

Synthesis and Crystal Structure of the Cadmium(II) Complex with Thiocyanate and 1,2-Diaminocyclohexane Ligands

Inn Hoe Kim*, Seung Wook Suh, Chong-Hyeak Kim^a, Jin-Gyu Kim^b and Il-Hwan Suh^{b*}

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

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

^bDepartment of Physics, Chungnam National University, Daejeon 305-764, Korea

Thiocyanate 및 1,2-Diaminocyclohexane 리간드로 구성된 카드뮴(II) 착물의 합성 및 결정구조

김인회* · 서승욱 · 김종혁^a · 김진규^b · 서일환^{b*}

건양대학교 화학과, ^a한국화학연구원 분석실, ^b충남대학교 물리학과

Abstract

The crystal structure of the title complex, $\text{Cd}(\text{SCN})_2(\text{C}_6\text{H}_{10}(\text{NH}_2)_2)_2$ (1), has been analyzed by X-ray single crystallography. The complex 1 crystallizes in the monoclinic system, $P2_1/c$ space group with $a = 11.842(2)$, $b = 7.926(2)$, $c = 11.291(2)$ Å, $\beta = 106.74(3)^\circ$, $V = 1014.8(4)$ Å³, $Z = 2$, $R_1 = 0.0518$ and $\omega R_2 = 0.1315$ for 1775 independent reflections. The central Cd(II) atom of this complex has a slightly distorted octahedral coordination geometry, with the 1,2-diaminocyclohexane ligands functioning as an N,N' -bidentate and the thiocyanate ligands bonding through the sulfur atom in a *trans* arrangement.

요 약

$\text{Cd}(\text{SCN})_2(\text{C}_6\text{H}_{10}(\text{NH}_2)_2)_2$ 착물을 합성하고 단결정 X-선 회절법으로 구조를 규명하였다. 이 착물은 단사정계, 공간군 $P2_1/c$, $a = 11.842(2)$, $b = 7.926(2)$, $c = 11.291(2)$ Å, $\beta = 106.74(3)^\circ$, $V = 1014.8(4)$ Å³, $Z = 2$ 로 결정화되었으며, 1775 개의 독립적인 회절반점에 대한 최종 신뢰도 인자 R_1 및 ωR_2 값은 각각 0.0518 및 0.1315이었다. 이 착물의 결정 구조는 2개의 1,2-diaminocyclohexane 리간드의 질소 원자가 xy 평면에서 Cd(II) 금속 원자에 chelate되어 5-membered ring을 형성하며, 2개의 thiocyanate 리간드의 황 원자가 z 축 방향에서 Cd(II) 금속 원자에 트란스 형태로 결합함으로써 z 축 방향으로 약간 늘어진 팔면체 구조의 단핵 착물을 형성한다.

1. Introduction

The supramolecular architecture of one- (1D), two- (2D), and three-dimensional (3D) frameworks with organic-inorganic hybrid compositions has become of great interest recently.¹⁻²⁾ It has been reported that they have useful properties as catalytic, electronic, magnetic, and optical materials.³⁾ For designing infinite multi-dimensional frameworks, one

of us⁴⁾ and other workers⁵⁻⁶⁾ have used the coordination properties of various pseudohalide ions such as CN^- , SCN^- , OCN^- , SeCN^- , CNO^- , N_3^- , and the complementary organic ligands. Generally, they are known to build up one-, two-, and three-dimensional framework linking one metal atom M to another metal atom M' alternately.⁷⁾

Among these pseudohalide metal complexes, the transition-metal thiocyanate complexes with various

amine ligands such as aliphatic amines, aromatic amines, and cyclic amines have been intensively studied by X-ray single crystallography.⁸⁻¹³⁾ As an extension of this study, our research is focused on the development of novel two- (2D) and/or three-dimensional (3D) framework structures using metal-thiocyanate interactions and chelating behaviour of the diamine ligands. In this paper, we report the synthesis and crystal structure of the cadmium(II) thiocyanate complex (**1**) with 1,2-diaminocyclohexane ligands.

2. Experimental Section

Preparation and Characterization of Cd(SCN)₂{C₆H₁₀(NH₂)₂}₂ (1**).** To a 30 ml of aqueous ethanol (1 : 1) solution, 1 mmol (0.23 g) of CdCl₂ · 2.5H₂O and 2 mmol (0.02 g) of NaSCN were introduced successively under stirring. To this solution, 2 mmol (0.21 g) of 1,2-diaminocyclohexane was added with stirring. After the 1,2-diaminocyclohexane was added, fine white precipitates formed. A small amount of the white precipitate was filtered off, and the aqueous ethanol solution was allowed to stand in a refrigerator at 5°C. After a few weeks, the pale yellow block crystals were obtained.

IR spectrum of the obtained crystal was recorded on a BioRad Digilab FTS-165 infrared spectrophotometer by KBr pellet methods. The assignment of the relevant absorption bands confirmed the presence of 1,2-diaminocyclohexane and thiocyanate ligand.¹⁴⁾ The quantitative analysis of Cd²⁺ ion was conducted by a Perkin-Elmer 2380 atomic absorption spectrometer, and the analyses of the carbon, hydrogen, nitrogen, and sulfur contents were made on a CE EA-1110 elemental analyzer. The composition of the crystal **1** was deduced from the elemental analyses; the formula of Cd(SCN)₂{C₆H₁₀(NH₂)₂}₂ is consistent with results of the single crystal X-ray diffraction analysis. *Anal. Found:* C, 37.16; H, 6.27; N, 19.03; S, 14.01; Cd, 24.3%. *Calc. for CdC₁₄H₂₈N₆S₂:* C, 36.80; H, 6.18; N, 18.39; S, 14.03; Cd, 24.60%.

X-ray Single Crystallography. A pale yellow block crystal (0.50 × 0.30 × 0.30 mm) of the title complex was coated with epoxy glue in order to

prevent degradation of the specimen under ambient conditions. The crystal was mounted on an Enraf-Nonius CAD4 X-ray diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$) in the ω -2 θ scan mode. The cell parameters and an orientation matrix were determined from the least-squares fit of 25 accurately centered reflections in the θ range of 11.21 to 14.40°.¹⁵⁾ One orientation reflection was checked every 200 reflections and three standard reflections were monitored every 300 minutes. The intensity variation was less than 0.3% over the course of data collection, and no decay correction was applied. Lorentz and polarization corrections were applied to the intensity data, and a semi-empirical absorption correction based on the ϕ -scans was applied.

All calculations in the structural solution and refinements were performed using the Siemens SHELXTL crystallographic software package.¹⁶⁾ The space group was assigned on the basis of the systematic absences and intensity statistics, and was confirmed by successful refinements. The structure was solved by the direct method¹⁷⁾ and refined by successive least-squares methods followed by difference Fourier maps. All the non-hydrogen atoms were refined anisotropically; all the hydrogen atoms fixed at calculated positions with isotropic thermal parameters were included in the final structure-factor calculations. The final difference electron density map contained no significant features.

3. Results and Discussion

The crystallographic and experimental data are summarized in Table 1. The refined atomic parameters and the selected bond lengths and bond angles are listed in Tables 2 and 3, respectively. Fig. 1 and Fig. 2 show a molecular structure with the atomic numbering scheme and a perspective view of the cadmium(II) complex (**1**), respectively.

As shown in Fig. 1, the central cadmium(II) atom rests on a crystallographic inversion center and is six-coordinated by a pair of sulfur atoms from two thiocyanate groups and by a pair of 1,2-diaminocyclohexane ligands functioning as an *N,N'*-bidentate. Two thiocyanate groups take axial positions with

Table 1. Crystallographic and experimental data for 1

Empirical formula	C ₁₄ H ₂₈ CdN ₆ S ₂
Formula weight	456.94
Temperature	293(2) K
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 11.842(2) Å <i>b</i> = 7.926(2) Å <i>c</i> = 11.291(2) Å β = 106.74(3)°
Volume	1014.8(4) Å ³
Z	2
Density (calculated)	1.495 g/cm ³
Absorption coefficient	1.289 mm ⁻¹
<i>F</i> (000)	468
θ range for data collection	3.14 to 24.97°
Limiting indices	-14 ≤ <i>h</i> ≤ 0, 0 ≤ <i>k</i> ≤ 9, -12 ≤ <i>l</i> ≤ 13
Reflections collected/unique	1864/1775 (<i>R</i> _{int} = 0.0188)
Data/restraints/parameters	1775/0/106
Goodness-of-fit on <i>F</i> ²	1.066
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0518, <i>wR</i> ₂ = 0.1315
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0615, <i>wR</i> ₂ = 0.1397
Largest diff. peak and hole	1.007 and -0.369 eÅ ⁻³

trans-configurations. On the other hand, two 1,2-diaminocyclohexane ligands take equatorial positions and forms 5-membered chelate rings with the central cadmium(II) atom. This result suggests that the *trans* geometry is favored when the amine ligand is bulkier. Therefore, the coordination geom-

Table 2. Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å²×10³) for 1

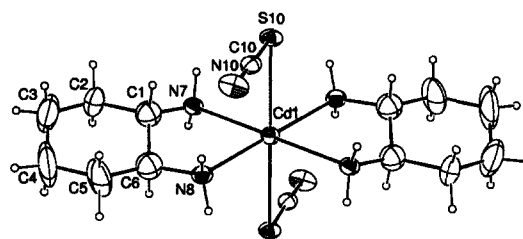
atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Cd(1)	5000	0	0	60(1)
S(10)	5316(2)	203(2)	2566(1)	73(1)
C(10)	6437(6)	1467(7)	2826(5)	72(2)
N(10)	7292(6)	2334(8)	3018(5)	102(2)
C(1)	7569(8)	-1186(12)	282(12)	143(4)
C(2)	7033(8)	-2509(11)	806(11)	135(3)
C(3)	7636(10)	-4225(13)	892(11)	144(4)
C(4)	8883(14)	-4070(20)	1290(20)	237(9)
C(5)	9367(13)	-2900(30)	680(20)	284(11)
C(6)	8828(8)	-1153(17)	645(14)	180(5)
N(7)	6988(4)	462(7)	252(5)	74(1)
N(8)	5762(5)	-2661(5)	304(4)	72(1)

*U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Table 3. Bond lengths (Å) and angles (°) for 1

Cd(1)-S(10)	2.817(2)	S(10)-C(10)	1.621(7)
C(10)-N(10)	1.19(1)	Cd(1)-N(7)	2.317(5)
Cd(1)-N(8)	2.281(4)	C(1)-C(2)	1.44(1)
C(2)-C(3)	1.53(1)	C(3)-C(4)	1.42(2)
C(4)-C(5)	1.37(2)	C(5)-C(6)	1.52(2)
C(6)-C(1)	1.43(1)	C(1)-N(7)	1.47(1)
C(2)-N(8)	1.45(1)		
S(10)-Cd(1)-N(7)	92.0(1)	S(10)-Cd(1)-N(8)	88.2(1)
S(10)-Cd(1)-N(7) ⁱ	88.0(1)	S(10)-Cd(1)-N(8) ⁱ	91.8(1)
S(10)-Cd(1)-S(10) ^j	180.00(7)	N(7)-Cd(1)-N(8)	77.5(2)
N(7)-Cd(1)-N(7) ⁱ	180.00(5)	N(7)-Cd(1)-N(8) ⁱ	102.5(2)
N(8)-Cd(1)-N(8) ⁱ	180.0(3)	Cd(1)-S(10)-C(10)	94.7(2)
Cd(1)-N(7)-C(1)	108.3(5)	Cd(1)-N(8)-C(2)	107.6(4)
S(10)-C(10)-N(10)	177.0(6)	C(1)-C(2)-C(3)	115.0(8)
C(2)-C(3)-C(4)	111.8(9)	C(3)-C(4)-C(5)	116.5(9)
C(4)-C(5)-C(6)	113.3(9)	C(5)-C(6)-C(1)	112.7(9)
C(6)-C(1)-C(2)	116.3(9)	N(7)-C(1)-C(2)	113.4(7)
N(7)-C(1)-C(6)	115.7(9)	N(8)-C(2)-C(1)	115.5(7)
N(8)-C(2)-C(3)	111.4(8)		

Symmetry code : (i) -*x* + 1, -*y*, -*z*.

**Fig. 1. The coordination environment around the Cd(II) atom in 1 with ellipsoids at the 30% probability level. The hydrogen atoms are shown as small circles of arbitrary radii.**

etry of the central cadmium(II) atom adopts a slightly distorted octahedral environment with CdS₂N₄ composition. The Cd-S_{SCN} bond length of 2.817(2) Å and the average Cd-N_{diaminocyclohexane} bond length of 2.299(5) Å are similar to those observed in the cadmium(II) thiocyanate complexes with amine ligands.⁸⁻¹³ The average S_{SCN}-Cd-N_{diaminocyclohexane} bond angle is 90.0(1)°, and the intra and inter N-Cd-N bond angles are 77.5(2)° and 102.5(2)°, respectively. As listed in Table 3, bond lengths and angles of thiocyanate and 1,2-diaminocyclohexane ligands are not unusual.¹⁸⁻²⁰

As shown in Fig. 2, the molecular packing of the

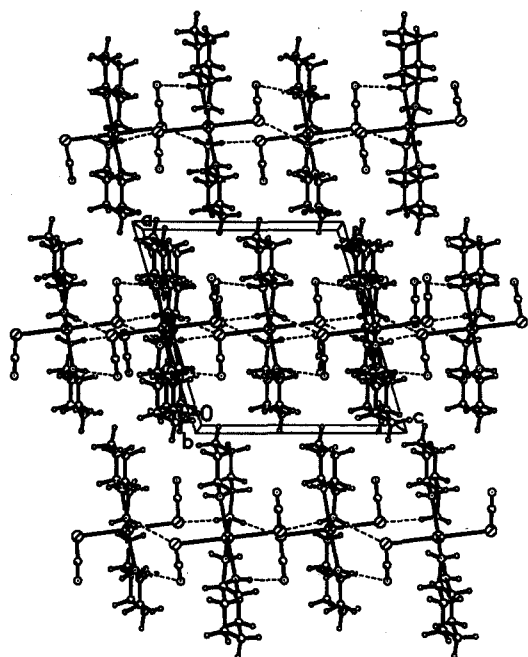


Fig. 2. A perspective view of the unit cell of **1** along the *b*-axis.

title complex lies on an array parallel to the *c*-axis. The sulfur atoms of the thiocyanate ligands are coordinated to the octahedral cadmium(II) atoms, while the nitrogen atoms of the thiocyanate ligands are uncoordinated. This is quite different from other cadmium(II) thiocyanate complexes¹⁸⁻¹⁹ that are doubly bridged by the thiocyanate (SCN^-) group and isothiocyanate (NCS^-) group through both ends. The 1,2-diaminocyclohexane ligand has a 6-membered cyclohexane ring in a chair conformation, and its cyclohexyl ring is approximately perpendicular to the plane of the *ac*-plane. The N atoms of 1,2-diaminocyclohexane and the N atoms of thiocyanate are linked together in a hydrogen-bonded chain along *c*-axis. Furthermore, these hydrogen bonding chains are crosslinked in the *bc*-plane by the weak N7-H \cdots N10 hydrogen bond [3.17(1) Å, 179.2°]. In summary, the title compound, (**1**), is an octahedral mononuclear complex of cadmium(II) with the thiocyanate monodentate ligands and 1,2-diaminocyclohexane chelating ligands, and the crystal structure is further reinforced by weak hydrogen-bonding networks.

4. Supplementary Material

Tables of crystallographic details, atomic coordinates, interatomic distances and angles, torsional angles, hydrogen atom coordinates, anisotropic displacement parameters, and structure factors are available from I. H. Kim.

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