Synthesis and Characterisation of Zinc(II) Complex With 2-Amino-5-bromopyridine Ligand

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ABSTRACT

The synthesis and characterisation of zinc(II) complex with 2-amino-5-bromopyridine ($C_5H_5BrN_2$) ligand have been described. The complex was structurally characterised *via* X-ray crystallography, in the title compound, (2-amino-5-bromopyridinium) $[ZnCl_3(2\text{-amino-5-bromopyridine})]$ or which is also called ($C_5H_6BrN_2$) $[ZnCl_3(C_5H_5BrN_2)]$. The Zn(II) atom is four-coordinated by three Cl atoms and one imine N-atom of 2-amino-5-bromopyridine ligand, forming a distorted tetrahedral coordination geometry. The complex was also investigated by elemental analysis, 1H NMR, IR spectroscopy and UV-Visible absorption. The protonation behaviour upon coordination is discussed.

Keywords: molecular structure, single crystal, coordination geometry, protonation

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The synthesis and characterisation of zinc(II) complex with 2-amino-5-bromopyridine ($C_5H_5BrN_2$) ligand have been described. The complex was structurally characterised *via* X-ray crystallography, in the title compound, (2-amino-5-bromopyridinium) $[ZnCl_3(2\text{-amino-5-bromopyridine})]$ or which is also called ($C_5H_6BrN_2$) $[ZnCl_3(C_5H_5BrN_2)]$. The Zn(II) atom is four-coordinated by three Cl atoms and one imine N-atom of 2-amino-5-bromopyridine ligand, forming a distorted tetrahedral coordination geometry. The complex was also investigated by elemental analysis, 1H NMR, IR spectroscopy and UV-Visible absorption. The protonation behaviour upon coordination is discussed.

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INTRODUCTION

Heterocyclic compounds analogues and derivatives have received considerable interest in the last many years due to their ability to coordinate to metal ions and known to have various chemical and biological properties. Pyridine is a type of heterocyclic organic compound with the chemical formula C_5H_5N . It is structurally related to benzene, with one CH group replaced by a nitrogen atom. In recent years, pyridine and its derivatives are found to be suitable ligands for transition metal coordination compounds involving Fe(II) ; Ni(II) [1], Cu(II) ; Co(II) [2] and Zn(II) [3]. Several pyridine derivatives play

important roles in biological properties such as antifungal and antibacterial activities [4] as well as electrochemical properties [5].

The 2-amino-5-bromopyridine is one of the pyridine derivatives, used to form the metal complex, which has an ortho substituent next to the N atom and para position with respect to the amino substituent. In an attempt to prepare the metal complex of this type, we present here the synthesis and X-ray crystal structure of zinc(II) chloride with 2-amino-5-bromopyridine, which is a monodentate N-donor ligand. The spectroscopic properties of the compound and the X-ray crystal structure of zinc(II) complex are also presented and discussed.

MATERIALS AND METHODS

Raw Material

2-amino-5-bromopyridine, $C_5H_5BrN_2$ A.R. grade and zinc(II) chloride, $ZnCl_2$ L.R grade were purchased from Aldrich Chemical Company and Fisher Scientific Company, respectively. All chemicals and solvents were purchased as A.R. grade products and were used without further purification.

Sample Preparation

The $(C_5H_6BrN_2) [ZnCl_3(C_5H_5BrN_2)]$ complex was prepared by direct reaction between zinc(II) chloride, $ZnCl_2$ with 2-amino-5-bromopyridine, $C_5H_5BrN_2$ under suitable condition. The colourless needle crystals of the complex were obtained from the filtrate after keeping to evaporate at

room temperature. The $(C_5H_6BrN_2) [ZnCl_3(C_5H_5BrN_2)]$ complex was characterised using elemental analysis 1H NMR, IR spectroscopy and UV-Visible absorption. The crystal structure of zinc(II) complex was determined by means of X-ray single crystal diffraction analysis. The cell parameters and diffraction data of zinc(II) complex were performed at room temperature on Bruker APEX CCD diffractometer. The Shelx program was used for solving and refining the crystal structure.

The elemental analysis data of the complex were given as follow. $(C_5H_6BrN_2) [ZnCl_3(C_5H_5BrN_2)]$ Yield (440 mg ; 28 %). m.p: 188–190 °C. Anal. Calcd. for $(C_5H_6BrN_2) [ZnCl_3(C_5H_5BrN_2)]$: C, 23.15; H, 2.14; N, 10.80 %. Found: C, 23.31; H, 2.09; N, 10.64 %.

RESULTS

X-ray crystallography

Table 1. Summarised crystallographic data for $(C_5H_6BrN_2) [ZnCl_3(C_5H_5BrN_2)]$ complex.

Empirical formula	$C_{10}H_{11}Br_2Cl_3N_4Zn$
Formula weight	518.77
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 9.4238(4)$ Å $\alpha = 90^\circ$ $b = 13.6544(6)$ Å $\beta = 104.3490(10)^\circ$ $c = 13.5679(6)$ Å $\alpha = 90^\circ$
Volume	$1691.40(13)$ Å ³
Z	4
Density (calculated)	2.037 Mg/m ³
Absorption coefficient	6.644 mm ⁻¹
$F(000)$	1000
Crystal size	$0.257 \times 0.162 \times 0.083$ mm ³
Theta range for data collection	2.15 to 25.00°
Index ranges	$-11 \leq h \leq 11, -16 \leq k \leq 16, -16 \leq l \leq 16$
Reflections collected	18043
Independent reflections	2979 [$R(int) = 0.0335$]
Completeness to $\theta = 25.00^\circ$	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.664
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters

2979 / 5 / 196

Goodness-of-fit on F^2

1.024

Final R indices [$I > 2\sigma(I)$]

$R1 = 0.0334$, $wR2 = 0.0813$

R indices (all data)

$R1 = 0.0423$, $wR2 = 0.0861$

Largest diff. peak and hole

1.230 and -0.397 e^-

Figure 1. The structure of $(\text{C}_5\text{H}_6\text{BrN}_2) [\text{ZnCl}_3(\text{C}_5\text{H}_5\text{BrN}_2)]$ showing the atom numbering scheme.

DISCUSSION

Structural description of zinc(II) complex $(\text{C}_5\text{H}_6\text{BrN}_2) [\text{ZnCl}_3(\text{C}_5\text{H}_5\text{BrN}_2)]$

The asymmetric unit of this complex consists of discrete $[\text{ZnCl}_3(\text{C}_5\text{H}_5\text{BrN}_2)]^-$ complex anion and $[\text{C}_5\text{H}_6\text{BrN}_2]^+$ cation. The Zn(II) atom in the $[\text{ZnCl}_3(\text{C}_5\text{H}_5\text{BrN}_2)]^-$ complex anion is coordinated by three Cl atoms and one imine N-atom of 2-amino-5-bromopyridine ligand, within a distorted tetrahedral coordination environment. Moreover, the protonated form of pyridine nitrogen atom of a 2-amino-5-bromopyridine ligand is observed.

The protonated N-atom of pyridinium ring and the amino group of the cation are linked to the Zn(II) complex anion, *via* inter- and intra-molecular $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds. A perspective view of the asymmetric unit of the complex with the atom numbering scheme is depicted in Figure 1. Crystal data and structure

refinement for the complex are summarised in Table 1.

NMR Spectra

The ^1H NMR spectra of the zinc(II) complex was recorded in $\text{DMSO}-d_6$ as solvent, occurs at $\delta = 6.68 \text{ ppm} - 6.70 \text{ ppm}$ as doublet, $\delta = 7.77 \text{ ppm} - 7.79 \text{ ppm}$ as doublet of doublet (dd), and $\delta = 8.09 \text{ ppm} - 8.10 \text{ ppm}$ as doublet peak. Meanwhile, the existence of the complex in the protonated form is confirmed by the disappearance of the signal from the amino group whereas the nitrogen atom of the 2-amino-5-bromopyridine ligand is protonated upon complexation. As the result the protonation of nitrogen atom in zinc(II) complex $(\text{C}_5\text{H}_6\text{BrN}_2) [\text{ZnCl}_3(\text{C}_5\text{H}_5\text{BrN}_2)]$ is observed and which is also evident from X-ray result (Figure 1). However, the differences of chemical shift of pyridine H atoms indicate that the N atom of pyridine coordinate to the metal ion [6].

IR Spectra

The IR spectra of the free ligand 2-amino-5-bromopyridine shows the characteristic bands at 3453 cm^{-1} and 3293 cm^{-1} , 1623 cm^{-1} and 1591 cm^{-1} , 1474 cm^{-1} , 1387 cm^{-1} , 515 cm^{-1} , assignable to $\nu(\text{NH}_2)$, $\nu(\text{C}=\text{C})$, $\nu(\text{C}=\text{N})$, $\nu(\text{C}-\text{N})$, $\nu(\text{C}-\text{Br})$ stretching modes, respectively. Meanwhile in $(\text{C}_5\text{H}_6\text{BrN}_2) [\text{ZnCl}_3(\text{C}_5\text{H}_5\text{BrN}_2)]$ complex, the characteristic bands of pyridine occur at 1636 cm^{-1} and 1609 cm^{-1} , 1498 cm^{-1} , 1332 cm^{-1} , 500 cm^{-1} , assigned for $\nu(\text{C}=\text{C})$, $\nu(\text{C}=\text{N})$, $\nu(\text{C}-\text{N})$, $\nu(\text{C}-\text{Br})$ stretching modes, respectively. The appearance of the band in the strong intensity at 456 cm^{-1} due to $\nu(\text{Zn}-\text{Cl})$ stretching vibration while the band at 533 cm^{-1} is attributed to $\nu(\text{Zn}-\text{N})$ stretching vibration. The coordination of the nitrogen atom to metal ion is confirmed with the presence of this band [7].

Table 2. ^1H NMR spectral data of $(\text{C}_5\text{H}_6\text{BrN}_2) [\text{ZnCl}_3(\text{C}_5\text{H}_5\text{BrN}_2)]$ complex.

H-position	^1H NMR spectral data		
	δ (ppm)	Amount of H	Peak
3, 3'	6.68 – 6.70	2	d
4, 4'	7.77 – 7.79	2	dd
6, 6'	8.09 – 8.10	2	d

Figure 2. The molecular structure of $(\text{C}_5\text{H}_6\text{BrN}_2) [\text{ZnCl}_3(\text{C}_5\text{H}_5\text{BrN}_2)]$ complex with proton numbering system.

Figure 3. ^1H NMR spectrum of $(\text{C}_5\text{H}_6\text{BrN}_2) [\text{ZnCl}_3(\text{C}_5\text{H}_5\text{BrN}_2)]$ complex in $\text{DMSO}-d_6$ solvent.

Figure 4. The infrared spectra of 2-amino-5-bromopyridine ligand.

Figure 5. The infrared spectra of $(\text{C}_5\text{H}_6\text{BrN}_2) [\text{ZnCl}_3(\text{C}_5\text{H}_5\text{BrN}_2)]$ complex.

UV-Visible Absorption Spectra

The electronic spectra of the free ligand and its zinc(II) complex were recorded using Dimethyl Formamide (DMF) as solvent in the region of 200 – 800 nm at ambient temperature. As can be seen from the Table 3 and Figure 6, show the comparison of the electronic spectra between the free ligand of 2-amino-5-bromopyridine with zinc(II) complex, $(C_5H_6BrN_2) [ZnCl_3(C_5H_5BrN_2)]$. The electronic absorption data of the ligand exhibit two bands in the UV region. The

band at 265 nm in the electronic spectra of the ligand is being assigned to $\pi \rightarrow \pi^*$ transition, while the band at 311 nm corresponds to charge – transfer ($n \rightarrow \pi^*$) transition from the lone pair electron of the C=N group to the metal ion. In contrast to $(C_5H_6BrN_2) [ZnCl_3(C_5H_5BrN_2)]$ complex, $\pi \rightarrow \pi^*$ transition has a little red shift compared to the free ligand at 268 nm, confirming the ligand was coordinated to Zn(II) ion through nitrogen atom upon complexation [8].

Table 3. Electronic spectra of the free ligand and its zinc(II) complex in DMF solution.

Compounds	UV-Visible Absorption λ_{max} (nm)
2-amino-5-bromopyridine ligand	265 nm , 311 nm
$(C_5H_6BrN_2) [ZnCl_3(C_5H_5BrN_2)]$ complex	268 nm

Figure 6. UV-Visible absorption spectra of the 2-amino-5-bromopyridine ligand and its zinc(II) complex $(C_5H_6BrN_2) [ZnCl_3(C_5H_5BrN_2)]$ in DMF solution.

Remark : — = 2-amino-5-bromopyridine ligand
— = $(C_5H_6BrN_2) [ZnCl_3(C_5H_5BrN_2)]$ complex

CONCLUSION

In summary, determination of the crystal structure of zinc(II) complex by X-ray diffraction analysis shows a distorted tetrahedral coordination environment for $(C_5H_6BrN_2) [ZnCl_3(C_5H_5BrN_2)]$ complex. The Zn(II) atom in the $[ZnCl_3(C_5H_5BrN_2)]^-$ complex anion is coordinated by three Cl atoms and one imine N-atom of 2-amino-5-bromopyridine ligand. In addition, the

pyridine N-atom of 2-amino-5-bromopyridine ligand is protonated. The elemental analysis and 1H NMR technique confirmed the formula of the complex. Result from the elemental analysis showed that the calculated values of the complex was satisfactory when compared with the experimental values. Furthermore, the IR spectroscopy and UV-Visible absorption of the ligand and its zinc(II) complex were also studied and identified.

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