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Macromolecules

An Indian Journal

Full Paper

MMAIJ, 3(3), 2007 [91-95]

Synthesis And Spectral Studies Of New Schiff Base Macrocyclic Zn(II) Complexes

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Received: 10th July, 2007 ; Accepted: 15th July, 2007

ABSTRACT

Ten new types of Zn(II) complexes were synthesized by template effect by reaction of 2,6-diaminopyridine with $Zn(ClO_4)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and salicylaldehyde derivatives in chloroform-methanol. The complexes have been characterized by elemental analysis, IR, ¹H NMR, UV-vis spectra, magnetic susceptibility, conductivity measurements and mass spectra. On the bases of the spectral studies four coordinated tetrahedral geometry may be assigned to these complexes.

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KEYWORDS

Macrocyclic schiff bases;
Salicylaldehyde derivatives;
Zn(II) complexes.

INTRODUCTION

The chemistry of macrocyclic complexes has received much attention in recent years on account of its various applications in bioinorganic chemistry^[1-3]. Macrocyclic ligands containing a heteroatom are important complexing agents for cations, anions and molecules^[4-5]. The stability of macrocyclic metal complexes depends upon a number of factors, including the number and type of donor atoms present in the ligand and their relative positions within the macrocyclic skeleton, as well as the number and size of the chelate rings formed on complexation. For transition metal ions, features such as the nature and magnitude of crystal-field effects play also an important role^[6]. Synthetic macrocycles are a growing class of compounds with varying chemistry a wide range of different molecular topologies and sets of donor atoms^[7-13]. Zinc is the second most abundant

trace metal in human body and plays an important role in many biological systems^[14-15]. Synthetic 1:1 Zn(II) macrocyclic polyamine complexes are especially interesting because of their importance in modelling the chemistry of zinc(II) containing enzymes, such as carbonic anhydrases^[16-19]. The Zn(II) ion has a very flexible and adaptable coordination sphere, but in most of the structurally characterised enzymes is found with a coordination number of four or five. Because of this most modelling studies have concentrated on tetradentate and pentadentate complexes of zinc and have paid less attention to investigating chelate complexes in which Zn(II) has a higher coordination number. In the present work, we have synthesized ten macrocyclic Schiff base complexes by reaction of ligands with $Zn(ClO_4)_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$. Then spectral, magnetic properties of the new compounds were studied in detail.

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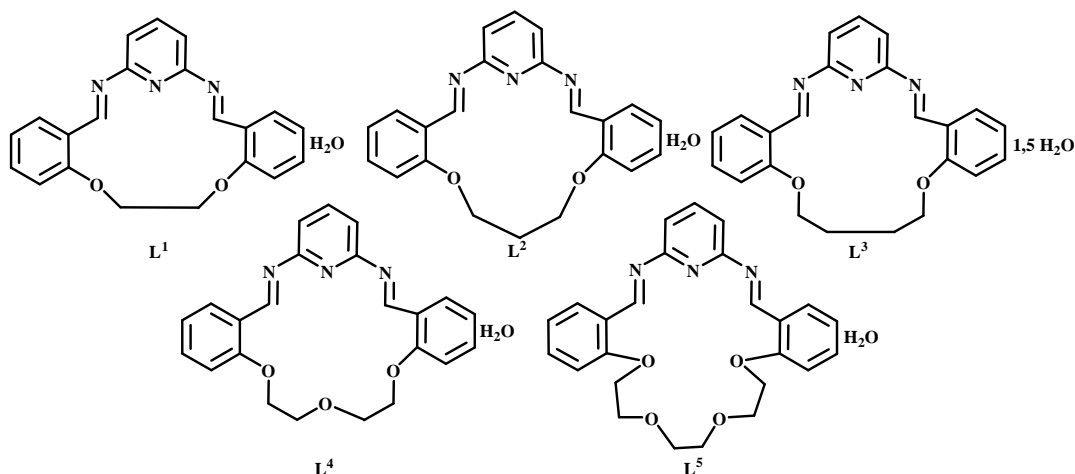


Figure 1 : The structure of the ligands

EXPERIMENTAL

Methods

Elemental analysis was carried out on a LECO CHNS model 932 elemental analyzer. $^1\text{H-NMR}$ spectra were recorded using a model Bruker Avance DPX-400 NMR spectrometer. IR spectra were recorded on a Perkin Elmer Spectrum RX1 FTIR spectrophotometer on KBr pellets in the wave number range of $4000\text{--}400\text{cm}^{-1}$. Electronic spectral studies were conducted on a Shimadzu model 160 UV Visible spectrophotometer in the wavelength $200\text{--}600\text{nm}$. Molar conductivity was measured with a WTW LF model 330 conductivity meter, using prepared solution of the complexes in DMSO solvent. Mass spectra were recorded using an Agilent model 1100 MSD mass spectrometer.

Chemical and starting materials

The ligands (Figure 1) used in the synthesis were prepared from salicylaldehyde derivatives with 2,6-diaminopyridine by the literature method^[20]. All the chemicals and solvents were of analytical grade and used as received.

Synthesis of complexes

To a stirred solution of ligands (2mmol) in chloroform (60mL) was added $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2mmol) in methanol (40mL) by dropwise. After the addition was completed, the stirring was continued for 2h. Then precipitate was filtered and washed with chloroform and methanol. Then dried in air.

Spectral characterization of $[\text{ZnL}^1(\text{ClO}_4)_2] \cdot \text{H}_2\text{O}$

Yield: 0.23g (18.4%). Anal Calcd. for $\text{ZnC}_{21}\text{N}_3\text{O}_{10}\text{Cl}_2 \cdot \text{H}_2\text{O}$: C, 40.32, H, 3.04, N, 6.72. Found: C, 40.62, H, 3.34, N, 6.78. $^1\text{H-NMR}$ (DMSO- d_6 , δ ppm): 3.41 (H_2O), 4.34 (s, 4H, $-\text{OCH}_2$), 7.00–8.02 (m, 11H, Ar-H), 10.38 (s, 2H, $\text{HC}=\text{N}$). Selected IR data (KBr, ν cm^{-1}): 3369 ν (H_2O), 3136 ν (Ar-CH), 2965, 2886 ν (Alph.-CH), 1661 ν (C=N), 1598 ν [(C=N)(pyridine)], 1455, 1450 ν (Ar-C=C), 1117, 626 ν (ClO_4^-), 1274, 1242 ν (Ar-O), 1141, 1038 ν (R-O), 755 ν (Substituted benzene), 515 ν (Zn-N). $\Lambda_M = 18 \text{ W}^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^2$ (in DMSO-DMF(1:1)). UV-vis (λ_{max} , nm) in DMSO-DMF(1:1): 274, 325, 377. Mass spectra (m/z): 625 $[[\text{ZnL}^1(\text{ClO}_4)_2] \cdot \text{H}_2\text{O}]^+$.

Yield: 0.35g (25.9%). Anal Calcd. for $\text{ZnC}_{22}\text{H}_{19}\text{N}_3\text{O}_{10}\text{Cl}_2 \cdot 3\text{H}_2\text{O}$: C, 42.24, H, 3.70, N, 6.22. Found: C, 42.35, H, 3.77, N, 6.18. $^1\text{H-NMR}$ (DMSO- d_6 , δ ppm): $\delta = 2.32$ (t, 2H, $J = 5.9 \text{ Hz}$) (CH_2), $\delta = 3.41$ (H_2O), $\delta = 4.36$ (t, 4H, $J = 6.2 \text{ Hz}$) (OCH_2), $\delta = 6.96\text{--}8.05$ (m, 11H, Ar-H), $\delta = 10.41$ (s, 2H, $\text{HC}=\text{N}$). Selected IR data (KBr, ν cm^{-1}): 3376 ν (H_2O), 3074 ν (Ar-CH), 2959, 2883 ν (Alph.-CH), 1655 ν (C=N), 1598 ν [(C=N)(pyridine)], 1491, 1456 ν (Ar-C=C), 1119, 624 ν (ClO_4^-), 1294, 1243 ν (Ar-O), 1161, 1043, ν (R-O), 755 ν (Substituted benzene), 519 ν (Zn-N). $\Lambda_M = 26 \text{ W}^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^2$ (in DMSO-DMF(1:1)). UV-vis (λ_{max} , nm) in DMSO-DMF(1:1): 278, 323, 374. Mass spectra (m/z): 622 $[\text{ZnL}^2(\text{ClO}_4)_2 + \text{H}]^+$.

Spectral characterization of $[\text{ZnL}^2(\text{ClO}_4)_2] \cdot 3\text{H}_2\text{O}$

Yield: 0.21g (15.6%). Anal Calcd. for $\text{ZnC}_{23}\text{H}_{21}\text{N}_3\text{O}_{10}\text{Cl}_2 \cdot 2\text{H}_2\text{O}$: C, 41.13, H, 3.26, N, 6.26. Found: C, 41.24, H, 3.46, N, 6.19. $^1\text{H-NMR}$ (DMSO- d_6 , δ ppm): $\delta = 2.32$ (t, 2H, $J = 5.9 \text{ Hz}$) (CH_2), $\delta = 3.41$ (H_2O), $\delta = 4.36$ (t, 4H, $J = 6.2 \text{ Hz}$) (OCH_2), $\delta = 6.96\text{--}8.05$ (m, 11H, Ar-H), $\delta = 10.41$ (s, 2H, $\text{HC}=\text{N}$). Selected IR data (KBr, ν cm^{-1}): 3376 ν (H_2O), 3074 ν (Ar-CH), 2959, 2883 ν (Alph.-CH), 1655 ν (C=N), 1598 ν [(C=N)(pyridine)], 1491, 1456 ν (Ar-C=C), 1119, 624 ν (ClO_4^-), 1294, 1243 ν (Ar-O), 1161, 1043, ν (R-O), 755 ν (Substituted benzene), 519 ν (Zn-N). $\Lambda_M = 26 \text{ W}^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^2$ (in DMSO-DMF(1:1)). UV-vis (λ_{max} , nm) in DMSO-DMF(1:1): 278, 323, 374. Mass spectra (m/z): 622 $[\text{ZnL}^2(\text{ClO}_4)_2 + \text{H}]^+$.

Spectral characterization of $[\text{ZnL}^3(\text{ClO}_4)_2] \cdot 2\text{H}_2\text{O}$

Yield: 0.21g (15.6%). Anal Calcd. for $\text{ZnC}_{23}\text{H}_{21}\text{N}_3\text{O}_{10}\text{Cl}_2 \cdot 2\text{H}_2\text{O}$: C, 41.13, H, 3.26, N, 6.26. Found: C, 41.24, H, 3.46, N, 6.19. $^1\text{H-NMR}$ (DMSO- d_6 , δ ppm): $\delta = 2.32$ (t, 2H, $J = 5.9 \text{ Hz}$) (CH_2), $\delta = 3.41$ (H_2O), $\delta = 4.36$ (t, 4H, $J = 6.2 \text{ Hz}$) (OCH_2), $\delta = 6.96\text{--}8.05$ (m, 11H, Ar-H), $\delta = 10.41$ (s, 2H, $\text{HC}=\text{N}$). Selected IR data (KBr, ν cm^{-1}): 3376 ν (H_2O), 3074 ν (Ar-CH), 2959, 2883 ν (Alph.-CH), 1655 ν (C=N), 1598 ν [(C=N)(pyridine)], 1491, 1456 ν (Ar-C=C), 1119, 624 ν (ClO_4^-), 1294, 1243 ν (Ar-O), 1161, 1043, ν (R-O), 755 ν (Substituted benzene), 519 ν (Zn-N). $\Lambda_M = 26 \text{ W}^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^2$ (in DMSO-DMF(1:1)). UV-vis (λ_{max} , nm) in DMSO-DMF(1:1): 278, 323, 374. Mass spectra (m/z): 622 $[\text{ZnL}^2(\text{ClO}_4)_2 + \text{H}]^+$.

δ ppm): $\delta=1,34$ (t, 4H, $J=7.2$ Hz)(CH₂), $\delta=3,42$ (H₂O), $\delta=4,22$ (t, 4H, $J=5.8$ Hz, OCH₂), $\delta=7,02-8,04$ (m, 11H, Ar-H), $\delta=10,39$ (s, 2H, HC=N). Selected IR data(KBr, vcm^{-1}): 3381 ν (H₂O), 3067 ν (Ar-CH), 2942 ν (Aliph.-CH), 1659 ν (C=N), 1598 ν [(C=N)(pyridine)], 1486, 1453 ν (Ar-C=C), 1281, 1242 ν (Ar-O), 1162 ν (R-O), 754 ν (Substitue benzene), 522 ν (Zn-N). $\Lambda_M=24 \text{ W}^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^2$ (in DMSO-DMF(1:1)). UV-vis (λ_{max} , nm) in DMSO-DMF: 274, 326, 376. Mass spectra(m/z): 634 [[ZnL³(ClO₄)₂]-H]⁺.

Spectral characterization of [ZnL⁴(ClO₄)₂]-H₂O

Yield: 0.44g(32.9%). Anal Calcd. for ZnC₂₃H₂₁N₃O₁₁Cl₂H₂O: C, 41.26, H, 3.44, N, 6.28. Found: C, 41.44, H, 3.48, N, 6.42. ¹H NMR(DMSO-d₆, δ ppm): $\delta=3.5$ (H₂O), $\delta=3.86$ (t, 4H, $J=4.5$ Hz)(OCH₂), $\delta=4.34$ (t, 4H, $J=4.4$ Hz)(CH₂Oph), $\delta=6.98-8.11$ (m, 11H, Ar-H), $\delta=10.39$ (s, 2H, HC=N). Selected IR data(KBr, vcm^{-1}): 3379 ν (H₂O), 3066 ν (Ar-CH), 2937 ν (Aliph.-CH), 1657 ν (C=N), 1598 ν [(C=N)(pyridine)], 1485, 1453 ν (Ar-C=C), 1285, 1243 ν (Ar-O), 1161 ν (R-O), 755 ν (Substitue benzene), 511 ν (Zn-N). $\Lambda=29 \text{ W}^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^2$ (in DMSO-DMF(1:1)). UV-vis (λ_{max} , nm)(DMF-DMSO(1:1)): 273, 324, 376. Mass spectra(m/z): 552 [ZnL⁴(ClO₄)]⁺.

Spectral characterization of [ZnL⁵(ClO₄)₂]-H₂O

Yield: 0.76g(53.3%). Anal Calcd. for ZnC₂₅H₂₅N₃O₁₂Cl₂H₂O: C, 42.08, H, 3.79, N, 5.89. Found: C, 42.04, H, 3.86, N, 5.95. ¹H NMR(DMSO-d₆, δ ppm): $\delta=3.36$ (t, 4H, $J=5.1$ Hz, H1), $\delta=3.46$ (H₂O), $\delta=3.83$ (t, 4H, $J=4.2$ Hz)(H2), $\delta=4.27$ (t, 4H, $J=4.25$ Hz)(H3), $\delta=7.02-8.00$ (m, 11H, Ar-H), $\delta=10.40$ (s, 2H, HC=N). Selected IR data(KBr, vcm^{-1}): 3371 ν (H₂O), 3068 ν (Ar-CH), 2938 ν (Aliph.-CH), 1656 ν (C=N), 1598 ν [(C=N)(pyridine)], 1487, 1452 ν (Ar-C=C), 1286, 1243 ν (Ar-O), 1161 ν (R-O), 755 ν (Substitue benzene), 514 ν (Zn-N). $\Lambda=31 \text{ W}^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^2$ (in DMSO-DMF(1:1)). UV-vis(λ_{max} , nm) in DMSO-DMF(1:1): 274, 325, 377. Mass spectra(m/z): 595 [ZnL⁵(ClO₄)]⁺.

9. Spectral characterization of [ZnL¹(NO₃)₂]-2H₂O

Yield: 0.65g(57.2%). Anal Calcd. for ZnC₂₁H₁₇N₅O₈·2H₂O: C, 44.37, H, 3.70, N, 12.32. Found: C, 44.47, H, 3.74, N, 12.28. ¹H NMR(DMSO-d₆, δ ppm): 3.40(H₂O), 4.35(s, 4H, -OCH₂), 6.99-8.01(m, 11H, Ar-H), 10.39(s, 2H, HC=N). Selected IR data(KBr, vcm^{-1}): 3372 ν (H₂O) 3071 ν (Ar-CH), 2967, 2882

ν (Alph.-CH), 1655 ν (C=N), 1598 ν [(C=N)(pyridine)], 1454, 1452 ν (Ar-C=C), 1164, 655 ν (NO₃⁻), 1276, 1242 ν (Ar-O), 1140, 1039 ν (R-O), 752 ν (Substitued benzene), 519 ν (Zn-N). $\Lambda_M=28 \text{ W}^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^2$ (in DMSO-DMF(1:1)). UV-vis(λ_{max} , nm) in DMSO-DMF(1:1): 276, 326, 374. Mass spectra(m/z): 533 [ZnL¹(NO₃)₂+H]⁺.

Spectral characterization of [ZnL²(NO₃)₂]-H₂O

Yield: 0.69g(61.2%). Anal Calcd. for ZnC₂₂H₁₉N₅O₈·H₂O: C, 46.81, H, 3.72, N, 12.41. Found: C, 47.04, H, 3.81, N, 12.32. ¹H NMR(DMSO-d₆, δ ppm): $\delta=2.33$ (t, 2H, $J=5.7$ Hz)(CH₂), $\delta=3.41$ (H₂O), $\delta=4.36$ (t, 4H, $J=6.1$ Hz)(OCH₂), $\delta=6.97-8.03$ (m, 11H, Ar-H), $\delta=10.40$ (s, 2H, HC=N). Selected IR data(KBr, vcm^{-1}): 3374 ν (H₂O), 3076 ν (Ar-CH), 2966, 2887 ν (Alph.-CH), 1654 ν (C=N), 1598 ν [(C=N)(pyridine)], 1488, 1452 ν (Ar-C=C), 1161, 654 ν (NO₃⁻), 1292, 1242 ν (Ar-O), 1162, 1046, ν (R-O), 752 ν (Substitued benzene), 526 ν (Zn-N). $\Lambda=29 \text{ W}^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^2$ (in DMSO-DMF(1:1)). UV-vis(λ_{max} , nm) in DMSO-DMF(1:1): 277, 325, 376. Mass spectra(m/z): 546 [ZnL²(NO₃)₂]⁺.

Spectral characterization of [ZnL³(NO₃)₂]-2H₂O

Yield: 0.72g(60.4%). Anal. Calcd. for ZnC₂₃H₂₁N₅O₈·2H₂O: C, 46.31, H, 4.19, N, 11.74. Found: C, 46.41, H, 4.26, N, 11.56. ¹H NMR(DMSO-d₆, δ ppm): $\delta=1,36$ (t, 4H, $J=6.2$ Hz)(CH₂), $\delta=3,43$ (H₂O), $\delta=4,26$ (t, 4H, $J=5.6$ Hz, OCH₂), $\delta=7,01-8,01$ (m, 11H, Ar-H), $\delta=10,39$ (s, 2H, HC=N). Selected IR data(KBr, vcm^{-1}): 3380 (H₂O), 3073 ν (Ar-CH), 2946 ν (Aliph.-CH), 1652 ν (C=N), 1598 ν [(C=N)(pyridine)], 1482, 1452 ν (Ar-C=C), 1282, 1241 ν (Ar-O), 1161 ν (R-O), 754 ν (Substitue benzene), 526 ν (Zn-N). $\Lambda=29 \text{ W}^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^2$ (in DMSO-DMF(1:1)). UV-vis(λ_{max} , nm) in DMSO-DMF: 276, 324, 377. Mass spectra(m/z): 561[[ZnL³(NO₃)₂]+H]⁺.

Spectral characterization of [ZnL⁴(NO₃)₂]-2H₂O

Yield: 0.70g(57.2%). Anal Calcd. for ZnC₂₃H₂₁N₅O₉·2H₂O: C, 45.10, H, 4.08, N, 11.44. Found: C, 45.04, H, 4.18, N, 11.52. ¹H NMR(DMSO-d₆, δ ppm): $\delta=3.5$ (H₂O), $\delta=3.83$ (t, 4H, $J=4.6$ Hz)(OCH₂), $\delta=4.36$ (t, 4H, $J=4.4$ Hz)(CH₂Oph), $\delta=6.95-8.07$ (m, 11H, Ar-H), $\delta=10.41$ (s, 2H, HC=N). Selected IR data(KBr, vcm^{-1}): 3373 ν (H₂O), 3067 ν (Ar-CH), 2936 ν (Aliph.-CH), 1656 ν (C=N), 1598 ν [(C=N)(pyridine)], 1487, 1451 ν (Ar-C=C), 1286, 1242 ν (Ar-O), 1159 ν (R-O), 752

Full Paper

$\nu(\text{Substitue benzene})$, 511 $\nu(\text{Zn-N})$. $\Lambda=29 \text{ W}^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^2$ in DMSO-DMF(1:1). UV-vis(λ_{max} , nm)(DMF-DMSO(1:1)): 273, 325, 377. Mass spectra(m/z): 515 $[\text{ZnL}^4(\text{NO}_3)_2\text{H}]^+$.

Spectral characterization of $[\text{ZnL}^5(\text{NO}_3)_2]\text{H}_2\text{O}$

Yield: 0.45 g(35.3%). Anal Calcd. for $\text{ZnC}_{25}\text{H}_{25}\text{N}_5\text{O}_{10}\text{H}_2\text{O}$: C, 47.02, H, 4.23, N, 10.97. Found: C, 47.04, H, 4.31, N, 10.85. $^1\text{H NMR}$ (DMSO- d_6 , δ ppm): $\delta=3.36$ (t, 4H, $J=5.2\text{Hz}$, H1), $\delta=3.43$ (H_2O), $\delta=3.84$ (t, 4H, $J=4.2\text{Hz}$)(H2), $\delta=4.25$ (t, 4H, $J=4.3\text{Hz}$)(H3), $\delta=7.00-8.02$ (m, 11H, Ar-H), $\delta=10.41$ (s, 2H, HC=N). Selected IR data(KBr, vcm^{-1}): 3376 $\nu(\text{H}_2\text{O})$, 3069 $\nu(\text{Ar-CH})$, 2936 $\nu(\text{Aliph.-CH})$, 1656 $\nu(\text{C=N})$, 1598 $\nu[(\text{C=N})(\text{pyridine})]$, 1487, 1451 $\nu(\text{Ar-C=C})$, 1288, 1242 $\nu(\text{Ar-O})$, 1161 $\nu(\text{R-O})$, 755 $\nu(\text{Substitue benzene})$, 520 $\nu(\text{Zn-N})$. $\Lambda=33 \text{ W}^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^2$ (in DMSO-DMF(1:1)). UV-vis(λ_{max} , nm) in DMSO-DMF(1:1): 275, 325, 375. Mass spectra(m/z): 496 $[\text{ZnL}^5]^+$.

RESULT AND DISCUSSION

Macrocyclic schiff base complexes

In this work, we have found that in the reaction between schiff base macrocyclic ligands(dissolved in chloroform) with zinc(II) perchlorate or zinc(II) nitrate(dissolved in methanol), the [1+1] macrocycle Schiff-base complexes are formed as the major product. The macrocyclic complexes were characterized by elemental analysis, mass, IR and UV-Vis spectrometry. The mass spectrum of complexes plays an important role in confirming the monomeric [1+1](ligands and metal salt) nature of complexes. On the bases of the spectral studies four coordinated tetrahedral geometry may be assigned to these complexes(Figure 2). The ligand is soluble

in DMSO, DMF, CHCl_3 , CH_2Cl_2 and CH_3CN but insoluble H_2O , EtOH and MeOH. The complexes are air stable, partly soluble in DMF, DMSO and insoluble CHCl_3 , CH_2Cl_2 and CH_3CN . As the crystals were unsuitable for single-crystal X-ray structure determination and are insoluble in most common solvents, including water, ethanol, ethyl acetate, and acetonitrile.

The characteristic infrared spectrum data are given in the experimental section. Infrared spectra of Zn(II) complexes were recorded in KBr pellet from 4000 to 400cm^{-1} . The IR spectra of all complexes shows $\nu(\text{C=N})$ bands at $1650-1665\text{cm}^{-1}$ [221] and it is found that the $\nu(\text{C=N})$ bands in the complexes are shifted by about ca. 35cm^{-1} to lower energy regions compared to that in the free ligands(L). This phenomenon appears to be due to the coordinated of azomethine nitrogen to the metal ion[22]. The broad bands within the range $3380-3360\text{cm}^{-1}$ for all Zn(II) complexes can be attributed to stretching vibrations of water molecule $\nu(\text{H}_2\text{O})$ [23]. In the spectra of all the Zn(II) metal complexes are dominated by bands between $2960-2890 \text{cm}^{-1}$ due to $\nu(\text{Alph.-CH})$ groups[24]. The absorptions of the nitrate counterions, at ca. $1460-1452(\nu_3)$, $1300(\nu_1)$ and $1040(\nu_2)\text{cm}^{-1}$ suggest the presence of bidentate nitrate groups. An intense band at 1384cm^{-1} is attributed to the presence of the ionic nitrate[25]. The IR spectra of the complexes clearly demonstrated that the COC and CCO stretching vibrations are altered compared to ligands due to conformational changes. The fact that the C-O-C absorptions of the complexes are shifted to lower wave numbers compared to that of the ligand also confirms the complex formation[26]. Conclusive evidence of the bonding is also shown by the observation that new bands in the IR spectra of the Zn(II) complexes appear at $510-530\text{cm}^{-1}$ assigned to $\nu(\text{Zn-N})$

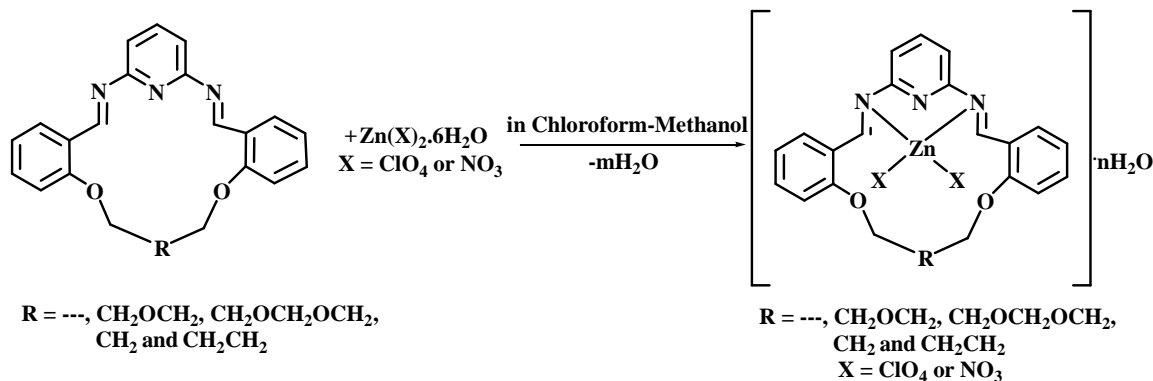


Figure 2 : Synthesis and suggested structure of the complexes

stretching vibrations^[27].

Electronic absorption spectral data of Zn(II) complexes in dimethylsulfoxide-dimethylformamide (DMSO-DMF) at room temperature that are presented in experimental section. The electronic spectra of Zn(II) complexes in DMSO-DMF show three peaks in the visible-ultraviolet region. The absorption bands below 300nm are practically identical and can be attributed to $\pi \rightarrow \pi^*$ transitions in the benzene ring and azomethine (-C=N) groups. The absorption bands observed within the 320-380nm range are most probably due to the transitions of $n \rightarrow \pi^*$ of imine groups^[28].

¹H NMR of the the complexes in DMSO-d₆ solution show that they are NMR active. The ¹H NMR spectrum of the free ligand showed a singlet at 10.4 ppm due to the imine protons, multiplet in the range 7.1-8.0ppm due to the aromatic protons, and H₂O proton at 3.4ppm. The ¹H NMR spectra of the complexes exhibited almost the same values with that of the ligand. Although we expected a shift on the position of CH=N signal for the NMR spectra of the complexes, no significant shift could not be observed^[21, 23, 24, 28].

The molar conductivities of the compounds in DMSO-DMF(1:1) are range 27-44 $\Omega^{-1}\text{mol}^{-1}\text{cm}^{-2}$ reported for non electrolytes^[21, 23, 24, 28].

The mass spectrum of Zn(II) with L¹, L², L³, L⁴, L⁵ play an important role in conforming the monomeric [1+1] (dicarbonyl and diamine) nature of the complexes. The mass spectra of the complexes of zinc peaks attributable to the molecular ions 625[[ZnL¹(ClO₄)₂·H₂O]⁺, 622 [ZnL²(ClO₄)₂+H]⁺, 634[[ZnL³(ClO₄)₂]-H]⁺, 552 [ZnL⁴(ClO₄)₂]⁺, 595 [ZnL⁵(ClO₄)₂]⁺, 533[ZnL¹(NO₃)₂+H]⁺, 546 [ZnL²(NO₃)₂]⁺, 561 [[ZnL³(NO₃)₂]+H]⁺, 515 [ZnL⁴(NO₃)₂+H]⁺, 496 [ZnL⁵]⁺ [29, 30].

REFERENCES

- [1] N.Raman, C.Thangaraja; Trans, Metal Chem., **30**, 317 (2005).
- [2] S.E.Castillo-Blum, N.Barbu-Behrens; Coord.Chem. Rev., **196**, 3 (2000).
- [3] S.Chandra, S.D.Sharma, U.Kumar; Synth.React. Inorg.Met.-Org.Chem., **34**, 79 (2004).
- [4] R.M.Izatt, K.Pawlak, J.S.Bradshaw; Chem.Rev., **95**, 2529 (1995).
- [5] A.A.Khandar, S.A.Hosseini-Yazdi, M.Khatamian, P.McArdle, S.A.Zarei; Polyhedron, **26**, 33 (2007).
- [6] L.Vance, N.W.Alcock, D.H.Busch, J.A.Heppert; Inorg.Chem., **36**, 5132 (1997).
- [7] K.Y.Choi, H.Y.Lee, B.Park, J.H.Kim, J.Kim, M.W.Kim, J.W.Ryu; Polyhedron, **20**, 2003 (2001).
- [8] T.W.Hambley, L.F.Lindoy, J.R.Reimers, P.Turner, W.Wei, A.N.W.Cooper; J.Chem.Soc., Dalton Trans., 614 (2001).
- [9] S.Chandra, L.K.Gupta, J.Saudi; Chem.Soc., **8**, 85 (2004); E.Q.Gao, H.Y.Sun, D.Z.Liao, Z.H.Jiang, S.P.Yan; Polyhedron, **21**, 359 (2002).
- [10] D.E.Fenton, R.Gauci, P.C.Junk, L.F.Lindoy, R.C.Luckay, G.V.Meehan, J.R.Price, P.Turner, G.Wei; J.Chem.Soc.Dalton Trans., 2185 (2002).
- [11] S.Chandra, K.Gupta; Trans.Met.Chem., **27**, 196 (2002).
- [12] S.Chandra, D.Jain, L.K.Gupta; J.Saudi Chem.Soc., **7** (2003).
- [13] S.Chandra, L.K.Gupta; Spectrochimica Acta, **A62**, 307 (2005).
- [14] W.N.Lipscomb, N.Straeter; Chem.Rev., **96**, 2375 (1996).
- [15] G.Parkin; J.Chem.Soc.Comm., 1971 (2000).
- [16] Kirchner, B.Kerbs; Inorg.Chem., **26**, 3569 (1987).
- [17] T.Koike, T.Gotoh, S.Aoki, E.Kimura, M.Shiro; Inorg.Chim.Acta, **270**, 424 (1998).
- [18] J.D.Curry, D.H.Busch; J.Am.Chem.Soc., **86**, 592 (1964).
- [19] H.Keypour, H.Khanmohammadi, K.P.Wainwright; Inorganica Chimica Acta, **355**, 286-291 (2003).
- [20] H.Temel, S.Ilhan; Spectrochimica Acta, Part A (in press).
- [21] S.Ilhan, H.Temel, I.Yilmaz, M.Sekerci; Polyhedron, **12**, 2795 (2007).
- [22] U.Cakyr, H.Temel, S.Ilhan, H.I.Ugras; Spectroscopy Letters, **36(5-6)**, 429 (2003).
- [23] S.Ilhan, H.Temel, I.Yilmaz, A.Kylyc; Trans, Metal.Chem., **32**, 3 (2007).
- [24] S.Ilhan, H.Temel, I.Yilmaz, M.Sekerci; Org.Chem., in press.
- [25] S.Ilhan, H.Temel, A.Kylyc; J.of Coord.Chem., (in press).
- [26] H.Temel, H.Hogoren, M.Boybay; Spectroscopy Letters, **34(5)**, 1 (2001).
- [27] S.Ylhan, H.Temel, A.Kylyc, E.Ta; J.Coord.Chem., in press.
- [28] S.Ylhan, H.Temel, R.Ziyadanogullary, M.Sekerci; Trans.Metal Chem., (2007).
- [29] Lodeiro, R.Batida, E.Bertolo, A.Macias, A.Rodriguez; Inorg.Chim.Acta, **343**, 133 (2003).
- [30] Lodeiro, R.Batida, E.Bertolo, A.Rodriguez; Can. J.Chem., **82**, 437 (2004).