



Crystal structure analysis of dichloridobis(2-Isopropylimidazole)Zinc(II)

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Abstract: The Crystal structure of dichloridobis(2-Isopropylimidazole)Zinc(II)[Zn(2-Isopropylimidazole)₂Cl₂]. The structure of title compound, [C₁₂H₂₀Cl₂N₄Zn], Consists of centrosymmetric monomeric units, in which the Zn^{II} atom has a tetragonally distorted coordination involving two imidazole N atoms and two Cl atoms in the square plane [Zn-N = 1.998(1)Å and Zn-Cl = 2.2541(7)Å. The angles Cl-Zn-Cl and N-Zn-N are 110.34(4)° and 116.07(12)°, respectively. In the crystal there are no classical hydrogen bonds present. Crystal data were collected using CrysAlis CCD Oxford Diffraction X-ray diffractometer. The structure was solved by direct methods and refined on F² by full-matrix least-squares procedures to the final R₁ of 0.0370 using SHELXL programs.

Key Words: Imidazole, Zinc(II) and crystal structure.

Introduction

Recently, we are interested in the synthesis, structures and thermal properties of coordination polymers based on zinc(II) halides and N-donor ligands¹, we have started systematic investigation of their thermal behavior because we have demonstrated that new ligand-deficient coordination polymers can be conveniently prepared by thermal decomposition of suitable ligand-rich precursor compounds^{2,3}. We have found for example that most of the ligand rich compounds can be transformed into ligand deficient compounds on heating. Starting from these findings we have initiated systematic investigations on this topic. In these investigations we have reacted zinc(II) chloride with bis(2-Isopropylimidazole).

Experimental

X-ray Structure Determination

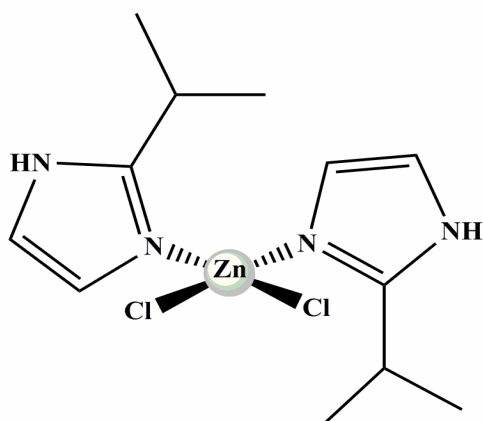
Single crystal of the compound suitable for x-ray diffraction was obtained by slow evaporation method. Three dimensional intensity data were collected on a CrysAlis CCD⁴ Oxford diffraction Xcalibur diffractometer with Eos detector using graphite monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å) at Department of Chemistry, Department of Chemistry, Pondicherry University, Pondicherry 605 014, India. The structure was solved by direct methods and refined on F² by full-matrix least-squares procedures using the SHELXL programs⁵. All the non-hydrogen atoms were refined using isotropic and later anisotropic thermal parameters. The hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model, but not refined. Images were created with ORTEP-3⁶. The crystallographic data for the compound are listed in Table 1.

Table 1: Crystal data and structure refinement of the titled compound

Compound	Parameters
Empirical formula	C ₁₂ H ₂₀ Cl ₂ N ₄ Zn
Formula weight	475.45
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbcn
Unit cell dimensions	a = 11.1856(3) Å alpha = 90° b = 11.3266(4) Å beta = 90° c = 13.0627(6) Å gamma = 90°
Empirical formula	
Volume	1654.98(11) Å ³
Z, Calculated density	3, 1.431 Mg/m ³
Absorption coefficient	1.799 mm ⁻¹
F(000)	736
Crystal size	0.20 x 0.24 x 0.28 mm
Theta range for data collection	3.92 to 29.33°
Limiting indices	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected / unique	10733 / 2056 [R(int) = 0.0372]
Completeness to theta = 29.33	90.80%
Max. and min. transmission	0.9655 and 0.9488
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2056 / 0 / 89
Goodness-of-fit on F ²	1.024
Final R indices [I > 2σ(I)]	R1 = 0.0349 , wR2 = 0.0897
R indices (all data)	R1 = 0.0658, wR2 = 0.1017
Extinction coefficient	0.0023(4)
Largest diff. peak and hole	0.544 and -0.316 e.Å ⁻³

Synthesis of the compound

Zinc(II) complexes with organic ligands show typical electronic properties that potentially give great advantages in the field of catalysis. The interest is also increasing, owing to the relevance of these compounds in basic and applied research in various fields to chemistry, material science, life science, and so forth. Furthermore, from the materials viewpoint, the metallic complexes can exhibit a full spectrum of new magnetic, optical, and redox properties. To an ethanol solution (30 mL) of 2-isopropyl imidazole (2 M) was added to an ethanol solution (10 mL) of ZnCl₂ (1 M) and the mixture was stirred for 5 hours at room temperature. The reaction mixture was stirred under a blanket of argon during which time a microcrystalline white solid precipitated from the solution. After repeated recrystallization the white solid was intensified into X-ray quality colorless crystals. The crystals were filtered, washed with cold ethanol, and dried in desiccators over CaCl₂. The scheme diagram is given below.



Results and Discussion

The symmetric unit of the title compound is shown in Fig. 1. The dihedral angle between the mean planes of the two imidazole five-membered rings is $47.7(18)^\circ$. For the ring comprising atoms N1/C1/C2/N2/C3, the out-of-plane distance are 0.201\AA for Zn1, 2.298\AA for C11 and 0.005\AA for Cl2, with two Cl atoms on the same side of the mean plane. The two imidazole rings connected at Zn with the torsion angle C1-N1-Zn1-N1a of $-137.24(17)^\circ$ indicating a -Anti-clinal conformation for this group. Atoms C5 and C6 deviate from the imidazole ring which it is attached by -1.035\AA and 1.412\AA , respectively. In the crystal, molecule are linked by N---H...Cl hydrogen bonds, forming Zigzag and chains along c axis (Fig. 2). There are a number of $\pi-\pi$ interactions present linking the ribbons and forming a three dimensional structure. The selected bond lengths and angles are listed in table 3 and 4, respectively.

Table 2: Hydrogen-bond geometry [\AA]

Distance (\AA)				Angle ($^\circ$)
D—H...A	D—H	H...A	D...A	D—H...A
N2-H2A...Cl1	0.86	2.52	3.358(2)	166

Symmetry code: i) $1/2-x, -1/2+y, z$

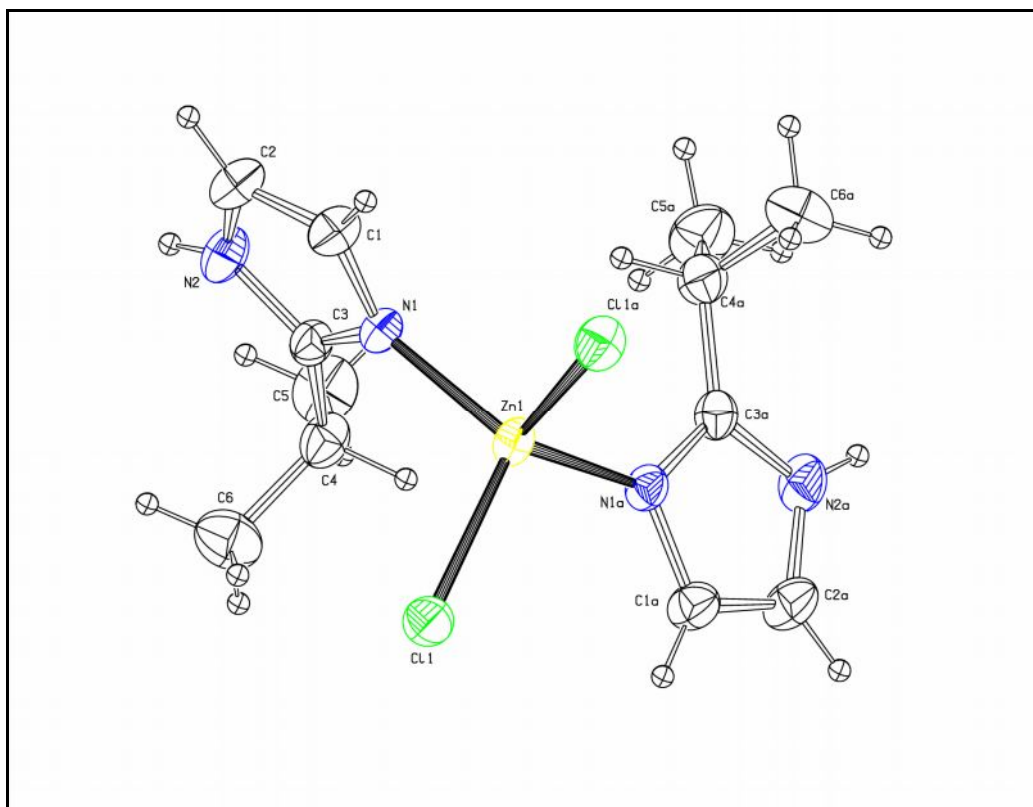


Fig.1. The molecular structure of the title compound, with the atom-numbering scheme. The displacement ellipsoids are drawn at 30% probability level. H atoms are shown as spheres of arbitrary radius.

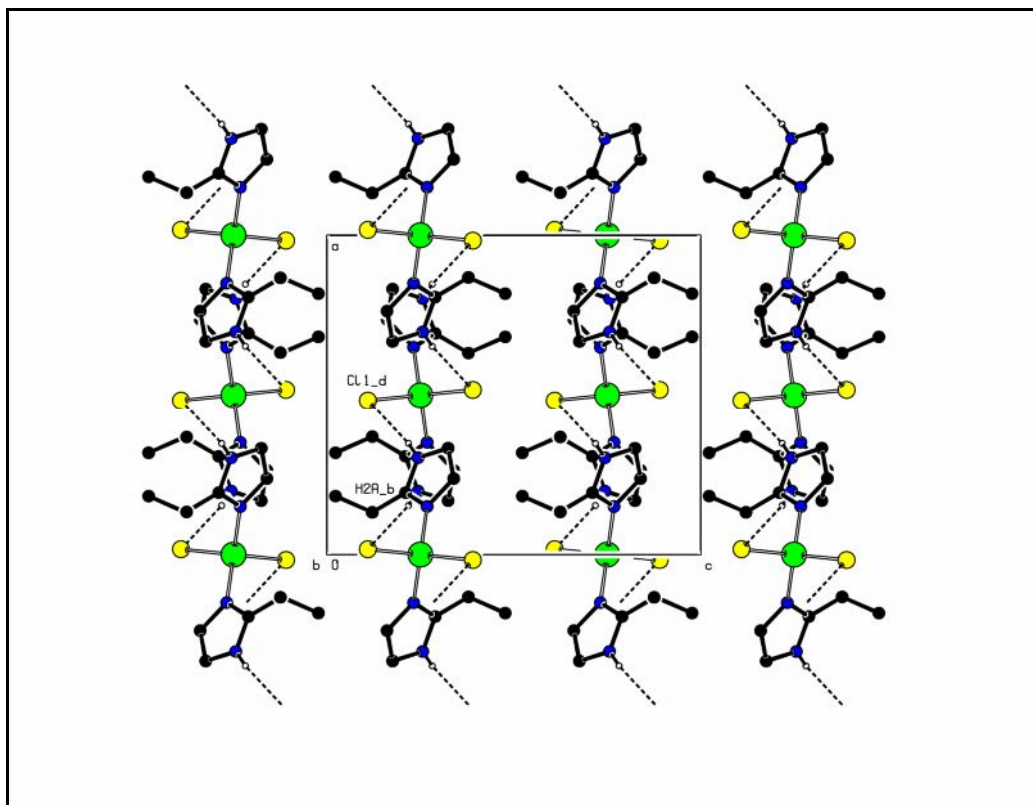


Fig.2. The crystal packing of the title compound, viewed along b axis, showing N2---H2A...Cl1 hydrogen bonds chains parallel to c axis. Hydrogen bond omitted clarity(see Table 2 for details).

Table 3: Selected Bond lengths (Å) Table 4: Selected Bond angles (°)

Bond	Length	Bond	Angle
C(1)-C(2)	1.339(3)	C(2)-C(1)-N(1)	109.3(2)
C(1)-N(1)	1.380(3)	C(2)-C(1)-H(1)	125.4
C(1)-H(1)	0.93	N(1)-C(1)-H(1)	125.4
C(2)-N(2)	1.361(3)	C(1)-C(2)-N(2)	105.5(2)
C(2)-H(2)	0.93	C(1)-C(2)-H(2)	127.2
C(3)-N(1)	1.323(3)	N(2)-C(2)-H(2)	127.2
C(3)-N(2)	1.333(3)	N(1)-C(3)-N(2)	108.8(2)
C(3)-C(4)	1.481(3)	N(1)-C(3)-C(4)	125.5(2)
C(4)-C(6)	1.511(4)	N(2)-C(3)-C(4)	125.7(2)
C(4)-C(5)	1.520(4)	C(3)-C(4)-C(6)	110.2(2)
C(4)-H(4)	0.98	C(3)-C(4)-C(5)	112.6(2)
C(5)-H(5A)	0.96	C(6)-C(4)-C(5)	112.7(2)
C(5)-H(5B)	0.96	C(3)-C(4)-H(4)	107
C(5)-H(5C)	0.96	C(6)-C(4)-H(4)	107
C(6)-H(6A)	0.96	C(5)-C(4)-H(4)	107
C(6)-H(6B)	0.96	C(4)-C(5)-H(5A)	109.5
C(6)-H(6C)	0.96	C(4)-C(5)-H(5B)	109.5
N(1)-Zn(1)	1.9967(18)	H(5A)-C(5)-H(5B)	109.5
N(2)-H(2A)	0.86	C(4)-C(5)-H(5C)	109.5
Zn(1)-N(1)#1	1.9968(18)	H(5A)-C(5)-H(5C)	109.5
Zn(1)-Cl(1)	2.2542(7)	H(5B)-C(5)-H(5C)	109.5
Zn(1)-Cl(1)#1	2.2542(7)	C(4)-C(6)-H(6A)	109.5

Conclusion

The crystal structure analysis of a novel dichloridobis(2-Isopropylimidazole)Zinc(II) compound was studied using x-ray diffraction method. In the crystal, molecule are linked by N---H...Cl hydrogen bonds, forming Zigzag and chains along c axis. There are a number of π — π interactions present linking the ribbons and forming a three dimensional structure.

Acknowledgments

KA is thankful to CSIR, New Delhi (Lr: No. 01 (2570)/12/EMR-II/3.4.2012) for financial support through a major research project. The authors are thankful to the Department of Chemistry, Pondicherry University, for the single-crystal XRD instrumentation facility.

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