

Preparation and One-Dimensional Coordination Structure of the Bis(morpholine)dithiocyanatocadmium(II) Complex, $[\text{Cd}(\text{SCN})_2(\text{C}_4\text{H}_9\text{NO})_2]$

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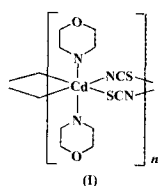
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Extensive studies have been carried out on the constructions of infinite one- (1D), two- (2D), and three-dimensional (3D) networks with organic-inorganic mixed compounds.^{1,2} It has been reported that they have useful properties as an electronic, magnetic, optical, and catalytic materials.³ For designing of infinite multi-dimensional inorganic-organic mixed frameworks, one of authors⁴ and other workers^{5,6} have used the coordination properties of various pseudohalide ions and complementary organic ligands. Generally, they are known to build up one-, two-, and three-dimensional frameworks linking one metal atom M to another metal atom M' alternately.⁷

The chemistry of transition metal pseudohalide complexes has been intensively studied in the area of metal thiocyanato complexes⁸ with monodentate and/or bidentate ligands such as aliphatic amines, aromatic amines, cyclic amines. However, the coordination behaviour of morpholine in the transition metal-morpholine complexes is controversial. More specifically, the morpholine in the complexes acts either as N-bonded monodentate ligand⁹⁻¹¹ or as bidentate ligand.^{12,13} Therefore, as an extension of the study, we have introduced the thiocyanate ligand and heterocyclic morpholine compound as a complementary ligand in order to develop novel multi-dimensional framework structures. We report herein the preparation and crystal structure of one-dimensional inorganic-organic composite coordination polymer of the title compound $[\text{Cd}(\text{SCN})_2(\text{C}_4\text{H}_9\text{NO})_2]$, (I).



Experimental Section

Preparation and analysis of $[\text{Cd}(\text{SCN})_2(\text{C}_4\text{H}_9\text{NO})_2]$. $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (1.14 g, 5 mmol) and KSCN (2.91 g, 10 mmol) were dissolved in 30 mL of distilled water. To the solution, 1.7 mL (20 mmol) of neat morpholine was added dropwise with stirring. After the morpholine 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 aqueous solution was allowed to stand in a refrigerator at 278 K. After a few

weeks crystals were obtained.

The quantitative analysis of Cd^{2+} ion was conducted on a Perkin-Elmer 2380 atomic absorption spectrometer. The analyses of carbon, hydrogen, nitrogen, oxygen and sulfur contents were made on a CE EA-1110 elemental analyzer. Anal. Found: Cd, 27.5; C, 29.66; H, 4.51; N, 13.80; O, 8.14; S, 15.74%. Calc. for $\text{CdC}_{10}\text{H}_{18}\text{N}_4\text{O}_2\text{S}_2$: Cd, 27.91; C, 29.82; H, 4.50; N, 13.91; O, 7.94; S, 15.92%.

X-ray crystallography. A single crystal of the title compound was coated with epoxy resin in order to prevent degradation of the specimen under ambient conditions. The intensity data were collected at room temperature on a Siemens P4 four-circle X-ray diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$). Accurate unit cell dimensions were refined using $3\hat{9}$ reflections with 2θ ranges $5.04\text{--}20.16^\circ$. Three standard reflections were measured every 97 reflections and no remarkable decays were observed. The reflections used with the intensities $|I| > 2\sigma|I|$ were Lorentz and polarization corrected by the semi-empirical absorption correction applying psi-scans. A total of 2225 reflections was collected in the 2θ range $4\text{--}55^\circ$ using $\theta\text{--}2\theta$ scan mode.¹⁴

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

Results and Discussion

The crystallographic data are listed in Table 1. The selected bond lengths and bond angles are summarized in Table 2. Asymmetric unit and a perspective drawing of the compound together with the atomic numbering schemes are shown in Figures 1 and 2, respectively.

As shown in Figures 1 and 2, the cadmium(II) atom is six-coordinated by two thiocyanate (SCN) sulfur atoms, two isothiocyanate (NCS) nitrogen atoms, and two morpholine nitrogen atoms. Two thiocyanate and two isothiocyanate groups

Table 1. Crystallographic data for [Cd(SCN)₂(C₄H₉NO)₂]

Formula	C ₁₀ H ₁₈ N ₄ O ₂ S ₂ Cd
Formula weight	402.80
Crystal system	triclinic
Space group	<i>P</i> 1̄
<i>a</i> (Å)	5.9340(6)
<i>b</i> (Å)	6.7565(6)
<i>c</i> (Å)	10.0757(13)
α (°)	84.277(9)
β (°)	82.495(10)
γ (°)	70.349(8)
<i>V</i> (Å ³)	376.51(7)
<i>Z</i>	1
<i>D_c</i> , <i>D_m</i> (g/cm ³)	1.777, 1.78(1)
<i>F</i> (000)	202
μ (Mo-Kα) (mm ⁻¹)	1.730
2θ range for data (°)	4.08–55.00
Limiting indices	-7 ≤ <i>h</i> ≤ 1, -8 ≤ <i>k</i> ≤ 8, -13 ≤ <i>l</i> ≤ 13
Reflections collected	2225
Independent reflections	1728 [<i>R</i> _{int} = 0.0246]
Parameters	88
Goodness-of-fit on <i>F</i> ²	1.140
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0190, <i>wR</i> ₂ = 0.0524

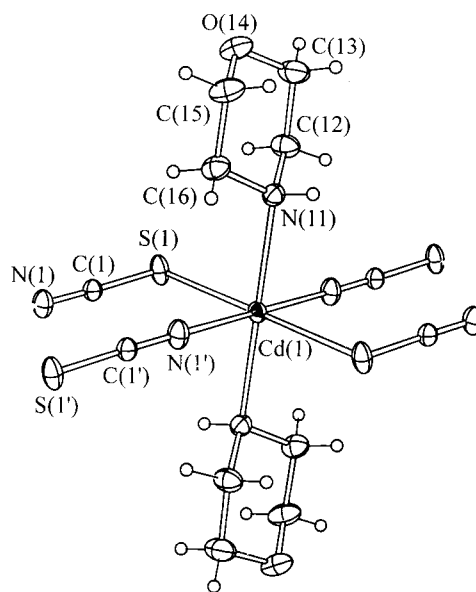
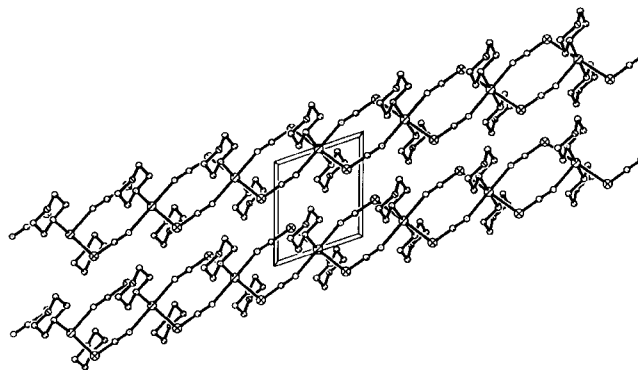
Table 2. Selected bond lengths (Å) and angles (°) for [Cd(SCN)₂(C₄H₉NO)₂]

Cd(1)-S(1)	2.7536(6)	Cd(1)-N(1) ^{*1}	2.3234(17)
Cd(1)-N(11)	2.3710(16)	S(1)-C(1)	1.6403(19)
C(1)-N(1)	1.149(2)	N(11)-C(12)	1.479(3)
C(12)-C(13)	1.518(3)	C(13)-O(14)	1.414(3)
O(14)-C(15)	1.420(3)	C(15)-C(16)	1.517(3)
C(16)-N(11)	1.472(3)		
S(1)-Cd(1)-N(11)	90.14(4)	N(1) ^{*1} -Cd(1)-N(11)	90.99(7)
S(1)-Cd(1)-N(1) ^{*1}	92.81(5)	Cd(1)-S(1)-C(1)	98.82(6)
Cd(1) ^{*2} -N(1)-C(1)	163.94(17)	Cd(1)-N(11)-C(12)	115.55(13)
Cd(1)-N(11)-C(16)	112.27(13)	S(1)-C(1)-N(1)	177.95(17)
N(11)-C(12)-C(13)	112.04(19)	C(12)-C(13)-O(14)	111.4(2)
C(13)-O(14)-C(15)	109.92(19)	O(14)-C(15)-C(16)	110.89(19)
C(15)-C(16)-N(11)	112.4(2)	C(16)-N(11)-C(12)	109.27(16)

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

take equatorial positions, and two morpholine ligands take axial positions with all in *trans*-configurations, respectively. The central cadmium(II) atom adopts a distorted octahedral geometry. The Cd-S_{SCN} bond length of 2.7536(6) Å is longer than the Cd-N_{NCS} bond length of 2.3234(17) Å.^{17,18} The equatorial Cd-N_{NCS} bond length is shorter than the axial Cd-N_{morpholine} bond length of 2.3710(16) Å. The Cd-S-C_{SCN} bond angle of 115.55(13)° and Cd-N-C_{NCS} bond angle of 163.94(17)° are similar to the values previously observed in the thiocyanate bridging transition metal complexes.^{19,20} Bond lengths and angles of thiocyanate and morpholine ligands in the title compound are not unusual.

As shown in Figure 2, the octahedral Cd centers make an

**Figure 1.** Coordination geometry around the cadmium(II) atom in **I** showing the atomic labelling scheme and 30% probability thermal ellipsoids except for the hydrogen atoms.**Figure 2.** A perspective view of the unit cell of **I** along the *c*-axis; H atoms have been omitted for clarity.

array in parallel to the *a*-axis, and are doubly bridged with neighboring Cd centers by the thiocyanate and isothiocyanate ligands; one of them is S-coordinated and the other one is N-coordinated to the same side metal atom. This eight-membered ring with a repeating unit of Cd-S-C-N-Cd'-S'-C'-N'- makes an array in parallel to the *ab*-plane of the unit cell. On the other hand, two morpholine ligands are coordinated to each octahedral Cd center *via* morpholine nitrogen atoms occupying the axial sites, and take the chair conformation by the alicyclic skeleton of morpholine molecules. Unlike other reported compounds, such as Cd(ben)(SCN)₂ (ben = bis(2-aminoethyl)amine),²¹ [Ag(SCN)L]_n (L = 2-methylpyridine, 3-methylpyridine),²² and CoHg(SCN)₄(H₂O)₂ · 2{CH₃CON-(CH₃)₂},²³ the title compound shows one of the unique one-dimensional infinite chain structure with monodentate N-bonded character of morpholine.

Supporting information available. Tables of crystallographic details, atomic coordinates, interatomic distances and angles, torsional angles, hydrogen atom coordinates, anisotropic displacement parameters, and structure factors for title

compound are available. Supplementary materials are available from C. H. Kim (Phone: +82-42-860-7721, Fax: +82-42-860-7704, e-mail: chkim@pado.kriect.re.kr).

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