Synthesis, Structure and Fluorescence Properties of a Trinuclear Zn(II) Complex with $N,N,O$-donor Schiff Base Ligands and Bridging Acetates

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A new centrosymmetric trinuclear Zn(II) complex $[\text{Zn}_3\text{L}_2(\text{CH}_3\text{COO})_4]_\text{i}$ (I) has been synthesized by the reaction of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ with a tridentate $N,N,O$-donor Schiff base ligand $\text{HL} = \text{C}_5\text{H}_4\text{NC}(\text{CH}_3)=\text{NC}_6\text{H}_4(\text{OH})$ and systematically characterized by elemental analysis, FT-IR, UV/Vis and thermal methods. Single crystal X-ray structure analysis reveals that three Zn(II) centers are in two different coordination environments. Two terminal Zn(II) centers adopt a distorted square-pyramidal geometry leaving the central Zn(II) in a distorted octahedral environment. Two adjacent metal centers are connected through single $\mu_2$-phenolato as well as double $\mu$-acetato-$\text{O},\text{O}^\prime$-syn-$\text{syn}$ bridges. Fluorescence properties of the complex as compared to the ligand indicate that the former can serve as a potential photoactive material.

Key words: Trinuclear Schiff Base Complex, Five- and Six-coordinated Zinc(II), Crystal Structure, $\mu_2$-Phenolato and Double $\mu$-Acetato-$\text{O},\text{O}^\prime$-syn-$\text{syn}$ Bridges, Fluorescence

Introduction

Multidentate Schiff base ligands have played an important role in the development of coordination chemistry as they readily form reasonably stable complexes with most transition metal ions [1 – 3]. Schiff base transition metal complexes have been of great interest for many years [4] due to their important role in homogeneous or heterogeneous catalysis [5 – 9] and magnetism [10], and offer wide applications as antibacterial, antiviral and antifungal agents [11]. Schiff bases are also considered as potential anticancer drugs [12], and when administered as their metal complexes, the anticancer activity is enhanced in comparison to the free ligand [13, 14]. Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest [15, 16] because of their ability to possess unusual configurations, structural lability, and sensitivity to molecular environments [17]. Moreover, the design and synthesis of novel coordination compounds based on transition or non-transition metals and multifunctional bridging ligands is of great research interest, due to the interesting topologies and potential applications of the complexes as functional materials. Schiff base ligands have been proven to be very effective in constructing supramolecular architectures such as coordination polymers, including double and triple helicates [18, 19], due to their capacity to function as chelator as well as connector. In this connection, various bridging ligands have been used, such as carboxylates which are very effective due to their versatile bridging modes. Thus transition metal complexes with Schiff base ligands and bridging carboxylates have been of great interest for a long time.

Zinc(II) cations, due to their $d^{10}$ electronic configuration, form complexes with a flexible coordination environment, and the geometries of these complexes can vary from tetrahedral to octahedral, and severe distortions of the ideal polyhedra occur easily. Due to the general lability of $d^{10}$ metal ion complexes, the formation of coordination bonds is reversible which enables metal ions and ligands to rearrange during the process of self-organization to give highly ordered network structures. The terminal or blocking co-ligands, which are usually used along with the bridging ligand to complete the metal coordination sphere, can alter the supramolecular assembly and consequently the type of structure formed taking advantage of the flexibility of the coordination sphere. Zinc(II) chemistry plays an
important role in biological systems. Zinc-containing carboxylato-bridged complexes form a variety of structural motifs in hydrolytic metalloenzymes, such as phosphatases and aminopeptidases [20, 21]. The catalytic role of zinc comprises Lewis acid activation of the substrate, generation of a reactive nucleophile (Zn–OH) and stabilization of leaving groups. Zinc(II) Schiff base complexes have often been found to be photochemically active.

Working on Schiff base zinc(II) complexes [22, 23] with bridging carboxylates, we report herein a new centrosymmetric trinuclear zinc(II) Schiff base complex \([\text{Zn}_3\text{L}_2(\text{CH}_3\text{COO})_4]\) (1), obtained by the reaction of \(\text{Zn(CH}_3\text{COO})_2\cdot2\text{H}_2\text{O}\) with a tridentate \(\text{N,N,O}\)-donor Schiff base ligand \(\text{HL} = \text{C}_5\text{H}_4\text{NC(CH}_3\text{)=NC}_6\text{H}_4(\text{OH})\) (Scheme 1). Systematic characterization of the complex was done by microanalytical, FT-IR, UV/Vis and thermal methods. Single crystal X-ray structural analysis has revealed that two terminal and one central zinc(II) ions in 1 adopt distorted square pyramidal and distorted octahedral geometry, respectively. The trinuclear units are held together through \(\mu_2\)-phenolato and double \(\mu\)-acetato-\(\text{O,O'}\) syn-syn bridging modes. Fluorescent properties of 1 indicate its potential to act as a promising photoactive material.

**Results and Discussion**

**Fourier transform infrared spectra**

The solid-state Fourier transform infrared spectra of HL and 1 were recorded on an FT-IR spectrophotometer in the range 4000 – 200 cm\(^{-1}\). The samples were studied as powder dispersed in KBr pellets. For HL, a sharp strong peak for the imine (CH=N) group and a broad band for the phenolic OH group were observed at 1645 and 3398 cm\(^{-1}\), respectively. HL shows strong sharp bands at 1586, 1473 and 1430 cm\(^{-1}\) corresponding to the pyridine skeleton [24a].

However, the azomethine stretching frequency is lowered by 25 cm\(^{-1}\) in 1 and observed at 1620 cm\(^{-1}\), indicating the coordination of the imine (CH=N) nitrogen atom, as further supported by bands in the range 459 cm\(^{-1}\) corresponding to a \(v(\text{Zn–N})\) vibration. The absence of a peak around 3398 cm\(^{-1}\) in 1 indicates the absence of \(v(\text{OH})\) due to deprotonation followed by complexation [24b]. The bidentate bridging coordination mode of the acetate ion is revealed by the characteristic asymmetric and symmetric stretching vibrations at 1596 and 1446 cm\(^{-1}\), respectively. The difference, \(\Delta \nu [v_{\text{asym}}(\text{COO} – v_{\text{sym}}(\text{COO}))\] of 150 cm\(^{-1}\) is quite low as compared to 164 cm\(^{-1}\) observed in the ionic acetate [24c]. An additional medium band assigned to \(v(\text{Zn–O})\) at 365 cm\(^{-1}\) is observed for 1 [23]. Complex 1 also exhibits strong sharp bands in the regions 1605 – 1597, 1485 – 1460, 1445 – 1420, 1055 – 1040 and 1015 – 1005 cm\(^{-1}\), corresponding to the coordinated pyridine ring [24a].

**X-Ray crystal structure of \([\text{Zn}_3\text{L}_2(\text{CH}_3\text{COO})_4]\) (1)**

The crystal structure of 1 as revealed from the X-ray diffraction study consists of a trinuclear molecule with a central Zn(II) ion lying on a center of inversion. Fig. 1 shows an ORTEP view of 1 with the atom labeling scheme adopted. The trinuclear complex is built up of two mononuclear \(\text{ZnL}\) moieties linked through bridging acetate and \(\mu_2\)-phenolato groups to the central Zn atom. This structure is analogous to a previously reported manganese complex [25a]. The coordination geometry around the terminal Zn centers (Zn1 and Zn1#1) may be regarded as distorted square pyramidal, described by the Addison distortion parameter (\(\tau = 0.32\)) [25b] [the cisoid angles vary in the range of 76.11(5) – 118.98(5)\(^\circ\) and the transoid angles vary in the range of 133.61(5) – 152.61(5)\(^\circ\), respectively]. The equatorial plane of a terminal Zn atom (Zn1) is formed by the pyridine nitro-
Table 1. Selected bond lengths (Å) and angles (deg) for 1, with estimated standard deviations in parentheses.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(1)–O(3)</td>
<td>1.9826(13)</td>
<td>Zn(1)–O(5)</td>
</tr>
<tr>
<td>Zn(1)–O(1)</td>
<td>2.0214(12)</td>
<td>Zn(1)–N(2)</td>
</tr>
<tr>
<td>Zn(1)–N(1)</td>
<td>2.1486(14)</td>
<td>Zn(2)–O(1)</td>
</tr>
<tr>
<td>Zn(2)–O(4)</td>
<td>2.0852(12)</td>
<td>Zn(2)–O(2)</td>
</tr>
<tr>
<td>O(1)–Zn(1)–N(1)</td>
<td>76.11(5)</td>
<td>O(1)–Zn(2)–O(1)</td>
</tr>
<tr>
<td>O(2)–Zn(2)–O(2)</td>
<td>86.13(5)</td>
<td>O(3)–Zn(1)–O(1)</td>
</tr>
<tr>
<td>O(3)–Zn(1)–N(2)</td>
<td>95.90(5)</td>
<td>O(1)–Zn(1)–O(5)</td>
</tr>
<tr>
<td>O(5)–Zn(1)–N(1)</td>
<td>133.61(5)</td>
<td>O(3)–Zn(1)–O(5)</td>
</tr>
<tr>
<td>N(2)–Zn(1)–N(1)</td>
<td>76.11(5)</td>
<td>O(5)–Zn(1)–O(1)</td>
</tr>
<tr>
<td>O(1)–Zn(2)–O(4)</td>
<td>89.35(5)</td>
<td>O(5)–Zn(1)–N(2)</td>
</tr>
<tr>
<td>O(1)–Zn(2)–O(2)</td>
<td>90.18(5)</td>
<td>O(3)–Zn(1)–N(1)</td>
</tr>
<tr>
<td>O(4)–Zn(2)–O(2)</td>
<td>93.87(5)</td>
<td>O(3)–Zn(1)–O(5)</td>
</tr>
</tbody>
</table>

Equivalent atoms generated by symmetry code: (x, -y, z-2).

Table 2. Hydrogen bonding parameters (Å, deg) for 1.

<table>
<thead>
<tr>
<th>D–H···A</th>
<th>D–H</th>
<th>H···A</th>
<th>D···A</th>
<th>Z···D–H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(6)–H(6)–O(2)</td>
<td>0.95</td>
<td>2.47</td>
<td>3.163(3)</td>
<td>130</td>
</tr>
<tr>
<td>C(9)–H(9)–O(3)</td>
<td>0.95</td>
<td>2.46</td>
<td>3.329(2)</td>
<td>152</td>
</tr>
<tr>
<td>C(15)–H(15)–O(2)</td>
<td>0.95</td>
<td>2.54</td>
<td>3.399(2)</td>
<td>138</td>
</tr>
<tr>
<td>C(15)–H(15)–O(1)</td>
<td>0.95</td>
<td>2.46</td>
<td>3.311(2)</td>
<td>150</td>
</tr>
</tbody>
</table>

Equivalent atoms generated by symmetry codes: (x, -y, z-2).

Fig. 1. ORTEP view of 1 with crystallographic labeling scheme adopted. Displacement ellipsoids are shown at the 50% probability level. (Symmetry code to equivalent positions: #1 2, -x, -y, 2-z).

The three zinc ions are in a perfectly linear arrangement, with the terminal zinc ions. Thus two Schiff base ligands and acetate ions which coordinate the terminal zinc ions. Thus two Schiff base ligands and four acetate ions act as bridges between the two terminal zinc ions (Zn1 and Zn1#1) and the central zinc ion (Zn2). The four equatorial positions are occupied by the phenolato oxygen atoms O1/O1#1 in the phenolato oxygen atoms O1/O1#1 in the trans position [Zn2–O1 2.0706(12) Å], and two oxygen atoms O4/O4#1 of two acetate groups [Zn2–O4 2.0852(12) Å]. The two axial positions are occupied by O2/O2#1 [Zn2–O2 2.1295(13) Å] from the other two bridging acetate ligands. cisoid angles vary in the range observed for similar systems [25c].

There is no classical hydrogen bonding present, but there are several CH···O hydrogen bonds, the closest C···O distance being 2.46 Å. Selected bond lengths and angles are presented in Table 1, and the relevant hydrogen bonding parameters are summarized in Table 2, respectively.

Thermogravimetric analysis

The TGA curve of complex 1 indicates that the compound is stable up to 190 °C, above which it undergoes decomposition in two steps. A total mass loss of 27.6% per formula unit corresponds to the release of four acetate groups in the temperature range 191–289 °C, followed by the loss of two molecules of Schiff base ligand between 290–350 °C, corresponding to a total mass loss of 68.19%.

Absorption and fluorescence spectra of HL and I

The electronic absorption and emission spectra of HL and I recorded in dilute methanolic solutions are shown in the Fig. 2. The absorption spectrum of HL shows absorptions at 342 and 405 nm while I exhibits two absorption peaks at 382 and 445 nm. The absorption profile of I...
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properties of the complex, the normalized photoluminescence spectrum of 1 in methanolic solution was also recorded (Fig. 3). The emission maximum wavelength was found at 511 nm when 1 was exposed to light of 390 nm wavelength.

Conclusion

In this paper we have reported the synthesis and the spectral and structural characterization of a new trinuclear centrosymmetric zinc(II) Schiff base complex. The Zn(II) centers are in two different coordination environments. The two terminal Zn(II) centers are five-coordinate with distorted square-pyramidal geometry whilst the central Zn(II) is six-coordinate and adopts a distorted octahedral geometry. Terminal Zn(II) ions are attached to the central Zn(II) ion through double \( \mu_2 \)-phenolato as well as through double \( \mu \)-acetato-O,O’ syn-syn bridges. Fluorescence properties of the complex indicate that it can serve as potential photoactive material.

Experimental Section

Materials

All chemicals and solvents used for the syntheses were of analytical grade. Zn(CH\(_3\)COO\(_2\) \( \cdot \) 2H\(_2\)O (Fluka), 2-aminophenol (E. Merck), and 2-acetylpyridine (Aldrich Chemical Co. Inc.) were used as received.

Physical techniques

The Fourier transform infrared spectra of HL and 1 were recorded on a Perkin Elmer Spectrum RX I FT-IR spectrophotometer with a KBr disc in the range 4000 – 200 cm\(^{-1}\). Elemental analyses (C, H, and N) were carried out using a Perkin Elmer 2400 II elemental analyzer. Thermogravimetric analyses were carried out at a heating rate of 10 °C/min with a Mettler-Toledo star TGA/SDTA-851 e thermal analyzer system in a dynamic atmosphere of N\(_2\) (flow rate 80 mL/min) in an alumina crucible for the range 25 – 400 °C. The electronic absorption and fluorescence spectra were recorded on a Perkin Elmer Lambda-40 UV/Vis spectrometer and a Spex fluorolog II spectrofluorimeter, respectively.

Preparation of the ligand and the complex

Schiff base ligand: \([C_5H_4NC(CH_3)=N C_6H_4(OH)] (HL)\)

To have a better understanding of the effect of the ligand conformations on the photoluminescent properties of the complex, the normalized photoluminescence spectrum of 1 in methanolic solution was also recorded (Fig. 3). The emission maximum wavelength was found at 511 nm when 1 was exposed to light of 390 nm wavelength.

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