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FORMATION OF BENZIMIDAZOLIUM SALT IN THE COMPLEXATION OF 2–SUBSTITUTED BENZIMIDAZOLE DERIVATIVE

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Abstract: In an attempted synthesis of Zn(II) complex of a tridentate ligand[2-((1H-benzimidazol-2-yl)methylamino)acetic acid] (BIG), benzimidazolium salt was formed instead of Zn(II) complex . Benzimidazolium salt was structurally characterized by single crystal X-ray diffraction . The compound is crystallized in the monoclinic system and crystallographic details of X-Ray structure of benzimidazolium salt are : Space group: $P2_1/c$, a (Å) = 7.021(6), b (Å) = 19.934(18), c (Å) = 9.869(9), V (Å^3) = 1371(2), α (º) = 90, β (º)= 96.858(14), γ (º)= 90, Z= 4, R factor was 0.1080 for 7381 observed reflections.

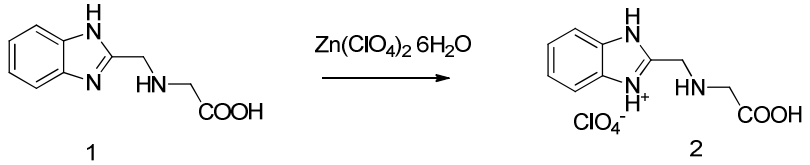
Keywords: Benzimidazolium salt, crystal structure , tridentate ligand

Introduction:

Benzimidazole based ligands are known to be strong chelating agents. These ligands are potential N donors and react easily with metal ions to give stable complexes. Several benzimidazole ligands [I,II] forms stable complexes with Zn(II) ions. Benzimidazole compounds possess broad spectrum of biological activities and were investigated for their anti HIV [III,IV], anticancer [V,VI], antibacterial, anti-inflammatory etc activities. The biological activity of most of the benzimidazole ligand systems was found to undergo significant enhancement on complexation. Hence in the present work an attempt is made to synthesise Zn(II) complexes of 2-((1H-benzimidazol-2-yl)methylamino)acetic acid ,BIG.

Experimental Section:

Synthesis of [BIGH]ClO_4.H_2O(2): 2-((6-R-1H-benzimidazol-2-yl)methylamino)acetic acid (0.250g, 1.12mmol) was dissolved in 25 mL water, to which 5 ml aqueous solution of $Zn(ClO_4)_2.6H_2O$ (0.450 g, 1.12 mmol) was added slowly and stirred for 5 min. The colourless solution obtained was filtered and kept for crystallization in desiccator over H_2SO_4. Good quality colorless single crystals obtained were collected after ten days. Yield: 0.20g (0.62 mmol, 51.2%).



1 2

Scheme 1

X-ray crystallography:

X-ray data was collected for **[BIGH]$ClO_4.H_2O$(2)** on a BRUKER-AXS SMART APEX CCD X-ray diffractometer, using graphite-monochromatic Mo Kα radiation (= 0.71073 Å). Data was reduced using SAINTPLUS[VII], and a multi-scan absorption correction using SADABS[VIII] was performed. The structures were solved using SHELXS-97[IX] and full matrix least-squares refinements against F^2 were carried out using SHELXL-97[X]. All ring hydrogen atoms were assigned on the basis of geometrical considerations and were allowed to ride upon the respective carbon atoms. All hydrogen atoms were assigned fixed U_{iso} values, equal to $1.2U_{eq}$ of the parent atom for ring and $1.5U_{eq}$ for methyl hydrogens. Crystallographic data and structure refinement parameters are presented in Table**1**.

Results and Discussion:

Crystal Structure [BIGH]$ClO_4.H_2O$(2): An attempted synthesis of complex of Zn(II) with BIG was not successful. The tridentate BIG did not coordinate to form a complex with Zn(II) ion. Instead of formation of a complex of Zn(II) , a benzimidazolium salt was formed. [BIGH]$ClO_4.H_2O$ has three nitrogen atoms, two in imadazole ring and another in secondary amine, two carboxylic oxygen atoms, one perchlorate ion and nine hydrogen atoms with a probability of hydrogen bonding interactions. Analysis of crystal structure obtained indicates the presence of one water molecule and one perchlorate ion. The ORTEP view of the compound **2** with labeling of non hydrogen atoms is shown in Figure 1. The crystal system is monoclinic and $P2_1/c$ space group with four molecules of BIG and four molecules of water and perchlorate ions. The data of analysis of bond lengths and bond angles are listed in Table 2&3. In this compound, the carboxylic acid oxygens are forming hydrogen bonds with nitrogen of imadazole ring (N—H···O) and methylene carbon of the 2° amine (C—H···O). These hydrogen bonds results in a dimeric unit and the perchlorate ion stands in the cavity of the dimeric unit.

Table 1: Crystallographic data and structure refinement for Quaternary ammonium salt.

Formula	$C_{10}H_{14}ClN_3O_7$	ρ_{calcd} (g cm^{-3})	1.568
Formula weight	323.69	μ (mm^{-1})	0.317
Crystal system	Monoclinic	θ Range (º)	2.04 to 25.00
a (Å)	7.021(6)	*h*/*k*/*l* indices	–8, 8/ –23, 23/ –11, 11
b (Å)	19.934(18)	Reflections collected	7381
c (Å)	9.869(9)	Unique reflection, R_{int}	1933, 0.0503
α (º)	90	GooF	1.469
β (º)	96.858(14)	$R_1[I > 2\sigma(I)]$	0.1080
γ (º)	90	wR_2 [all data]	0.4069
V (Å^3)	1371(2)	$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e.Å^{-3})	0.442, –0.503
Space group	$P2_1/c$	ρ_{calcd} (g cm^{-3})	1.568
Z	4	μ (mm^{-1})	0.317
T (K)	298(2)	θ Range (º)	2.04 to 25.00

Figure 1: ORTEP view of **[BIGH]$ClO_4.H_2O$**. The thermal ellipsoids are represented at the 30% probability level.

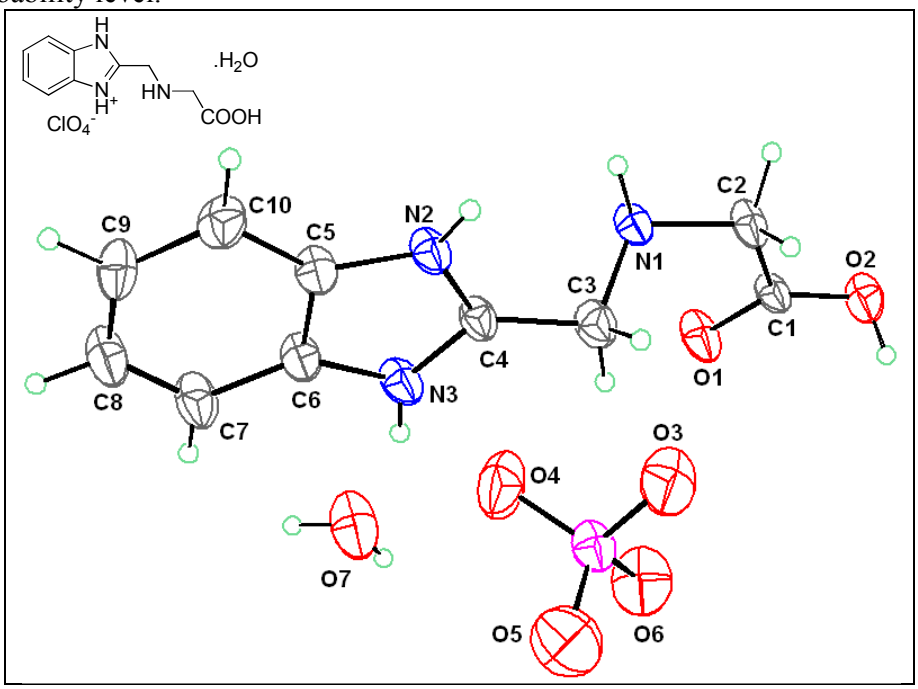


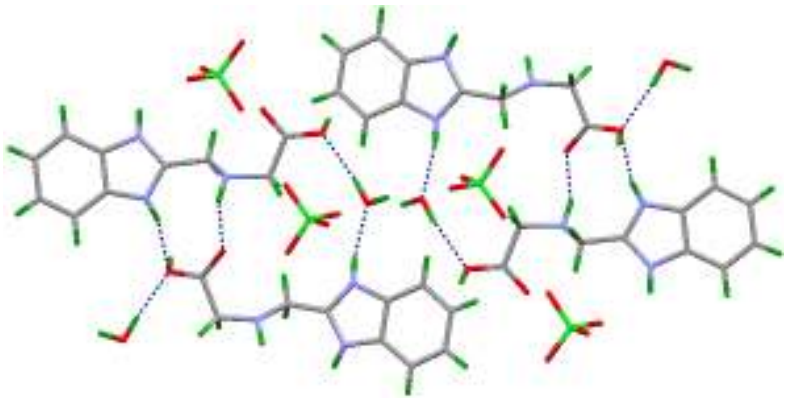
Table 2: Selected bond lengths (Å) for compound **[BIGH]$ClO_4.H_2O$**

Bond	Bond length(Å)	Bond	Bond length(Å)	Bond	Bond length(Å)
C1-O1	1.242(7)	C4-N3	1.349(8)	C8-C9	1.373(11)
C1-O2	1.259(8)	C5-N2	1.377(8)	C9-C10	1.365(10)
C1-C2	1.516(7)	C5-C10	1.403(9)	O3-Cl1	1.424(6)
C2-N1	1.499(8)	C5-C6	1.379(9)	O4-Cl1	1.421(7)
C3-C4	1.495(9)	C6-N3	1.387(8)	O5-Cl1	1.416(6)
C3-N1	1.487(9)	C6-C7	1.410(9)	O6-Cl1	1.431(8)
C4-N2	1.335(7)	C7-C8	1.361(11)		

Table 3: Selected bond angles (°) for compound **[BIGH]$ClO_4.H_2O$**

Angle	Bond angle(°)	Angle	Bond angle(°)	Angle	Bond angle(°)
O1-C1-O2	127.0(5)	N2-C5-C10	132.7(6)	C3-N1-C2	113.1(6)
O1-C1-C2	116.5(6)	C5-C6-C10	120.6(6)	C4-N2-C5	109.9(5)
O2-C1-C2	116.6(5)	C5-C6-N3	106.6(5)	C4-N3-C6	109.0(5)
N1-C2-C1	112.1(5)	C5-C6-C7	122.0(6)	O5-Cl1-O4	110.8(5)
N2-C4-N3	107.8(5)	N3-C6-C7	131.4(6)	O5-Cl1-O3	110.3(4)
N1-C3-C4	112.3(6)	C8-C7-C6	116.2(7)	O4-Cl1-O4	109.5(4)
N2-C4-C3	126.6(5)	C7-C8-C9	121.6(7)	O5-Cl1-O6	108.1(5)
N3-C4-C3	125.5(5)	C10-C9-C8	123.4(7)	O4-Cl1-O6	110.9(6)
N2-C5-C6	106.6(5)	C9-C10-C5	116.1(7)	O3-Cl1-O6	107.1(5)

Figure 2: View of the dimeric unit of Quaternary ammonium salt through hydrogen bonds.



Conclusion:

The result shows that instead formation of Zn(II)-BIG complex , benzimidazolium salt was formed as evidenced by the single crystal X-ray diffraction.

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