A soluble complex of Zn(II) with $N_2O_4$ core: A structural study

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A soluble complex of Zn(II) with 1-hydroxy-3-hydroxy-2-hydroxymethyl-2-(5′-formyl-salicylidimino) propane resulting in a distorted octahedral Zn$_2$O$_4$ core has been synthesized and characterized by analytical and spectral methods and the structure has been established by single crystal XRD.

Zinc is the second most abundant essential trace element found in the human body after iron and has been found to play important roles in catalyzing various reactions in biological systems as well as structurally stabilize various proteins by being present as Zn(II) ion in all such systems. Hence bioinorganic chemistry of zinc is certainly a challenging field of metalloenzymes. This demands for the development of zinc model complexes which are structurally diverse. Before checking their functional relevance the synthesized molecules are to be structurally characterized. As the complexes of similar type reported by us earlier were not water soluble the present studies were taken up with a view to synthesize a water soluble complex. Thus our group reported the metal ion complexes of the ligands, 1-hydroxy-2-methyl-2-salicylidimino propane, 1-hydroxy-3-hydroxy-2-methyl-2-salicylidimino propane and 1-hydroxy-3-hydroxy-2-hydroxymethyl-2-salicylidimino propane, using Ti(IV)\footnote{Department of Chemistry, University of Jyvaskyla, Jyvaskyla, Fin 40351, Finland}, mono- and di-oxoV(V)\footnote{Received 20 December 2002; revised 31 March 2003}, cis-dioxoMo(VI)\footnote{Received 20 December 2002; revised 31 March 2003}, trans-dioxoU(VI)\footnote{Received 20 December 2002; revised 31 March 2003}, Ni(II)\footnote{Received 20 December 2002; revised 31 March 2003}, Cu(II)\footnote{Received 20 December 2002; revised 31 March 2003} and Zn(II)$^{11}$ metal ion species.

**Experimental**

The compounds reported in this note were synthesized as given in Scheme 1 and characterized by analytical and spectral methods already reported in our earlier papers. Crystal structure determination of 3 was performed adopting the procedures reported earlier\textsuperscript{12} and the details of data collection and refinement are provided in ref 13.

**HL**$^1$, 1: This was synthesized as per the reported procedure\textsuperscript{14} and the product was obtained in the yield, 11.2 g (47.7%). m.p. 113-115°C; FTIR (KBr matrix, cm$^{-1}$): 3223($\nu_{OH}$), 1654,1621($\nu_{C=O}$), 1$^1$H NMR (CDCl$_3$, 300 MHz, ppm): 11.565 (s, 1H, O$_2$H), 10.016 (s, 1H, $HC=O$), 9.948 (s, 1H, $HC=O$), 8.166 (d, 1H, Ar-H, $J$ = 2.2 Hz), 8.097 (dd, 1H, Ar-H, $J$ = 2.2, 6.6, 1.8 Hz) and 7.135 (d, 1H, Ar-H, $J$ = 8.4 Hz). Anal. (%) Caled for C$_9$H$_8$O$_4$: C, 64.00; H, 4.00, Found: C, 64.06; H, 3.82.

**H$\Delta$L$^2$, 2: The compound was obtained from the reaction of 1 (3.01 g, 19.9 mmol) and 2-amino-2-(hydroxymethyl)-1,3-propanediol (tris) (4.86 g, 32.6 mmol) in acetonitrile (75 ml) upon refluxing for 8 h. The crude product was purified by using chloroform and diethyl ether to yield 6.8 g (82.5%). mp. 173-175°C; FTIR (KBr matrix, cm$^{-1}$): 3376, 3284($\nu_{OH}$), 1634($\nu_{C=O}$), 14.401 (d, 1H, $J$ = 2.2 Hz, Ar-H), 7.652 (d, 1H, $J$ = 2.6 Hz, Ar-H), 7.652 (dd, 1H, J = 2.2, J = 8.4 Hz). Anal. (%) Caled for C$_{10}$H$_{12}$O$_{5}$: C, 64.06; H, 6.29, Found: C, 64.06; H, 6.29.

**[Zn(H$\Delta$L$^2$)$_2$]CH$_3$OH**, 3: The compound was obtained from the reaction of 2 (0.200 g, 0.87 mmol) in 10 ml methanol and zinc acetate dihydrate (0.44 g, 1.74 mmol) upon refluxing for 8 h. Diffraction quality single crystals, 3.CH$_3$OH were obtained upon recrystallisation. The yield of the purified product was found to be 0.35g, 80%, m.p. 245°C (decomposition); FTIR (KBr matrix, cm$^{-1}$): 3376, 3284 ($\nu_{OH}$), 1633 ($\nu_{C=O}$), 1595 ($\nu_{C=O}$), 1$^1$H NMR (DMF-d$_6$, 300 MHz, ppm) 9.587 (s, 2H, $HC=O$), 8.394 (s, 4H, $HC=O$), 7.571-7.535 (m, 4H, Ar-H), 6.475 (d, 2H, J = 8.6 Hz, Ar-H), 5.772 (s, 2H, O$_2$H), 5.256 (s, 4H, O$_2$H), 3.620 (s, 12H, CH$_2$); UV-vis (H$_2$O:MeOH; 1:1), $\lambda$/nm (e/M$^+$cm$^{-1}$): 312 (65980), 260 (70588), FAB MS: m/z
Scheme 1—Step-wise synthesis of \( L^1 \), \( L^2 \), \( L^3 \), and the mononuclear Zn(II) complex, \([\text{Zn}\{L^1\}^2]_2 \). 3: (i) HCHO, conc. HCl, HCl gas, 4hrs; (ii) hexamine, \( \text{CH}_3\text{COOH}, \) refluxed 1 hr, conc. HCl, water, left overnight; (iii) tris, \( \text{CH}_3\text{CN}, \) reflux, 8hrs; (iv) zinc acetate, MeOH, reflux, 6hrs.

569 [M]+ Anal. Calcd for \( C_{24}H_{37}N_2O_lZn\cdot\text{CH}_3\text{OH} \): C, 48.31; H, 4.99, N, 4.51. Found: C, 47.76; H, 4.71; N, 4.98.

Results and discussion

The di-aldehyde, 1 (synthesized by us) was condensed with tris to result in the corresponding Schiff base molecule where only the aldehyde group ortho- to OH was converted but not the one para- to OH, even if two equivalents of tris were used. Thus, 1 results in the mono-Schiff's base 2, having a free aldehyde group rather than the bis-Schiff's base. Mono-Schiff's base 2 was characterized by analytical and spectral methods including mass spectrometry. The spectral change observed in 1600-1650 cm\(^{-1}\) region of the FTIR spectrum is also supportive of the formation of mono-Schiff's base. UV-vis spectra of ligand 2 shows three bands in UV region at 374, 312 and 257 nm. However, in the Zn complex the band at 374 changes into a broad shoulder. All the absorption coefficients are higher in the complex 3 as compared to its precursor ligand, 2.

The Zn(II) product 3 was characterized by analytical, spectral and crystallographic methods. Based on the analytical data, the complex was found to be mononuclear with metal ion to ligand ratio being 1:2. On complexation with Zn metal ion, in \(^1\text{H} \) NMR spectrum the imine proton \(-\text{HC}=\text{N}-\) shifts from 8.58 to 8.40 ppm and in the FTIR spectrum the stretching vibration of this group, \( \nu_{\text{C}=\text{N}} \), shifted from 1604 to 1595 cm\(^{-1}\). Both these spectral changes are in support of the binding of Zn(II) to \(-\text{HC}=\text{N}-\) group through nitrogen. All the three alcoholic hydroxyl protons and the three \(-\text{CH}_2\text{OH}\) groups of the precursor ligand 2 exhibit its resonance in \(^1\text{H} \) NMR at 5.20 ppm as cross checked by D\(_2\)O exchange experiment. However, when the ligand is bound to the Zn(II) center in 3, the corresponding resonance splits into two sets of \(-\text{OH}\) signals with 1:2 intensity ratio, of which one of the resonance was shifted down field by about 0.6 ppm indicating the binding of one \(-\text{CH}_2\text{OH}\) group to the Zn(II) center without deprotonation. The other two \(-\text{CH}_2\text{OH}\) groups are not bound to the metal ion center in the complex. \(^1\text{H} \) NMR spectrum of the precursor ligand 2 exhibited its phenolic proton resonance at 14.41 ppm which was further cross checked by D\(_2\)O exchange. However, this signal disappeared from the spectrum upon complexation with the Zn(II) ion indicating the loss of phenolic proton. FAB mass spectrum provided the molecular ion peak consistent with that obtained from X-ray structure.

Molecular and crystal structure of 3

The Zn(II) complex 3 crystallizes in monoclinic crystal system with C2/c space group and the Zn(II) center in the complex sits on a center of symmetry. The complex was found to be neutral and octahedral with 1:2 metal ion to ligand ratio. In the structure, each ligand acts as tridentate mono-anionic with the coordination being extended through phenolic-O\(^{-}\), imine N and \(-\text{OH}\) of one of the alcoholic \(-\text{CH}_2\text{OH}\).
groups. This resulted in a complex with ZnO4N2 core. The structure of the complex is shown as ORTEP in Fig. 1. The bond length and bond angles of the coordination sphere are given in Table 1. The bond length observed for Zn-O(H)CH2 (2.199 Å) is quite normal and is consistent with the binding of alcoholic -OH group without deprotonation. Zn-Ophen distance is clearly indicative of binding through deprotonated phenolate form. Other bond lengths exhibited by 3 are quite normal. The observed trans-angles (163.7 and 167) and the cis- angles (78.3 and 101.1) are substantially away from the idealized geometries and hence are suggestive of highly distorted geometry around Zn(II) center. In addition to the Zn-complex unit, each asymmetric unit contains a MeOH molecule.

In the lattice, the molecule exhibits four O-H...O and three C-H...O type of hydrogen bond interactions as shown in Fig. 2 (Table 2). The solvent methanol molecule extends one of the O-H...O interactions. Due to the extensive intermolecular interactions, the molecules are arranged in layers, and adjacent layers are further connected by O-H...O type of interactions where the aldehydic oxygen of one layer is acting as acceptor and the bound -CH2OH of the neighbouring layer is acting as donor, forming zig-zag type structure.

Conclusions

The study clearly indicates the formation of a mono Schiff’s base with one free aldehydic function still present in the molecule. Reaction of this molecule with Zn(II) resulted in the formation of a distorted octahedral complex with ZnO4N2 core in a metal ion to ligand ratio of 1:2. The Zn(II) complex is soluble in water-MeOH mixture in a volume ratio of 3:1 due to the presence of the free aldehydic -CHO function when compared to the Zn(II) complexes not possessing such free -CHO function\textsuperscript{12}. Therefore, the Zn(II) complex reported in this note is expected to be biologically important due to its solubility in water, a prerequisite for studying biological activity of inorganic complexes.

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Table 1—Selected bond lengths (Å) and bond angles(°) for 3, associated with the coordination sphere

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<td>Zn(1)-O(2)</td>
<td>2.040(2)</td>
<td>2.092(2)</td>
<td>2.199(2)</td>
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<tr>
<td>Zn(1)-N(10)</td>
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<td>2.092(2)</td>
<td>2.199(2)</td>
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<td>Zn(1)-O(13)</td>
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<td>2.199(2)</td>
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<tr>
<th>Bond angles</th>
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<td>O(2)-Zn(1)-N(10)</td>
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<td>N(10)-Zn(1)-N(10)#</td>
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Table 2—Hydrogen bond data for 3

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<tr>
<th>D-H...A</th>
<th>d(D-H) (Å)</th>
<th>d(H...A) (Å)</th>
<th>d(D...A) (Å)</th>
<th>&lt;(DHA) (°)</th>
<th>Symmetry</th>
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<tr>
<td>O(15)-H(15)...O(2)</td>
<td>0.840</td>
<td>1.890</td>
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<td>1.926</td>
<td>2.760</td>
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<td>O(100)-H(100)...O(17)</td>
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<td>1.991</td>
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<td>O(13)-H(13)...O(19)</td>
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<td>1.912</td>
<td>2.632</td>
<td>169.4</td>
<td>x+1/2,y+1/2,z-1/2</td>
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<td>C(16)-H(16B)...O(2)</td>
<td>0.990</td>
<td>2.588</td>
<td>3.429</td>
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<td>C(7)-H(7)...O(100)</td>
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<td>3.4007</td>
<td>152.2</td>
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# ‘D’ refers to donor center, ‘H’ refers to hydrogen atom and ‘A’ refers to the acceptor center.
Acknowledgement

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References

13. Crystal data for 3. Empirical formula: C_{32}H_{35}Ni_{1}O_{11}Zn; Formula weight:601; Crystal system: Monoclinic C2/c; Unit cell dimension (Å): a = 12.294(5), b = 11.221(3), c = 20.599(1), β = 90°; Space group: P21/c; Z = 4, D = 1.514 g/cm³; Independent reflections: 2433; Final R indices: R = 0.0285; Final R indices (all data): R = 0.0269; wR2 = 0.0718 and R indices (all data): R = 0.0279; wR2 = 0.0724. The crystallographic data is deposited with the Cambridge Crystallographic Data Centre with CCDC No. 207386.