

SYNTHESIS AND CRYSTAL STRUCTURE OF A ZINC(II) COORDINATION POLYMER: N-(2-PYRIDYLMETHYL)-L-ALANINE)ISOTHIOCYANATE Zn(II)

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ABSTRACT. The title compound, N-(2-pyridylmethyl)-L-alanine) zinc(II), [Zn(C₁₀H₁₁N₃O₂S)], a coordination polymer derived from the mixed ligands, N-(2-pyridylmethyl)-L-alanine (HL1) and ammonium thiocyanide (L2) has been synthesized and characterized by IR spectroscopy, ¹H-NMR, elemental analysis, thermogravimetric analysis and single crystal x-ray structure determination. The single crystal X-ray structure analysis of the title compound reveals a molecular polymeric compound that crystallizes in the orthorhombic crystal system and P2(1)2(1)2(1) space group. The ligand acts as a bridge between adjacent zinc(II) centres, each of which adopts a five-coordinate geometry. Zinc bonds to two N atoms and one O atom of HL1, one N atom of L2 and one O atom of another HL1 ligand. This is confirmed by IR spectroscopy. Thermogravimetric analysis shows a one-step decomposition of the complex to leave a zinc sulfide residue.

KEY WORDS: Zinc(II), N-(2-pyridylmethyl)-(L)-alanine) ligand, Isothiocyanate, Coordination polymer, Single crystal structure

INTRODUCTION

Schiff bases as a class of important ligands have been used extensively due to their versatile synthesis and good solubility in common solvents [1, 2]. Schiff bases have remarkable coordination ability and are able to form complexes with a variety of transition metals and stabilize various oxidation states [2-4]. Schiff bases and their metal complexes have been shown to have potential biological, medicinal, catalytic and industrial applications [3-5]. The characteristic azomethine group (-N=CH-) in Schiff bases is essential for the observed properties and reactivity [3, 6].

Reduced Schiff bases have been shown to be relatively unreactive towards air oxidation and are highly coordinating ligands as a result of the reduction of the -N=C bond of the azomethine group, giving rise to a flexible ligand [7-9]. Reduced Schiff base ligands have been found to form multidentate network complexes because of the reduction of the C=N bond of the Schiff base which helps to overcome ligand instability [10]. Compared to the Schiff bases, the corresponding reduced Schiff bases are more stable and adaptable to form conformational flexible 5- or 6-membered rings upon complexation as they are not constrained to be planar [10-12]. Recent attention of scientist has been focused on the use of mixed-ligand assemblies as effective methods for constructing coordination frameworks with interesting topologies and desirable properties for potential applications in gas storage, conductivity, porosity, magnetism,

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catalysis and drug delivery systems [3, 7]. Multidimensional Zn(II) coordination polymers is an area of recent interest due to its numerous applications [13, 14]. Our recent focus has been on the synthesis of mixed ligand complexes involving tridentate reduced Schiff bases and the thiocyanate ion which also exhibit versatile coordinating abilities [15, 16]. We report herein, the synthesis, characterisation and x-ray crystal structure of a zinc(II) coordination polymer derived from ammonium thiocyanate and a reduced Schiff base mixed ligands.

EXPERIMENTAL

All reagents and solvents used for the synthesis were of reagent grade, obtained from commercial sources and used without any further purification.

Physical measurements

Elemental analysis (C, H, N) were performed on a Fisons instrument 1108 CHNS-O (University of Reims-France for the ligand) and a FLASH 2000 Organic Elemental Analyzer, CHNS-O analyser by Thermo Scientific (University of Manchester for the complex). Thermogravimetric analysis was investigated using a TGA/DSC1 STAR^c System; METTLER TOLEDO. Infrared spectra were recorded on a Perkin-Elmer model IR-457 spectrometer and a spectrum 100 FT-IR Perkin-Elmer spectrometer, while the UV/Vis spectrum was recorded using a Agilent HP8453 Diode Array UV/Vis Spectrometer.

Synthesis

The ligand, N-(2-pyridylmethyl)-L-alanine (Pyala) was synthesised using a published procedure [17] and recrystallized using methanol. Yield: 70%; mp: 202-203 °C; anal. calc. (found) C 60.01 (59.50), H 6.67 (6.60), N 15.55 (15.90).

The complex was synthesized by the reaction of zinc acetate, pyala and NH₄SCN as described below. Pyala, HL1 (0.18 g, 1 mmol,) in 10 mL water/ethanol mixture (1:1) was added dropwise to a 5 mL solution of Zn(OOC₂H₃)₂·2H₂O (0.2 g, 1 mmol), while stirring magnetically at room temperature. After stirring for a further 10 min, L2 (0.08 g, 1 mmol,) in 2 mL distilled water was added dropwise and stirring continued for two hours. Suitable rectangular white crystals for X-ray analysis were obtained from the solution by slow evaporation after a week. Yield (79%); mp: decomposed at 340-342 °C; anal calcd. for C₁₀H₁₁ZnN₃O₂S; C, 39.68; H, 3.66; N, 13.88; S, 10.59; Zn, 21.60; found: C, 39.84; H, 3.42; N, 13.89; S, 10.53; Zn, 21.68.

X-ray crystal structure determination and refinement

A suitable single crystal of [Zn(pyala)SCN] was mounted on a glass fiber on the goniometer head of a Bruker APEX diffractometer and data were collected using graphite monochromated Cu-K_α radiation ($\lambda = 1.54178 \text{ \AA}$) at a temperature of 100 K. The structure was solved by direct methods and refined by full-matrix least squares on F^2 . All non-H-atoms were refined anisotropically. Hydrogen atoms were included in calculated positions, assigned isotropic thermal parameters and allowed to ride on their parent carbon atoms. All calculations were carried out using the SHELXTL package [18, 19]. Selected crystal data collection parameters and X-ray structure refinement details are given in Table 1. CCDC deposition number 1419825 contains the supplementary crystallographic data for this paper. These data can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Table 1. Selected crystal data collection parameters and X-ray structure refinement details for Zn(Pyala)SCN.

Empirical formula	C ₁₀ H ₁₁ N ₃ O ₂ S Zn
Formula weight	302.65
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 7.7994(4) Å α = 90 ^o b = 7.9234(4) Å β = 90 ^o c = 19.6699(9) Å γ = 90 ^o
Volume	1215.56(10) Å ³
Z	4
Density (calculated)	1.654 mg/m ³
Absorption coefficient	4.374 mm ⁻¹
F(000)	616
Crystal size	0.28 x 0.19 x 0.02 mm ³
Theta range for data collection	4.50 to 72.23 ^o
Index ranges	-9<=h<=7, -9<=k<=9, -24<=l<=24
Reflections collected	7688
Independent reflections	2322 [R(int) = 0.0358]
Completeness to theta = 67.00	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9176 and 0.688078
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2322 / 0 / 159
Goodness-of-fit on F ²	1.158
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.1219
R indices (all data)	R1 = 0.0481, wR2 = 0.1224
Absolute structure parameter	0.10(5)
Largest diff. peak and hole	Largest diff. peak and hole

RESULTS AND DISCUSSION

Spectroscopic analysis

A broad but weak IR band observed at 2356 cm⁻¹ is attributed to the OH of the carboxylic group in the ligand IR spectrum (Figure 1a). The IR spectrum of the complex displays very strong absorption bands at 1609-1611 cm⁻¹ attributed to ν(C=C) and ν(C=N) of the pyridyl ring [20, 21], while the strong bands at 2095 cm⁻¹ and 769 cm⁻¹ suggest the presence of a terminal N-bonded N=C=S stretch [21] (Figure 1b, Table 2). This is confirmed by the single crystal structure of the compound. The ligand, HL1 presents a UV absorption band at 250-300 nm attributed to the spin allowed π-π* transitions of the delocalised electronic charge of the pyridine ring. This band is observed to be red shifted to 261 nm in the spectrum of the Zn(II) complex (Figure 2).

Table 2. IR Characteristic bands of Pyala and ZnPyalaSCN.

	<i>V</i> (OH)	<i>V</i> (N-H)	<i>V</i> (C=C, C=N)	<i>V</i> (NCS)	<i>V</i> (C=S)	<i>V</i> (C-H)
<i>Pyala</i>	2356	3033w	1571s			2835w
<i>ZnPyalaSCN</i>		3233w	1611vs	2095	769s	2911vw

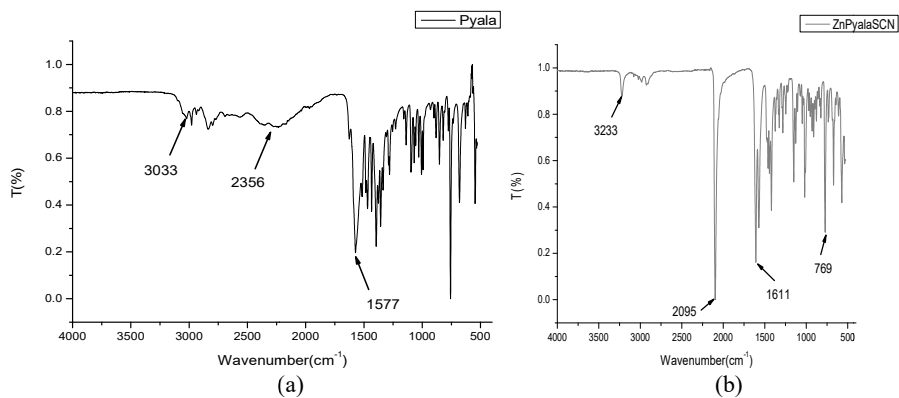


Figure 1. IR spectrum of (a) Pyala, HL1 and (b) Zn(Pyala)SCN.

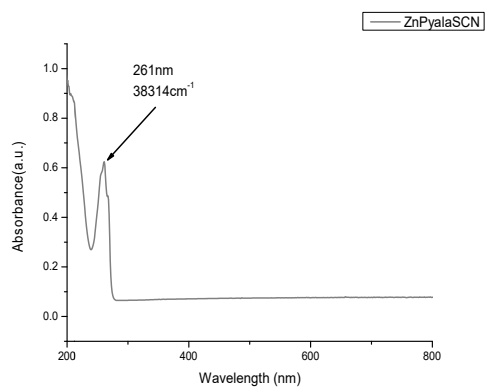


Figure 2. UV/Vis spectrum zinc mixed-ligand complex.

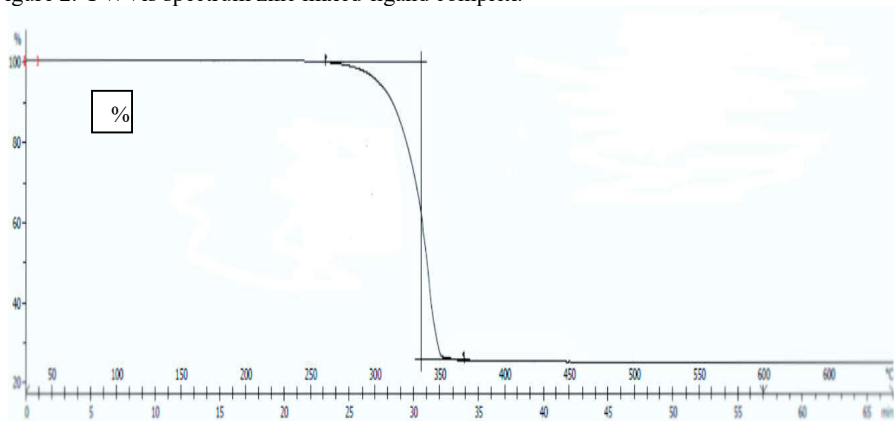


Figure 3. TGA Thermogram for Zn(Pyala)SCN.

Thermogravimetric analysis

The thermal behaviour of the Zn(II) complex is shown in Figure 3 which represents the thermogravimetric analysis thermogram recorded under a nitrogen atmosphere in the temperature range of 25 °C to 600 °C at a heating rate of 25 °C·min⁻¹. The thermogram shows a one-step decomposition pattern of the Zn(II) complex at 338 °C corresponding to the loss of the ligands, 72.5% (calc. 73.02%) which leaves a residue of 27.5% (calc. 26.98%) corresponding to ZnO.

Crystal structure of Zn(Pyala)SCN

The single crystal X-ray structure of N-(2-pyridylmethyl)-L-alanine isothiocyanate Zn(II) shows a polymeric structure that crystallizes in the orthorhombic system, space group, *P*2₁2₁2₁ as shown in Table 1. Selected important bond distances and bond angles are given in Table 3.

The ORTEP diagram for Zn(Pyala)SCN together with the atom numbering schemes are depicted in Figure 4. The structure of Zn(Pyala)SCN shows that the Zn(II) cation is coordinated in a tridentate fashion using two nitrogen atoms of L1 and through the nitrogen atom of the NCS (isothiocyanate) group (L2), as well as through a bridging oxygen atom of another L1, forming a polymer (Figure 5). The coordination geometry around the zinc atom can be described as a distorted square-pyramidal (Figure 6). The basal positions are defined by O2, N1 and N2 of the tridentate reduced Schiff base ligand, HL1 and by N3 of the thiocyanate ligand L2; while the apical position is occupied by the bridging O2 of another HL1 ligand as shown in Figure 6 [15]. The calculated trigonality index, $\tau = 0.15$ confirms a non-perfect square-pyramidal geometry, ($\tau = 1$ for a perfect trigonal bipyramidal geometry and $\tau = 0$ for a perfect square-pyramidal geometry [22]). The deviation from ideal geometry may be due to the fact that the amino hydrogen is in an abnormal position. The pyridyl N1-Zn1 bond length of 2.169(5) Å is longer than the amino N2-Zn1 bond length 2.076(6) Å. However, both N-Zn1 bond lengths of the HL1 ligand are longer than the isothiocyanate N3-Zn1 bond length, 1.969(5) Å, of the L2 ligand. Similarly, the O2-Zn1 bond length, 2.102(4) Å, of one L1 ligand is longer than the bridging O1-Zn1 bond length, 1.986(4) Å of another L1 ligand. However, the Zn-O2 bond length is in close agreement with other known axial M-O bond lengths. The Zn1-N3-C10 bond angles, 174.3(5)°, in compound (1) agrees with M-N-C metal isothiocyanates values in the literature [15, 23-25].

The packing diagram showing the unit cell is given in Figure 7a while the packing diagram showing chiral channels of the metal organic framework is illustrated in Figure 7b.

Table 3. Bond lengths [Å] and bond angles [°] for Zn(Pyala)SCN.

N1—Zn1	2.169(5)	C8—H8A	0.9800
N3—Zn1	1.969(5)	C8—H8B	0.9800
O1—Zn1 ¹	1.986(4)	C8—H8C	0.9800
O2—Zn1	2.102(4)	C9—O1	1.262(7)
Zn1—O1 ¹¹	1.986(4)	C9—O2	1.265(6)
Zn1—N2	2.076(6)	C10—N3	1.166(8)
N2—H2A	0.9900	C10—S1	1.624(6)
C6—H6A	1.07(12)		
C6—H6B	0.9900	N1—C1—C2	122.6(6)
C6—H2A	1.53(14)	N1—C1—H1	118.700
C7—N2	1.481(9)	C2—C1—H1	118.700
C7—C8	1.493(9)	C3—C2—C1	118.2(6)
C7—C9	1.517(7)	C3—C2—H2	120.900
C7—H7	1.0000	C1—C2—H2	120.900
C7—H2A	1.52(13)	C4—C3—C2	119.2(6)

C4—C3—H3	120.400	C1—N1—C5	118.6(5)
C2—C3—H3	120.400	C1—N1—Zn1	126.1(4)
C5—C4—C3	119.0(6)	C5—N1—Zn1	114.8(4)
C5—C4—H4	120.500	C10—N3—Zn1	174.3(5)
C3—C4—H4	120.500	C9—O1—Zn1 ⁱ	122.3(4)
N1—C5—C4	122.4(6)	C9—O2—Zn1	115.8(4)
N1—C5—C6	115.5(5)	N3—Zn1—O1 ⁱⁱ	102.5(2)
C4—C5—C6	122.0(5)	N3—Zn1—N2	146.5(3)
N2—C6—C5	110.7(5)	O1 ⁱⁱ —Zn1—N2	110.9(3)
N2—C6—H6A	109.500	N3—Zn1—O2	97.7(2)
C5—C6—H6A	109.500	O1 ⁱⁱ —Zn1—O2	100.18(18)
N2—C6—H6B	109.500	N2—Zn1—O2	78.9(2)
C5—C6—H6B	109.500	N3—Zn1—N1	99.0(2)
H6A—C6—H6B	108.100	O1 ⁱⁱ —Zn1—N1	93.68(18)
N2—C6—H2A	42.(4)	N2—Zn1—N1	77.2(2)
C5—C6—H2A	117.(5)	O2—Zn1—N1	155.40(16)
H6A—C6—H2A	68.300	C6—N2—C7	118.3(6)
H6B—C6—H2A	131.500	C6—N2—Zn1	115.8(5)
N2—C7—C8	109.7(7)	C7—N2—Zn1	113.4(4)
O1—C9—O2	123.8(5)	C6—N2—H2A	75.(8)
O1—C9—C7	116.3(5)	C7—N2—H2A	71.(7)
O2—C9—C7	119.9(5)	Zn1—N2—H2A	89.(7)
N3—C10—S1	178.6(6)		

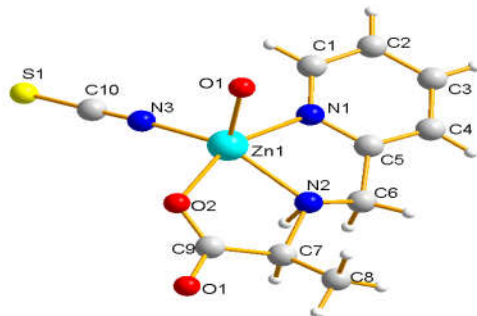


Figure 4. Monomer of Zn(Pyala)SCN showing the atom numbering scheme.

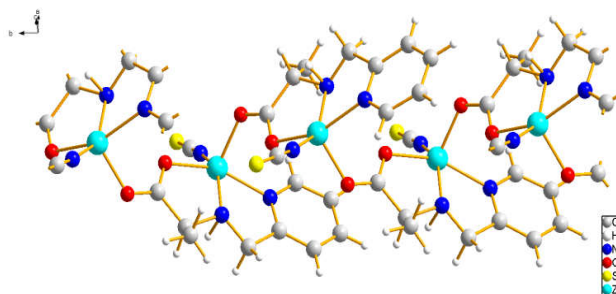


Figure 5. Polymer of Zn(Pyala)SCN) showing the atom numbering scheme.

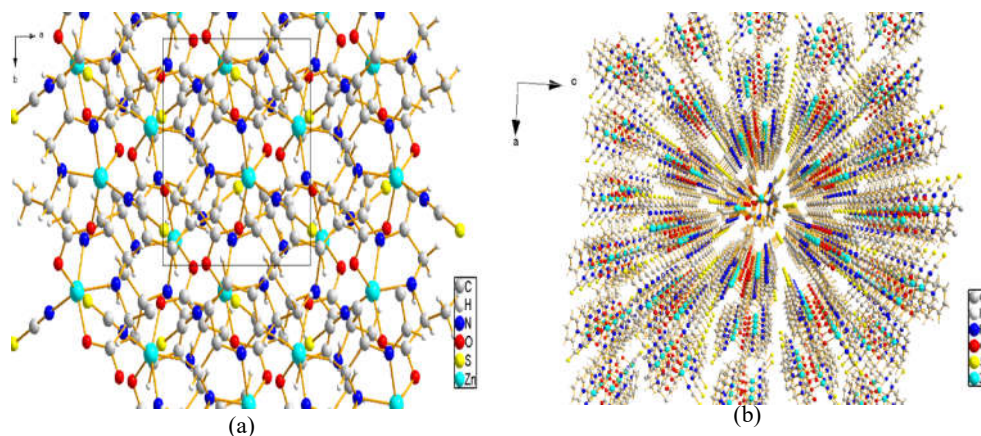


Figure 6. Coordination square pyramidal environment around the Zn1 atom.

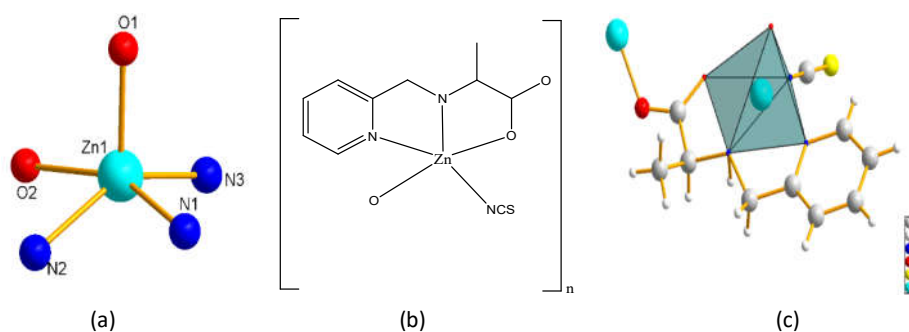


Figure 7. Packing diagram showing (a) unit cell and (b) stair case polymer viewed along the b-axis with chiral channels in Zn(Pyala)SCN.

CONCLUSION

A new zinc(II) isothiocyanide metal organic framework containing HL1 ligand has been synthesized and its single crystal structure was determined. The compound which undergoes a single step decomposition, is polymeric with the zinc(II) cation adopting a five coordinate geometry and having N-coordination to the isothiocyanato ligand, (M-NCS).

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