

Phenoxy-bridged binuclear Zn(II) complex holding salen ligand: Synthesis and structural characterization



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ABSTRACT

A novel binuclear phenoxy-bridged zinc complex obtained from the interaction of ligand, 2,2-(1E,1E)-(2,2-dimethylpropane-1,3-diyl)bis(azanylylidene) bis(methanylylidene)diphenol with zinc chloride is reported. The synthesized and isolated zinc complex has been characterized by FT-IR, ¹H- and ¹³C- NMR, ESI-MS, TGA/DTA and single crystal X-ray diffraction studies. The phenoxy-bridge in this binuclear Zn(II) complex is due to the phenolic oxygen of the salen ligand. The complex crystallizes in monoclinic P-1 space group, and different geometry has been assigned for both zinc ions in the complex.

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1. Introduction

Salen ligands and their complexes have been extremely useful in coordination chemistry and catalysis [1], have been reported to catalyze various reactions of Lewis basic substrates playing important role in the synthesis of various biological compounds [2,3]. Moreover, salen based complexes have also been used as catalysts for polymer synthesis viz., living polymerization of olefins [4,5], ring-opening polymerizations of lactones [6] and lactide etc [7]. Among various salen complexes, zinc complexes have played an excellent role in catalysis for ring-opening polymerization of esters and ethers [8], isobutene polymerizations and copolymerization [8], and therefore, considered as models for hydrolytically active zinc enzymes [9], enzyme inhibition [10] and for the role of structural zinc in protein folding [10]. It has been reported that alkoxide or phenoxide groups are needed for the formation of binucleating ligands to bridge between two metal centers, and the remainder of the ligand usually requires further coordinating groups to retain the metal atoms and prevent formation of multinuclear arrays [11,12]. In continuation of our ongoing interest on salen ligand derived from 2-hydroxybenzaldehyde and 2,2-dimethyl-1,3-diaminopropane and its coordination property [13,14], hereby we report the synthesis and characterization of binuclear Zn(II) complex with formula $[Zn_2\mu(O-O)(N-N)Cl_2H_2O]$.

Various studies viz., elemental analyses FT-IR, ¹H and ¹³C NMR, ESI-MS and X-ray diffraction analysis has been used to characterize the synthesized zinc complex. The thermal stability of the complex has been studied in nitrogen atmosphere by using TGA/DTA study.

2. Experimental

2.1. Materials and methods

2-Hydroxybenzaldehyde, zinc chloride and 2,2-dimethyl-1,3-diaminopropane were purchased from Sigma–Aldrich. The other reagents and solvents were analytical grade reagents and used as received.

Elemental analysis was carried out on Elementar Varrio EL analyzer. NMR spectra of the complex were recorded with a JEOL spectrometer at 400 MHz (¹H NMR) and 100 MHz (¹³C NMR). The chemical shifts (δ in ppm) were reported downfield from tetramethylsilane (TMS, δ scale) with *d*₆-DMSO resonance referenced as the internal standard. FT-IR (4000–400 cm⁻¹) spectra were recorded as KBr pellets on a Perkin Elmer 621 spectrophotometer. Mass spectrometry was performed with a Micromass Quattro Premier tandem MS fitted with an ESI interface and controlled by MassLynx 4.1 software. MS/MS detection was performed in electrospray positive ionization mode.

2.2. Synthesis of complex, $[Zn_2(\mu-O)_2(L)Cl_2H_2O]$

To the stirred solution of ligand (0.25 mmol, 77 mg) in 10 ml

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methanol [13], we added methanol solution of zinc chloride (0.50 mmol, 68 mg) followed by the addition of 1 ml Et₃N. The reaction mixture was stirred for 2 h. A white precipitate is formed which is removed by filtration. The resulting filtrate was allowed to evaporate slowly at room temperature. After one week, yellow colored crystals suitable for single crystal X-ray diffraction measurements were separated out.

Yield 70%, color Yellow, Mp. 340 °C; molecular formula C₂₀H₂₆Cl₂N₂O₄Zn₂; Anal. Calc. C, 42.89; H, 4.68; N, 5.00%; Found: C, 42.95; H, 4.78; N, 5.07%. ¹H NMR (DMSO-d₆): δ (ppm) 8.33 (s, –CH=N), 7.25–6.87 (m, 8H, Ar–H), 3.48 (s, 4H, –CH₂), 1.24 (s, 6H, –C(CH₃)₂), ¹³C NMR (DMSO-d₆, 100 MHz): δ (ppm) 170.0 (–C=O), 161.8 (–CH=N), 118.0–133.5 (–C–Ar), 116.9 (C_c–Ar), 35.8 (OH–CH₃), 38.9 (C–(CH₃)₂), 24.3 (CH₃)₂–C, 70.0 (C–(CH₂)₂); IR (KBr cm^{–1}), 1645 ν(–CH=N), 2840 ν(–C–H), 3486 coordinated H₂O.

2.3. X-ray data collection, structure determination, and refinement

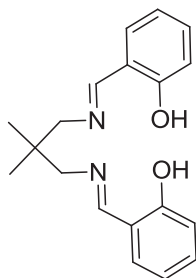
Single crystal X-ray diffraction data was collected on a Stoe IPDS-2 T diffractometer [$\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$, ω scan]. The structure was solved by direct methods using SHELXS-97 [15] and refined by full-matrix least squares methods using SHELXL-97 [16]. All non-hydrogen atoms were refined anisotropically. C-bound hydrogen atoms were placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. O-bound H atoms were located as residual electron density peaks and were refined isotropically without bond length restraints [17].

3. Results and discussion

The phenoxo-bridged zinc complex was synthesized by the reaction of ligand, H₂L with zinc chloride in 1:2 M ratio in methanol in basic medium (Scheme 1). The ligand, H₂L was synthesized by the condensation reaction of 2-hydroxybenzaldehyde and 2,2-dimethyl,1,3-diaminopropane in 2:1 M ratio in methanol following method reported in literature [13]. The complex was stable at room temperature, and soluble in common organic solvents. The structure of synthesized binuclear complex was confirmed on the basis of elemental analysis, ESI-MS, resonance signals in the ¹H and ¹³C NMR spectra and the characteristic bands in the FT-IR spectrum along with single crystal X-ray diffraction measurement.

3.1. Description of X-ray crystal structure

A perspective view of binuclear zinc complex is shown in Fig. 1. Crystal structure refinement, selected bond distances and angles are given in Tables 1–6. The crystal packing structure shows there are four crystallographically independent molecules in the asymmetric unit [Fig. 1S]. The coordination environment of Zn(II)



Scheme 1. Ligand, H₂L used in the synthesis of Zinc complex.

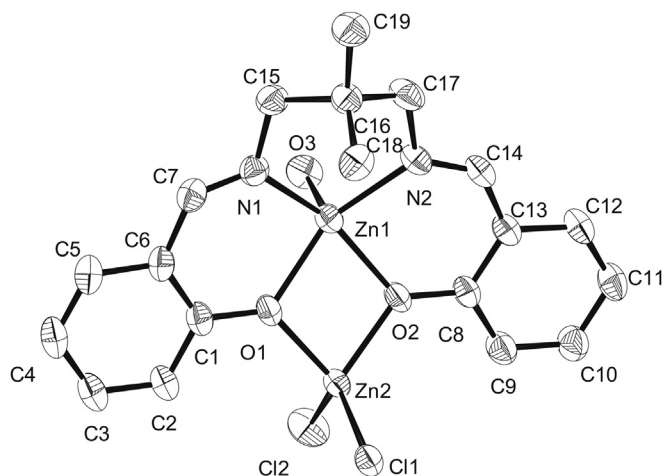


Fig. 1. Zinc complex showing ZnCl₂ moiety is two-fold disordered (in ratio 0.848(5):0.152(5)), only the predominant part is depicted. The water molecule at Zn₁ responds to this alternative environment by being disordered (over three sites).

Table 1

Crystal data and structure refinement for Zinc complex.

| | |
|-----------------------------------|---|
| Identification code | azam_a1_01 |
| Empirical formula | C ₂₀ H ₂₆ Cl ₂ N ₂ O ₄ Zn ₂ |
| Formula weight | 560.07 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Monoclinic, P21/n |
| Unit cell dimensions | a = 9.8027(6) Å alpha = 90° b = 19.5959(9) Å beta = 96.539(5)° c = 12.4891(7) Å gamma = 90° |
| Volume | 2383.5(2) Å ³ |
| Z, Calculated density | 4, 1.561 Mg/m ³ |
| Absorption coefficient | 2.264 mm ^{–1} |
| F(000) | 1144 |
| Crystal size | 0.24 × 0.20 × 0.15 mm |
| Theta range for data collection | 2.51–26.99° |
| Limiting indices | –11 ≤ h ≤ 12, –24 ≤ k ≤ 24, –15 ≤ l ≤ 15 |
| Reflections collected/unique | 18,398/5197 [R(int) = 0.0319] |
| Completeness to theta = 26.99 | 99.8% |
| Absorption correction | Integration |
| Max. and min. transmission | 0.7996 and 0.6516 |
| Refinement method | Full-matrix least-squares on F ² |
| Data/restraints/parameters | 5197/6/309 |
| Goodness-of-fit on F ² | 1.037 |
| Final R indices [I > 2sigma(I)] | R1 = 0.0299, wR2 = 0.0690 |
| R indices (all data) | R1 = 0.0427, wR2 = 0.0738 |
| Largest diff. peak and hole | 0.498 and –0.494 e.Å ^{–3} |

complex crystallize in monoclinic P-1 space group. There are two Zn(II) centers in the complex. One of which is five coordinated with pentagonal pyramidal geometry surrounded by two imine nitrogen atoms, two phenoxide oxygen atoms and one water molecule lying at the apex, while the second Zn(II) ion exists in square planar geometry surrounded by two phenoxide oxygen atoms and two chloride ions. The structure also contains one methanol molecule in the asymmetric unit. Its OH group points towards a Cl atom of the ZnCl₂ moiety. Moreover, two bridging oxygen atoms (μ -O–O) are located at the equatorial position of square pyramidal geometry, and the equatorial plane of the two zinc atoms are formed by these two phenoxo bridging anion. The μ -phenoxo oxygen atoms (O1 and O2) of the [Zn(salen)] chelates further coordinate to Zn₂ to form square planar. The Zn(1)–O(2) 2.0473(17) Å, Zn(1)–N(2) 2.049(2) Å, Zn(1)–N(1) 2.049(2) Å, Zn(1)–O(3) 2.055(2) Å, Zn(1)–O(1) 2.0573(17) Å bond distances are in the range observed for similar systems [18,19]. The observed angle for O(3)–Zn(1)–Zn(2) and N(1)–Zn(1)–

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