

Structural characterization and thermal behaviour of the bis(2-aminothiazole)bis(isothiocyanato)zinc(II) complex, $\text{Zn}(\text{NCS})_2(\text{C}_3\text{H}_4\text{N}_2\text{S})_2$

Seung Wook Suh, Inn Hoe Kim[★] and Chong-Hyeak Kim^a

Department of Chemistry, Konyang University, Nonsan 320-711, Korea

^aChemical Analysis Laboratory, Korea Research Institute of Chemical Technology, Daejeon 305-606, Korea

(Received August 3, 2005, Accepted September 22, 2005)

Abstract : The zinc(II) complex, $\text{Zn}(\text{NCS})_2(\text{C}_3\text{H}_4\text{N}_2\text{S})_2$, **I**, has been synthesized and characterized by single crystal X-ray diffraction, thermal analysis and infrared spectroscopy. The complex **I** crystallizes in the triclinic system, $P\bar{1}$ space group with $a = 7.587(1)$, $b = 8.815(1)$, $c = 12.432(2)$ Å, $\alpha = 75.584(8)$, $\beta = 83.533(9)$, $\gamma = 68.686(8)^\circ$, $V = 750.0(2)$ Å³, $Z = 2$, $R_1 = 0.036$ and $\omega R_2 = 0.101$. The central Zn(II) atom has a tetrahedral coordination geometry, with the heterocyclic nitrogen atoms of 2-aminothiazole ligands and the nitrogen atoms of isothiocyanate ligands. The crystal structure is stabilized by one-dimensional networks of the intermolecular N-H \cdots S hydrogen bonds between the amino group of 2-aminothiazole ligands and the sulfur atom of isothiocyanate ligands. Based on the results of thermal analysis, the thermal decomposition reaction of complex **I** was analyzed to have three distinctive stages such as the loss of 2-aminothiazole, the decomposition of isothiocyanate and the formation of metal oxide.

Key words : zinc complex, 2-aminothiazole, isothiocyanate, crystal structure, thermal behaviour

1. Introduction

The design and architecture of infinite multi-dimensional structures by crystal engineering has become of particular interest recently.^{1,2} Because, they have useful properties as a catalytic, electronic, magnetic and optical materials,^{3,4} it is important to be able to high-dimensionality systems. To design and architecture of infinite frameworks, one of authors⁵ and other workers^{6,7} have used the coordination properties of various pseudohalide ions such as CN^- , SCN^- , N_3^- , OCN^- , SeCN^- , CNO^- , and the complementary organic ligands. The pseudohalide ions are known to build up one-, two-, and three-dimensional framework

linking one metal atom M to another metal atom M', alternately.⁸ The complementary organic ligands such as aliphatic and aromatic amines are known to play an important role in stabilizing the multi-dimensional structures.

On the other hand, aromatic heterocycles such as imidazole, thiazole derivatives represent an important class of ligands in coordination chemistry. Especially, binding of imidazole derivatives to various metal complexes is a subject of great interest because of the frequent occurrence in biologically important metal complexes. A number of metal complexes of various imidazole derivatives have been synthesized and

[★] Corresponding author

Phone : +82-(0)41-730-5184 Fax : +82-(0)41-735-2782

E-mail: ihkim@konyang.ac.kr

characterized by X-ray single crystallography⁹⁻¹³ However, the frameworks of metal complexes containing thiazole derivatives have been less investigated compared with imidazole derivatives. Our interest in this area is focused to develop novel multi-dimensional framework structures^{14,15} using the terminal and bridging properties of the thiocyanate ligand and the coordination behaviour of the imidazole or thiazole derivatives as a complementary organic ligands. In this paper, we report the synthesis, crystal structure and thermal behaviour of the zinc(II) isothiocyanate complex **I** with 2-aminothiazole ligand.

2. Experimental

2.1. Synthesis and analysis

20 ml water-methanolic (2:1) solution of potassium thiocyanate (2 mmol, 0.19 g) was added to the 20 ml water-methanolic (2:1) solution of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (1 mmol, 0.29 g). To this mixture solution, 40 ml water-methanolic (2:1) solution of 2-aminothiazole (3 mmol, 0.30 g) was introduced with stirring. In the resulting solution a small amount of precipitate was formed and the precipitate was filtered off. The filtered water-methanolic solution was allowed to stand at room temperature. After few weeks, the pale yellow needle crystals was obtained.

IR spectrum was recorded on a BioRad Digilab FTS-155 infrared spectrophotometer. The 2-aminothiazole and isothiocyanate ligand were confirmed to assignment of the relevant IR absorption bands, respectively.¹⁶ The contents of the carbon, hydrogen, nitrogen, sulfur, and zinc were analyzed by a CE EA-1110 elemental analyzer and a Jobin-Yvon Ultima-C inductively coupled plasma-atomic emission spectrometer, respectively.

2.2. Crystal structure determination

Epoxy coated needle crystal was mounted on a Siemens P4 four-circle X-ray diffractometer equipped with graphite-monochromated Mo $\text{K}\alpha$ radiation. Unit cell dimensions were determined from the least-squares fit of 39 accurately centered reflections with θ range of 4.66 to 13.56°. Intensity data were collected by using a θ - 2θ scan mode. Lorentz and polarization corrections were applied to the intensity data, and a semi-empirical

absorption correction based on the psi-scans was applied.

All calculations were carried out using the Siemens SHELXTL crystallographic programs.¹⁸ The structure was solved by the direct method¹⁹ and refined by a full-matrix least-squares method followed by difference Fourier map. All non-hydrogen atoms were refined anisotropically; all hydrogen atoms were placed geometrically with the isotropic thermal parameters.

2.3. Thermal measurement

The thermal behaviour of the complex **I** was carried out with TA Instruments SDT Q600 simultaneous thermal analyzer. Sample was loaded into an alumina crucible in the range 7–13 mg. The data was recorded from room temperature to 1200°C with a heating rate of 10°C/min under air atmosphere. Air flow rate was 100 ml/min.

3. Results and Discussion

3.1. Analysis

The IR spectrum of the complex **I** exhibits absorption bands in the regions 2071, 712 and 486 cm^{-1} , which are identified as $\nu(\text{CN})$, $\nu(\text{CS})$ and $\delta(\text{NCS})$ modes, respectively. These wavenumbers are due to coordinated isothiocyanate groups and are in good agreement with those of similar modes in transition metal complexes.¹⁶ The typical peaks in the 3425, 1607, 1512, 1277, 1204, 1061 and 520 cm^{-1} are due to the presence of 2-aminothiazole ligand. The composition of the crystal **I** was deduced from the elemental analyses; the formula of $\text{Zn}(\text{NCS})_2(\text{C}_3\text{H}_4\text{N}_2\text{S})_2$ is consistent with the results of X-ray single crystallography. *Anal. Found:* C, 25.21; H, 1.94; N, 21.67; S, 35.22; Zn, 17.1% *Calc. for* $\text{C}_8\text{H}_8\text{N}_6\text{S}_4\text{Zn}$: C, 25.16; H, 2.11; N, 22.02; S, 33.59; Zn, 17.12%.

3.2. Crystal structure

The crystallographic and experimental data are summarized in *Table 1*. The selected bond lengths and bond angles are listed in *Table 2*. The molecular structure with the atomic numbering scheme and a perspective view of the complex **I** are shown in *Fig. 1* and *Fig. 2*, respectively.

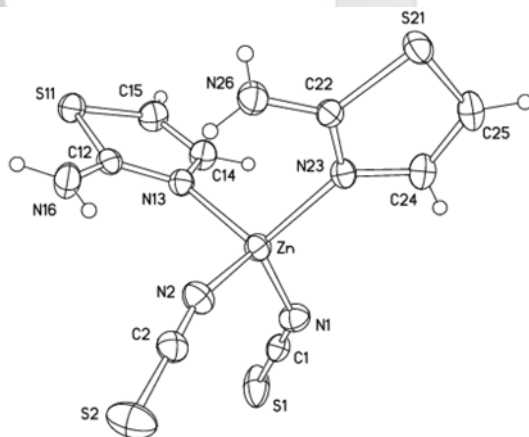
As shown in *Fig. 1*, the central zinc(II) atom has a

Table 1. Crystallographic and experimental data for Zn(NCS)₂-(C₃H₄N₂S)₂

Formula	C ₈ H ₈ N ₆ S ₄ Zn
Formula weight	381.81
Colour	pale yellow
Temperature (K)	295
λ (Mo-K α) (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	7.587(1)
<i>b</i> (Å)	8.815(1)
<i>c</i> (Å)	12.432(2)
α (°)	75.584(8)
β (°)	83.533(9)
γ (°)	68.686(8)
<i>V</i> (Å ³)	750.0(2)
<i>Z</i>	2
<i>D_c</i> (g/cm ³)	1.691
μ (mm ⁻¹)	2.187
<i>F</i> (000)	384
Crystal size (mm)	0.24×0.40×0.44
θ range for data collection (°)	2.6–26.5
Index range	0 ≤ <i>h</i> ≤ 9, -10 ≤ <i>k</i> ≤ 10, -15 ≤ <i>l</i> ≤ 15
Reflections collected/unique	3221/2688 [<i>R</i> _{int} = 0.0141]
Data/restraints/parameters	2688/0/173
Goodness-of-fit on <i>F</i> ²	1.057
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.036, ωR ₂ = 0.101

Table 2. Selected bond lengths (Å) and angles (°) for Zn(NCS)₂-(C₃H₄N₂S)₂

Zn-N(1)	1.943(3)	Zn-N(2)	1.967(3)
Zn-N(13)	2.027(2)	Zn-N(23)	2.001(2)
S(1)-C(1)	1.611(4)	C(1)-N(1)	1.153(4)
S(2)-C(2)	1.605(3)	C(2)-N(2)	1.158(4)
S(11)-C(12)	1.732(3)	C(12)-N(13)	1.322(4)
N(13)-C(14)	1.381(4)	C(14)-C(15)	1.337(5)
C(15)-S(11)	1.718(4)	C(12)-N(16)	1.326(4)
S(21)-C(22)	1.720(3)	C(22)-N(23)	1.315(4)
N(23)-C(24)	1.386(4)	C(24)-C(25)	1.345(5)
C(25)-S(21)	1.716(4)	C(22)-N(26)	1.347(4)
N(1)-Zn-N(2)	115.7(1)	N(1)-Zn-N(13)	103.7(1)
N(1)-Zn-N(23)	114.8(1)	N(2)-Zn-N(13)	107.5(1)
N(2)-Zn-N(23)	106.4(1)	N(13)-Zn-N(23)	108.4(1)
Zn-N(1)-C(1)	144.8(3)	Zn-N(2)-C(2)	164.0(3)
Zn-N(13)-C(12)	128.2(2)	Zn-N(13)-C(14)	120.6(2)
Zn-N(23)-C(22)	122.8(2)	Zn-N(23)-C(24)	126.0(2)
N(1)-C(1)-S(1)	179.6(3)	N(2)-C(2)-S(2)	179.1(3)
S(11)-C(12)-N(13)	113.3(2)	C(12)-N(13)-C(14)	111.1(3)
N(13)-C(14)-C(15)	115.3(3)	C(14)-C(15)-S(11)	110.7(3)
C(15)-S(11)-C(12)	89.5(2)	S(11)-C(12)-N(16)	122.0(2)
N(13)-C(12)-N(16)	124.7(3)	S(21)-C(22)-N(23)	113.8(2)

Fig. 1. The molecular structure of Zn(NCS)₂-(C₃H₄N₂S)₂ with the atomic numbering scheme and displacement ellipsoids at the 30% probability level.

tetrahedral coordination geometry and is tetra-coordinated by two heterocyclic nitrogen atoms of 2-aminothiazole ligands and by two nitrogen atoms of isothiocyanate groups. The average Zn-N_{aminothiazole} bond length of 2.014(2) Å and the average Zn-N_{NCS} bond length of 1.955(3) Å are similar to that observed in the zinc(II) isothiocyanate complexes.²⁰ The bond angles of N_{NCS}-Zn-N_{NCS} and N_{aminothiazole}-Zn-N_{aminothiazole} are 115.7(1) and 108.4(1)°, respectively. All bond lengths and angles of 2-aminothiazole ligands are similar to other reported compound, tetrakis(2-aminothiazole)bis(isothiocyanato) cobalt(II).²¹

A perspective view of complex **I** along the *b*-axis is shown in Fig. 2. The crystal packing of the complex lies on an array in parallel to the *ac*-plane. The nitrogen atoms of the isothiocyanate ligands are coordinated to the tetrahedral zinc(II) atoms, while the sulfur atoms of the isothiocyanate ligands are uncoordinated. It is quite different from the other transition metal(II) thiocyanate

complexes^{22,23} which are doubly bridged by the thiocyanate (SCN⁻) group and isothiocyanate (NCS⁻) group through both ends. The heterocyclic nitrogen atoms of 2-aminothiazole ligands are coordinated to central zinc(II) atoms. It is similar to other metal 2-aminothiazole

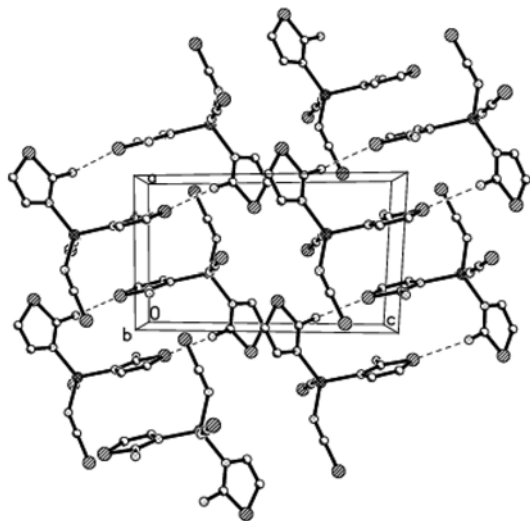


Fig. 2. Perspective view of the unit cell of $\text{Zn}(\text{NCS})_2 \cdot (\text{C}_3\text{H}_4\text{N}_2\text{S})_2$ along the b axis; hydrogen bonds are shown by broken lines.

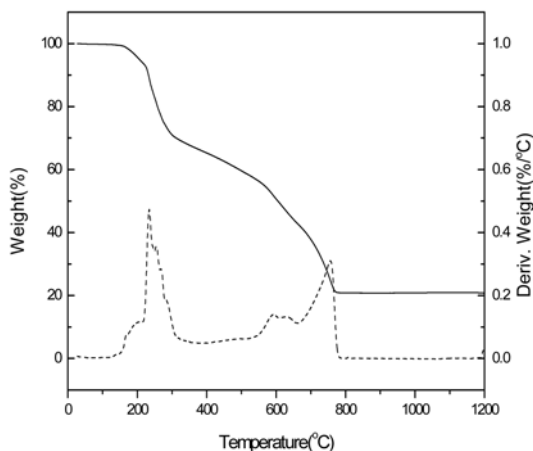


Fig. 3. Thermogravimetric and differential thermogravimetric analysis curves for $\text{Zn}(\text{NCS})_2(\text{C}_3\text{H}_4\text{N}_2\text{S})_2$ under air atmosphere.

complexes^{20,24} which are coordinated by heterocyclic nitrogen or heterocyclic sulfur atom of 2-aminothiazole ligands. The amino groups of 2-aminothiazole and the S atoms of isothiocyanate are linked together in intermolecular hydrogen bonding along ab -plane by the weak $\text{N-H}\cdots\text{S}$ hydrogen bond: $\text{N}(16)\text{-H}(16\text{b})\cdots\text{S}(1)$, $3.446(3)$ Å, 168.7° ; $\text{N}(26)\text{-H}(26\text{b})\cdots\text{S}(2)$, $3.401(3)$ Å, 167.5° . These $\text{N}_{\text{aminothiazole}}\text{-H}\cdots\text{S}_{\text{isothiocyanate}}$ one-dimensional hydrogen bonding networks contribute to stabilization of the crystal structure.

3.3. Thermal behaviour

The thermal behaviour of the complex **I** would proceed through three stages as shown in Fig. 3: the loss of 2-aminothiazole, the decomposition of isothiocyanate and the formation of metal oxide. The complex **I** thermally degrades to ZnO over the temperature range $120\sim 1200^\circ\text{C}$. Experimental and theoretical weight loss are 79.13 and 78.67%, respectively. The first step of thermal decomposition is the loss of 2-aminothiazole in the temperature of $120\sim 350^\circ\text{C}$. The second step occurs from 350 to 780°C and is the loss of isothiocyanate and remaining 2-aminothiazole. The higher decomposition temperature of 2-aminothiazole is due to intermolecular hydrogen bonding. A slow weight loss is observed which is consistent with the evolution of cyanogen from the isothiocyanate group.²¹ The final stage of the thermal decomposition starts at 780°C and the weight percentage of residue is 20.87%. This step leads to the metal oxide formation of ZnO and analyzed by an energy dispersive X-ray spectrometer.

References

1. T. Iwamoto, "Comprehensive Supramolecular Chemistry", Vol. 6, p. 643, D. D. MacNicol, F. Toda and R. Bishop, Eds., Pergamon Press, Oxford, U.K. (1996).
2. M. Fujita, "Comprehensive Supramolecular Chemistry", Vol. 9, p. 253, J. P. Sauvage and M. W. Hosseini, Eds., Pergamon Press, Oxford, U.K. (1996).
3. D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, **98**, 1375(1998).
4. O. M. Yaghi, H. L. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, **31**, 474(1998).
5. C. H. Kim, *Ph.D. Thesis*, The University of Tokyo, Japan (1996).
6. G. Demunno, G. Viau, M. Julve, F. Lloret and J. Faus, *Inorg. Chim. Acta*, **257**, 121(1997).
7. R. Cortes, M. K. Urriaga, L. Lezama, J. L. Pizarro, M. I. Arriortua and T. Rojo, *Inorg. Chem.*, **36**, 5016(1997).
8. K. Vrieze and G. V. Koten, "Comprehensive Coordination Chemistry", Vol. 2, p. 225, S. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Eds., Pergamon Press, Oxford, U.K. (1987).
9. H. J. Chen, G. Yang and X. M. Chen, *Acta Cryst.*, **C55**,