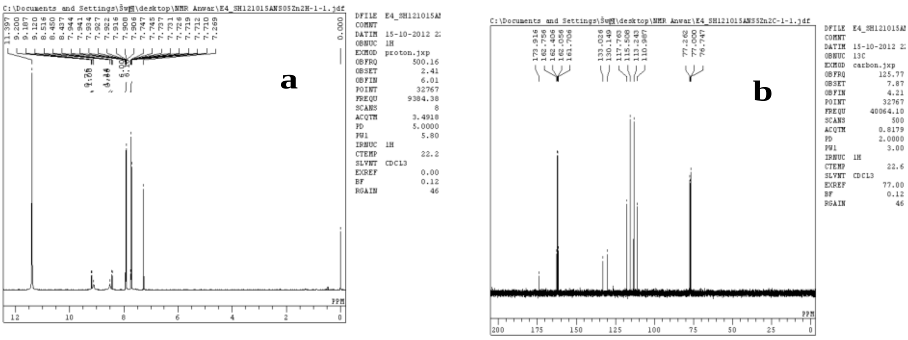


Fig. 2. a) ^{1}H-NMR, and b) ^{13}C-NMR of Zn(bpy)(pha).

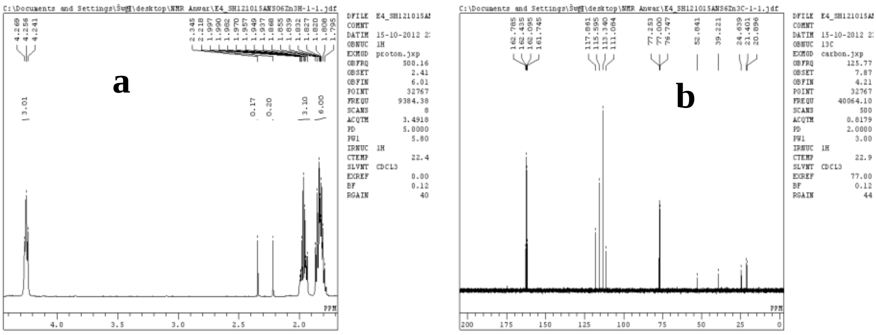


Fig. 3. a) ^{1}H-NMR, and b) ^{13}C-NMR of Zn(bpy)(leu).

Table 3. ^{1}H-NMR & ^{13}C-NMR spectral data of Zn(II) complexes.

Comp.	^{1}H-NMR spectral data	^{13}C-NMR spectral data
01	δ; 2.21 (s, 2H), 7.3 (t, 4H, Ar-H), 7.5 (m, 4H, Ar-H), 7.6 (m, 4H, Ar-H), 8.2 (m, 4H, Ar-H) 8.5 (d, 1H, Ar-H), 9.2 (d, 1H, NH) ppm	δ; 76 (-CH-), 110, 112, 115, 118(Aromatic carbons), 120, 126, 127, 128, 129, 145, 165 (C=O) ppm
02	δ; 7.3 (s, 7H, Ar-H), 7.75 (m, 6H, Ar-H), 7.90 (m, 6H, Ar-H), 8.5 (m, 1H, Ar-H) 9.20 (m, 1H, Ar-H) ppm	δ; 77 (-CH-), 110, 113, 115, 117(Aromatic carbons), 130, 133, 162(C=N), 173(C=O) ppm
03	δ; 1.82 (s, 6H,-CH_3), 1.83 (s, 3H-CH_2), 4.4 (s, 3H), 7.20 (s, 7H, Ar-H) ppm	δ; 20, 21, 24 (CH_3, CH_2), 39, 52, 75, 111(Aromatic carbons), 161, 162(C=N) ppm

As an additional support for the above conclusions, the FAB mass spectra of the complexes were recorded. In the FAB mass spectrum of complex 1, the molecular ion peak is observedd at *m*/*z* 460, which is in agreement with the molecular weight (460) of the proposed structure. The spectrum showed a peak at *m*/*z* 307, which is assigned to 4,4´-bipyridine. The molecular ion loses CH_3 giving an ion at *m*/*z* 289. This ion lost the rest of diphenic acid molecule giving an ion at *m*/*z* 154. The molecular ion gave a peak at *m*/*z* 89 for free metal ion.

In the FAB mass spectrum of complex 2, the molecular ion peak is observed at *m*/*z* 459, which is in agreement with the molecular weight (459) of the proposed structure. The spectrum showed a peak at *m*/*z* 307, which is assigned to 4,4´-bipyridine. The molecular ion loses CH_3 giving an ion at *m*/*z* 289. This ion lost the rest of phthalic acid molecule giving an ion at *m*/*z* 154. The molecular ion gave a peak at *m*/*z* 89 for free metal.

In the FAB mass spectrum of complex 3, the molecular ion peak is observed at *m*/*z* 458, which is in agreement with the molecular weight (458) of the proposed structure. The spectrum showed peaks at *m*/*z* 307 and *m*/*z* 154, which are assigned to luecine. The molecular ion finally lost leucine giving *m*/*z* at 57 for metal.

Table 4. FAB$^+$ mass spectral data of the Zn(II) complexes.

Comp.	FAB$^+$ mass spectral data
01	460.2, 307.2, 289.1, 154.1, 136.1, 107.0, 89.0
02	459.0, 307.2, 289.2, 154.1, 107, 89.
03	459.0, 307.2, 289.2,154.10, 136.10, 107.0, 89.0, 57.0

Magnetic susceptibility is recorded at room temperature on Faraday balance and the negative magnetic moments of complexes 1- 3 suggest that the central metal ion is diamagnetic. As the complexes have no unpaired electrons, the above complexes are expected to have the tetrahedral geometry [32].

The anti-inflammatory activities [27] of the test compounds were determined using the carrageenan-induced mice paw edema inhibition method [31] employing 1.0% carrageenan solution as the phlogistic agent. The test compounds were administered orally as suspensions in 3% DMSO, 30 min before the ingection of the phlogistic agents, at dose level of 10 mg/kg (p.o) body weight. Diclofenac sodium was used as a standard at a dose level of 10 mg/kg (p.o) body weight. 3% DMSO served as a control. Groups of four Swiss albino mice of either sex were used in each experiment. The volume of paw edema was measured with the help of plethysmograph by mercury displacement method at 0 h (immediately after injection of carrageenan). Then, the volume of paw edema was observed at 1, 2, 3 and 4 h. The results are presented in Table 5.

Table 5. Anti-inflammatory activity of the test compounds by carrageenan induced paw edema in mice.

Comounds	Dose (mg/kg	0.5 hr	1 hr	2 hr	3 hr
Comp-1	10	0.33	0.31	0.27	0.19
Comp-2	10	0.34	0.31	0.27	0.20
Comp-3	10	0.33	0.30	0.26	0.19

Inhibition of paws volume with respect to control (untreated) after incubation of carrageenan.

Number of mice in each group was three. Table 5 showed that volume of hinds paw edema decreased with time. In the carrageenan-induced mice paw edema test for acute inflammation, the test compounds at doses of 10 mg/kg showed that the volume of paw edema decreased with time. This has almost the same effect compared to the standard drug diclofenac sodium.

The analgesic activity of the test samples were studied [28] using acetic acid-induced writhing model in mice. Swiss albino mice of either sex were divided into control, standard and different test groups contained four mice in each. The control group received 3% DMSO and standard group was treated with diclofenac sodium at a dose level of 10 mg/kg (p.o.). Test samples and vehicle were administered orally 30 min before intraperitoneal administration of 0.6% acetic acid but diclofenac sodium was administered intraperitonially 15 min before injection of acetic acid. After an interval of 5 min, the mice were observed for specific contraction of body referred to as ‘writhing’ for the next 30 min. The results are given in Table 6.

Table 6. Effects of test compounds on acetic acid induced writhing test in mice.

Compounds	Dose (mg/kg)	No. of mice	No. of writhing	
			before administration	after administration
Comp-1	10	03	10	7
Comp-2	10	03	20	15
Comp-3	10	03	27	20

Table 6 showed the effect of the test compounds on acetic acid-induced writhing in mice. Percentage of inhibition was found to be 70-78% in statistical calculations considering diclofenac sodium as standard.

4. Conclusion

Synthesis and characterization of complexes containing N and O-donor ligands have been described in this paper. Based on analytical, conductance, magnetic and spectral data, all these complexes are assigned to be in tetrahedral geometry. 4, 4´-bipyridine coordinates through N^- and organic/amino acids through COO^- and NH_2 to Zn(II). Anti-inflammatory and analgesic activities of the test compounds at 50 mg/kg are quite comparable to those of standard drugs at 10 mg/kg.

Acknowledgment

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