

Synthesis, Characterization and Crystal Structure of a Mononuclear Zinc(II) Complex Derived from 2-[(2-Propylaminoethylimino)methyl]phenol

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Abstract A new zinc(II) complex, $[\text{Zn}(\text{C}_{12}\text{H}_{18}\text{N}_2\text{O})\text{Cl}_2] \cdot \text{CH}_3\text{CN}$, derived from the Schiff base ligand 2-[(2-propylaminoethylimino)methyl]phenol, has been synthesized and characterized by elemental analysis, IR spectra, and X-ray crystallography. The complex crystallizes in the orthorhombic space group *Pbcn* with unit cell dimensions $a = 26.387(9) \text{ \AA}$, $b = 7.389(2) \text{ \AA}$, $c = 18.731(6) \text{ \AA}$, $V = 3,652(2) \text{ \AA}^3$, $Z = 8$, $R_1 = 0.0455$ and $wR_2 = 0.1143$. The asymmetric unit of the compound contains a mononuclear $[\text{Zn}(\text{C}_{12}\text{H}_{18}\text{N}_2\text{O})\text{Cl}_2]$ complex and an acetonitrile molecule linked together by an intermolecular N–H $\cdots$ N hydrogen bond. Crystal packing is stabilized by intermolecular N–H $\cdots$ O hydrogen bonds linking the molecules into chains along the *b* axis of the unit cell.

Keywords Schiff base · Zinc(II) complex · Hydrogen bonds · Coordination chemistry

Introduction

Due to their biological activity, significance, and versatility in coordination modes, Schiff base compounds have received wide attention [1–3]. Zinc is an important life element, which acts as the active center of many enzymes [4, 5]. In our investigations of aggregates of Schiff base ligands with the zinc ion, we have recently reported the structure of a new mononuclear zinc complex [6]. In continuing our investigations of these compounds we now

report the synthesis and structure of a new mononuclear Schiff base zinc(II) complex derived from the Schiff base ligand 2-[(2-propylaminoethylimino)methyl]phenol.

Experimental

Materials and Measurements

All chemicals and reagents (AR grade) were commercially available and used without further purification. *N*-propylethane-1,2-diamine was purchased from Aldrich. C, H, and N elemental analyses were performed on a Perkin–Elmer 240C elemental analyzer. The IR spectra were measured with a Nicolet FT-IR 170-SX spectrophotometer. The ^1H NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer with tetramethylsilane as the internal reference.

Synthesis of 2-[(2-Propylaminoethylimino)methyl]phenol

The Schiff base ligand 2-[(2-propylaminoethylimino)methyl]phenol was synthesized according to the procedure described in Scheme 1. To a MeOH solution (10 mL) of salicylaldehyde (1.0 mmol, 122.1 mg) was added a MeOH solution (10 mL) of *N*-propylethane-1,2-diamine (1.0 mmol, 102.2 mg) with stirring. The mixture was stirred for 10 min at room temperature to give a clear yellow solution. The solvent was removed by distillation, yielding an orange oil. Analysis calculated for $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}$: C, 69.87; H, 8.80; N, 13.58%; found: C, 69.70; H, 8.93; N, 13.72%. Selected IR data (KBr, cm^{-1}): 3380 (w), 3217 (w), 3072 (w), 2926 (m), 2851 (m), 1632 (s), 1497 (w), 1282 (s), 759 (s). ^1H NMR data (CDCl_3 , ppm): $\delta = 8.07$ (s, 1H), 7.40 (d, 1H), 7.13

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(*m*, 1H), 6.81 (*m*, 1H), 6.72 (*d*, 1H), 4.32 (*s*, 1H), 3.73 (*t*, 2H), 2.88 (*m*, 2H), 2.53 (*m*, 2H), 1.87 (*m*, 1H), 1.46 (*m*, 2H), 0.98 (*t*, 3H).

Synthesis of the Complex $[\text{Zn}(\text{C}_{12}\text{H}_{18}\text{N}_2\text{O})\text{Cl}_2] \cdot \text{CH}_3\text{CN}$

A MeOH solution (5 mL) of ZnCl_2 (0.1 mmol, 13.6 mg) was added to a MeOH solution (10 mL) of 2-[(2-propylaminoethylimino)methyl]phenol (0.1 mmol, 20.6 mg) with stirring. The mixture was stirred at room temperature for 10 min to give a great deal of white precipitate. To the suspension was added with stirring an amount of 5 mL MeCN, the precipitate was dissolved in the mixed solvents. Upon keeping the final solution in air for a week, colorless block-shaped crystals suitable for X-ray single crystal analysis were formed at the bottom of the vessel on slow evaporation of the solvents. Analysis calculated for $\text{C}_{14}\text{H}_{21}\text{Cl}_2\text{N}_3\text{OZn}$: C, 43.83; H, 5.52; N, 10.95%; found: C, 43.65; H, 5.61; N, 11.04%. Selected IR data (KBr, cm^{-1}): 3327 (*w*), 2925 (*m*), 2851 (*m*), 2237 (*s*), 1635 (*s*), 1582 (*w*), 1497 (*w*), 1450 (*m*), 1279 (*s*), 1118 (*w*), 757 (*s*).

Crystal Structure Determination

Diffraction intensities for the complex were collected using a Bruker SMART Apex II CCD area detector equipped with graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 298(2) K. The crystal was enveloped with glue to avoid the efflorescence. Absorption correction was applied by SADABS [7]. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXTL package [8]. All of the non-hydrogen atoms were refined anisotropically. H atoms were generated geometrically, with C–H distances of 0.93–0.97 $\text{\AA}$, N–H distances of 0.90 $\text{\AA}$, and with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}(\text{C}, \text{N})$ and $1.5U_{\text{eq}}(\text{methyl C})$. The details of the crystallographic data are summarized in Table 1. Selected bond lengths and angles are summarized in Table 2. Hydrogen bonds are listed in Table 3.

Results and Discussion

The $[\text{Zn}(\text{C}_{12}\text{H}_{18}\text{N}_2\text{O})\text{Cl}_2]$ complex is slightly soluble in either MeOH or EtOH; however, it is soluble in a solution of MeOH/MeCN (V:V = 2:1) or EtOH/MeCN (V:V = 2:1).

Scheme 1 Synthesis of 2-[(2-propylaminoethylimino)methyl]phenol

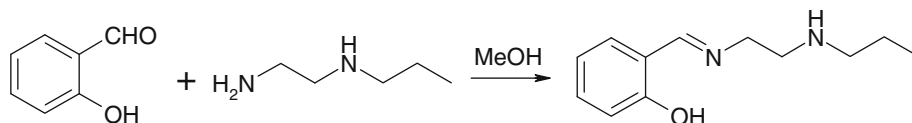


Table 1 Crystal data and refinement parameters for the complex

CCDC deposit no.	662571
Molecular formula	$\text{C}_{14}\text{H}_{21}\text{Cl}_2\text{N}_3\text{OZn}$
Molecular weight	383.61
Temperature (K)	298(2)
Radiation λ	Mo $K\alpha$ (0.71073 $\text{\AA}$)
Crystal system	Orthorhombic
Space group	<i>Pbcn</i>
<i>a</i> / $\text{\AA}$	26.387(9)
<i>b</i> / $\text{\AA}$	7.389(2)
<i>c</i> / $\text{\AA}$	18.731(6)
<i>V</i> / $\text{\AA}^3$	3,652(2)
<i>Z</i>	8
<i>D</i> _{calc} (g cm^{-3})	1.395
Crystal size (mm)	0.27 × 0.12 × 0.10
Crystal colour	Colorless
Absorption coefficient (mm^{-1})	1.639
Absorption correction <i>T</i> _{min} and <i>T</i> _{max}	0.666 and 0.853
<i>F</i> (000)	1,584
Reflections collected/unique	18,993/3,755 [<i>R</i> _{int} = 0.0618]
Range/indices (<i>h</i> , <i>k</i> , <i>l</i>)	−25, 32; −8, 9; −23, 16
θ limit ($^\circ$)	2.17–26.49
No. of observed data, <i>I</i> > 2 σ (<i>I</i>)	3,755
No. of variables	191
No. of restraints	0
Goodness of fit on <i>F</i> ²	1.030
Largest diff. Peak and hole ($\text{e \AA}^{-3}$)	0.427 and −0.529
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> ≥ 2 σ (<i>I</i>)] ^a	0.0455, 0.1143
<i>R</i> ₁ , <i>wR</i> ₂ (all data) ^a	0.0788, 0.1336

$$^a R_1 = \frac{\sum \|F_o| - |F_c|\|}{\sum |F_o|}, wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}, w = [\sigma^2(F_o^2) + (0.0434(F_o^2 + 2F_c^2)/3)^2]^{-1}$$

Table 2 Selected bond distances ($\text{\AA}$) and angles ($^\circ$) for the complex

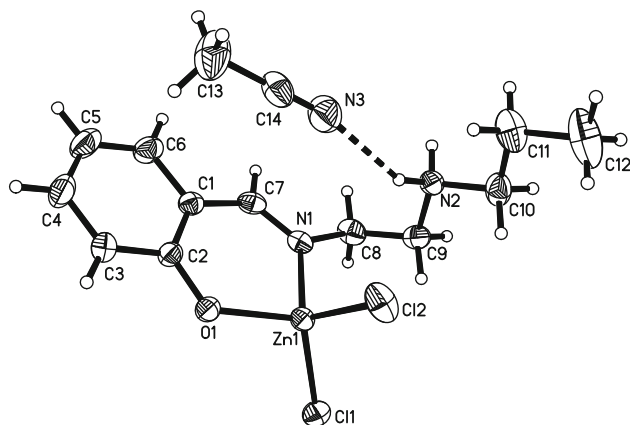
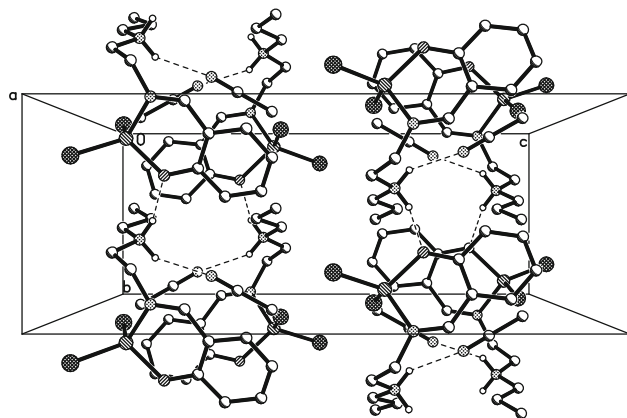
Bond distances			
Zn1–O1	1.948(2)	Zn1–N1	2.023(3)
Zn1–Cl1	2.2207(12)	Zn1–Cl2	2.2312(13)
Bond angles			
O1–Zn1–N1	95.55(12)	O1–Zn1–Cl1	111.05(8)
N1–Zn1–Cl1	112.98(9)	O1–Zn1–Cl2	112.27(9)
N1–Zn1–Cl2	111.06(9)	Cl1–Zn1–Cl2	112.79(5)

Description of the Crystal Structure of the Complex

The single crystal X-ray structural analysis shows that the complex consists of a mononuclear $[\text{Zn}(\text{C}_{12}\text{H}_{18}\text{N}_2\text{O})\text{Cl}_2]$

Table 3 Geometrical parameters for hydrogen bonds

Hydrogen bonds	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N2–H2A···O1 ^a	0.90	1.87	2.736(4)	161
N2–H2B···N3	0.90	2.22	3.024(5)	149

^a $x, -y, z$ **Fig. 1** Molecular structure of the asymmetric unit of the title compound, showing the $[\text{Zn}(\text{C}_{12}\text{H}_{18}\text{N}_2\text{O})\text{Cl}_2]$ complex and a CH_3CN molecule. Dashed lines indicate intermolecular N–H···N hydrogen bonds**Fig. 2** Molecular packing of the complex, viewed along the a axis. Intermolecular hydrogen bonds are shown as dashed lines. H atoms unrelated to hydrogen bonds are omitted for clarity

molecule and an acetonitrile molecule in the asymmetric unit (Fig. 1). The Zn atom is four-coordinated by the phenolic O and imine N atoms of the Schiff base ligand, and by two Cl atoms, forming a slightly distorted tetrahedron coordination. The amine N atom of the Schiff base ligand is protonated and therefore not coordinated to the Zn atom. The coordinated bond values (Table 2) are comparable to the values observed in similar Schiff base

zinc(II) complexes that we have recently reported [6]. The bond angles of the atoms coordinated to the Zn atom range from $95.55(12)$ to $112.98(9)^\circ$, which indicate a slightly distorted tetrahedral geometry. Crystal packing is stabilized by intermolecular N2–H2B···N3 and N2–H2A···O1 hydrogen bonds linking the molecules into chains along the b axis of the unit cell (Fig. 2). The N1–C8–C9–N2–C10–C11–C12 group in the complex adopts a zigzag pattern in the packing diagram most likely to minimize steric effects.

Conclusions

The present study shows that the Schiff base ligand 2-[(2-propylaminoethylimino)methyl]phenol coordinates to the Zn atom through the phenolic O and imine N atoms. The structure of the complex is stabilized by intermolecular N–H···N and N–H···O hydrogen bonds. The mixed solvent is a good choice to cultivate the single crystals of the complex.

Supplementary Material

CCDC 662571 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/const/retrieving.html> or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

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