

티오시아네이트 및 4-메틸이미다졸 리간드로 구성된 1차원 카드뮴(II) 착물의 합성과 구조 분석

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Synthesis and Structural Characterization of the One-Dimensional Cadmium(II) Complex with Thiocyanate and 4-Methylimidazole Ligands

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Abstract : One-dimensional coordination polymer of cadmium(II) complex, $[\text{Cd}(\text{SCN})_2(\text{C}_4\text{H}_6\text{N}_2)_2]_n$, has been prepared and characterized by X-ray single crystallography. Structure analysis reveals that each cadmium(II) atom is six-coordinated in distorted octahedral fashion with CdS_2N_4 composition. CdS_2N_4 composition contains two S and two N atoms from four thiocyanates and two N atoms from two 4-methylimidazole ligands. Central cadmium(II) atoms are run in parallel to the *a*-axis and are doubly bridged with neighboring cadmium(II) atoms by the thiocyanate and isothiocyanate ligands. Thus, this complex has a one-dimensional polymer structure in which the 4-methylimidazole is in the *trans* conformation.

Key words : cadmium complex, thiocyanate, 4-methylimidazole, polymeric 1D structure

1. Introduction

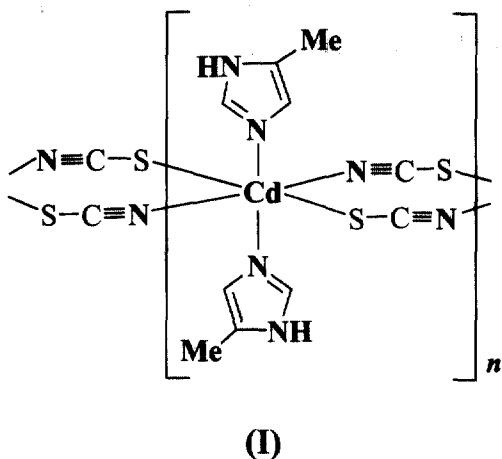
The supramolecular architecture of multi-dimensional networks with organic-inorganic hybrid composition has useful properties as an electronic, magnetic, optical, catalytic materials, and *etc.*¹⁻³ Therefore, designing of infinite one- (1D), two- (2D), and three-dimensional (3D) inorganic-organic mixed frameworks, has used the coordination properties of various pseudohalide ions such as CN^- , SCN^- , OCN^- , SeCN^- , CNO^- , N_3^- , and complementary organic ligands, by several workers.⁴⁻⁶

Chemistry of transition metal pseudohalide complexes has been intensively studied in the area of metal thiocyanato complexes⁷ with monodentate and/or bidentate ligands such as aliphatic amines, aromatic amines, cyclic amines. Many of them are in a linear polymeric form having double thiocyanate ion bridgings between any pair of adjacent metal atoms. Recently, we have also obtained the linear polymeric structure of $\text{Cd}(\text{SCN})_2(\text{aniline})_2$ ⁸, $\text{Cd}(\text{SCN})_2(\text{morpholine})_2$ ⁹ with aniline and morpholine as a complementary ligand, respectively. However, the coordination behaviour of imidazole in the transition metal-imidazole complexes is controversial. More specifically, the imidazole in the complexes acts either as *N*³-bonded monodentate ligand^{10,11} or as bidentate

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ligand^{12,13} via N^1 and N^3 atoms.

Therefore, as an extension of the study, we have introduced the thiocyanate ligand and 4-methylimidazole ligand as a imidazole derivative in order to develop novel 2D and/or 3D framework structures. However, we found that imidazole did not function as a bidendate ligand and report herein the preparation and crystal structure of 1D inorganic-organic composite coordination polymer of the title compound $[\text{Cd}(\text{SCN})_2(\text{C}_4\text{H}_6\text{N}_2)_2]_n$, (I).



2. Experimental

2.1. Preparation and Characterization of (I)

To 30 ml of distilled water, 5 mmol (1.14 g) of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and 10 mmol (2.91 g) of KSCN were introduced with stirring. To this mixture solution, 20 mmol (1.64 g) of 4-methylimidazole was added with stirring. After 4-methylimidazole was added, fine precipitates formed. Then the pH of the solution was adjusted to 9 by adding 2-aminoethanol and citric acid. A small amount of the precipitate was filtered off and the resulting solution was allowed to stand in refrigerator at 5 °C. After a few weeks the pale yellow block crystals were obtained with yield of 70 %.

IR spectrum was recorded on BioRad Digilab FTS-165 infrared spectrophotometer using KBr wafer methods. Assignment of relevant absorption bands

confirmed the presence of thiocyanate ligand and 4-methylimidazole ligand.¹⁴ The quantitative analysis of Cd^{2+} ion was conducted on 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. Composition of the crystal compound (I) was deduced from the elemental analyses; the formula of $[\text{Cd}(\text{SCN})_2(\text{C}_4\text{H}_6\text{N}_2)_2]_n$ is consistent with the results of single crystal X-ray diffraction analysis. *Anal. Found:* C, 30.23; H, 3.05; N, 21.05; S, 16.51; Cd, 28.1 %. *Calc. for $\text{CdC}_{10}\text{H}_{12}\text{N}_6\text{S}_2$:* C, 30.58; H, 3.08; N, 21.40; S, 16.33; Cd, 28.62 %.

2.2. X-ray Single Crystallography

A pale yellow block crystal of the title compound was coated with epoxy glue in order to prevent degradation of the specimen under ambient conditions. Intensity data were collected at room temperature on Siemens P4 four-circle X-ray diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å). Accurate unit cell dimensions were refined using 39 reflections with 2θ ranges 10–33°. Three standard reflections were measured every 97 reflections: no remarkable decays were observed. The reflections used with the intensities $|I| > 2\sigma |I|$ were Lorentz and polarization corrected; semi-empirical absorption correction based on psi-scans was applied. Total of 1132 reflections was collected in 2θ range 5.2–55.0° using θ - 2θ scan mode.

All calculations in structural solution and refinement were performed using Siemens SHELXTL crystallographic software.¹⁵ The space group was assigned based on systematic absences and intensity statistics, and was confirmed by successful refinements. The structure was solved by direct method¹⁶ and refined by successive full-matrix least-squares method followed by difference Fourier maps. All the non-hydrogen atoms were refined anisotropically; all hydrogen atoms were fixed at the calculated positions with isotropic thermal parameters. Final difference of electron density maps contained no significant features.

3. Results and Discussion

Crystallographic and experimental data are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2.

As shown in Fig. 1, the central cadmium(II) atom is hexa-coordinated by a pair of sulfur atoms from two thiocyanate (SCN) groups, a pair of nitrogen atoms from two isothiocyanate (NCS) groups, and two nitrogen (N^1) atoms from two 4-methylimidazole ligands. Two thiocyanate and two isothiocyanate groups take equatorial positions, and two 4-methylimidazole ligands take axial positions with all in *trans*-configurations, respectively. Thus, the coordination environment of the central cadmium(II) atom adopts distorted octahedral geometry with CdS_2N_4 composition.

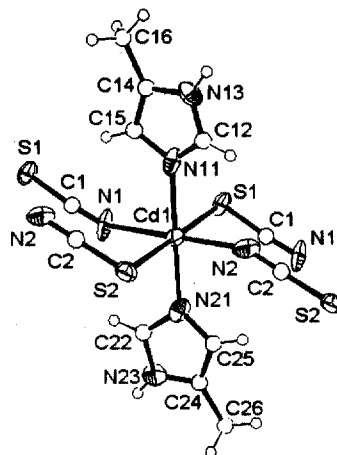


Fig. 1. The coordination environment around the Cd(II) atom in (I) with ellipsoids at the 30 % probability level. The hydrogen atoms are shown as small circles of arbitrary radii.

Table 1. Crystallographic and experimental data for (I)

Formula	$C_{10}H_{12}CdN_6S_2$
Formula weight	392.78
Crystal system	triclinic
Space group	$P1$
a (Å)	5.841(2)
b (Å)	8.229(2)
c (Å)	9.159(3)
α (°)	114.12(3)
β (°)	104.53(3)
γ (°)	97.80(3)
V (Å ³)	374.5(2)
Z	1
D_c (g/cm ³)	1.742
$F(000)$	194
μ (Mo-K α) (mm ⁻¹)	1.731
2θ range for data (°)	5.2 ~ 55.0
Limiting indices	$-7 \leq h \leq 6, -10 \leq k \leq 7, -10 \leq l \leq 6$
Reflections collected	1132
Independent reflections	1132 [$R_{int} = 0.0000$]
Parameters	172
Goodness-of-fit on F^2	1.146
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0298, wR_2 = 0.0737$

Table 2. Selected bond lengths (Å) and angles (°) for (I)

Cd(1)-S(1)	2.838(6)	Cd(1)-S(2)	2.826(6)
Cd(1)-N(1) ^{#2}	2.38(1)	Cd(1)-N(2) ^{#1}	2.29(2)
Cd(1)-N(11)	2.25(2)	Cd(1)-N(21)	2.27(2)
S(1)-C(1)	1.64(2)	C(1)-N(1)	1.12(2)
S(2)-C(2)	1.65(2)	C(2)-N(2)	1.18(2)
N(11)-C(12)	1.32(2)	C(12)-N(13)	1.34(2)
N(13)-C(14)	1.38(1)	C(14)-C(15)	1.36(2)
C(14)-C(16)	1.52(3)	C(15)-N(11)	1.39(2)
N(21)-C(22)	1.34(2)	C(22)-N(23)	1.36(2)
N(23)-C(24)	1.37(2)	C(24)-C(25)	1.36(2)
C(24)-C(26)	1.50(3)	C(25)-N(21)	1.37(2)
S(1)-Cd(1)-S(2)	179.4(3)	S(1)-Cd(1)-N(1) ^{#2}	89.0(5)
S(1)-Cd(1)-N(2) ^{#1}	90.7(5)	S(1)-Cd(1)-N(11)	89.7(5)
S(1)-Cd(1)-N(21)	88.8(6)	S(2)-Cd(1)-N(1) ^{#2}	91.2(5)
S(2)-Cd(1)-N(2) ^{#1}	89.0(5)	S(2)-Cd(1)-N(11)	89.8(6)
S(2)-Cd(1)-N(21)	91.7(6)	N(1) ^{#2} -Cd(1)-N(2) ^{#1}	179.8(1)
N(11)-Cd(1)-N(21)	178.5(1)	N(11)-Cd(1)-N(1) ^{#2}	90.1(7)
N(11)-Cd(1)-N(2) ^{#1}	89.9(7)	N(21)-Cd(1)-N(1) ^{#2}	89.8(7)
N(21)-Cd(1)-N(2) ^{#1}	90.2(7)	Cd(1)-S(1)-C(1)	95.0(8)
Cd(1)-S(2)-C(2)	97.0(7)	Cd(1) ^{#1} -N(1)-C(1)	149(2)
Cd(1) ^{#2} -N(2)-C(2)	150(2)	Cd(1)-N(11)-C(12)	125(1)
Cd(1)-N(11)-C(15)	127(1)	Cd(1)-N(21)-C(22)	124(1)
Cd(1)-N(21)-C(25)	133(1)	S(1)-C(1)-N(1)	175(3)
S(2)-C(2)-N(2)	179(2)	N(11)-C(12)-N(13)	110(2)
C(12)-N(13)-C(14)	107(2)	N(13)-C(14)-C(15)	107(2)
N(13)-C(14)-C(16)	118(2)	C(14)-C(15)-N(11)	107(2)
C(15)-N(11)-C(12)	107(2)	C(15)-C(14)-C(16)	135(2)
N(21)-C(22)-N(23)	112(2)	C(22)-N(23)-C(24)	107(2)
N(23)-C(24)-C(25)	105(2)	N(23)-C(24)-C(26)	125(2)
C(24)-C(25)-N(21)	112(2)	C(25)-N(21)-C(22)	103(2)
C(25)-C(24)-C(26)	130(2)		

Symmetry transformations used to generate equivalent atoms: ^{#1}: $x+1, y, z$ ^{#2}: $x-1, y, z$

Cd-S_{SCN} bond length of 2.826(6), 2.838(6) Å is longer than Cd-N_{NCS} bond length of 2.29(2), 2.38(1) Å. Axial Cd-N_{4-methylimidazole} bond length of 2.25(2) and 2.27(2) Å is similar to equatorial Cd-N_{NCS} bond length (2.29(2) and 2.38(1) Å). Cd-S-C_{SCN} bond angle of 95.0(8) and 97.0(7)° and Cd-N-C_{NCS} bond angle of 149(2) and 150(2)° are smaller than the values (98.1~99.6 and 163.8~165.5°) observed in the cadmium complexes, Cd(SCN)₂[(C₆H₅CH₂)₂NH]₂¹⁷ and [Cd(SCN)₂(CH₃C₃H₄N)₂]_n¹⁸, with doubly bridged thiocyanate ligands. As listed in Table 2, bond lengths and angles of thiocyanate and 4-methylimidazole ligands are not unusual.¹⁹

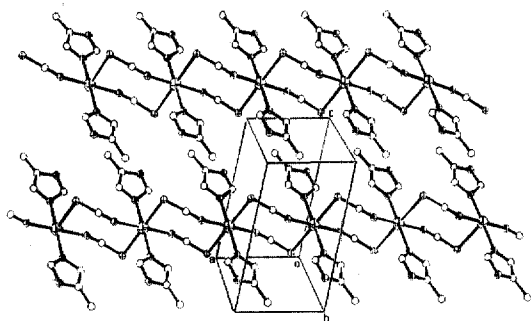


Fig. 2. Perspective view of the unit cell of (I) along the *b*-axis. Hydrogen atoms have been omitted for clarity.

As shown in Fig. 2, the octahedral cadmium(II) centers make an array in parallel to the *a*-axis, and each pair of adjacent cadmium(II) atoms are doubly bridged by the thiocyanate and isothiocyanate groups through both ends. Repeating unit of the cadmium(II)-thiocyanate group formed Cd-S-C-N-Cd-S'-C'-N'- eight-membered ring in a chair conformation. The chain-like structure makes an array in parallel to the *ac*-plane of the unit cell. On the other hand, a couple of the 4-methylimidazole ligands are coordinated to the octahedral cadmium(II) centers via 4-methylimidazole N¹ atoms occupying the axial sites because of steric effect. This structure is different from the other imidazole adducts^{11,12} which are coordinated to the cadmium(II) atom via imidazole N³ atoms. This cadmium(II) complex, [Cd(SCN)₂(C₄H₆N₂)₂]_n,

provides one-dimensional polymeric linear chain structure showing monodentate N¹-bonded character of 4-methylimidazole ligand as in case of the other cadmium(II) thiocyanate adducts.⁸⁻¹⁰

Supporting Information Available

Atomic coordinates, bond lengths and angles, thermal parameters, and hydrogen atom coordinates for title compound are available.

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