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Synthesis, and Crystal and Molecular Structure of Bis(benzylamine)bis(thiocyanato)cadmium(II), $[Cd(SCN)_2(C_6H_5CH_2NH_2)_2]$, in Planar Polymeric Form: Allotrope of the Linear Polymeric Complex

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Synopsis. The title complex (**1**), which is two-dimensional polymeric and an allotrope of the previously reported linear polymeric complex (**2**), was obtained and its crystal and molecular structure was determined by means of a single-crystal X-ray diffraction method. Since **1** is more soluble in organic solvents, **1** and **2** could be prepared, separately. The crystal of $CdC_{16}H_{18}N_4S_2$, F. W. 442.9, is monoclinic, space group $P2_1/c$, a=13.958(2), b=5.759(1), c=11.466(2) Å, β=99.24(1)°, U=909.8(3) Å^3, Z=2, D_m=1.61(3), D_x=1.62 g cm^{-3}, μ(Mo $K\alpha$)=14.2 cm^{-1}. The cadmium atom is in a trans-2*S*4*N*-hexa-coordinated octahedral geometry. Each cadmium atom is at the center of symmetry, and it is bridged to four cadmium atoms by an thiocyanate ion, respectively, and the complex network is extended on the bc-plane.

There have aleady been several structural reports concerning the one-, two-, and three-dimensional polymeric thiocyanato (SCN) complexes of metals.[1–4] In the case of thiocyanato complexes of cadmium, $Cs[Cd(SCN)_3]$ has a three-dimensional,[5] $Rb[Cd(SCN)_3]$ a two-dimensional,[5] and $[(CH_3)_4N][Cd(SCN)_3]$ a one-dimensional network,[6] respectively. However, in the Lewis base adducts of cadmium(II) thiocyanates, they are in a double-SCN-ion-bridging one-dimensional polymeric form,[7–10] like cobalt thiocyanate.[4]

Recently, we found that other types of crystals were mixed in the sample of the benzylamine adduct of cadmium(II) thiocyanate, previously reported,[10] which gave the same chemical analysis and almost the same infrared spectrum, though they were found to have a different unit-cell.

Therefore, we investigated how to separated the previously reported adduct **2** and this new compound **1**; moreover, the crystal and molecular structure of **1** was determined by a single-crystal X-ray diffraction method.

Experimental

Syntheses of Both Types of Bis(benzylamine)bis(thiocyanato)cadmium(II), (1,2). The product obtained by mixing cadmium thiocyanate and benzylamine in the stoichiometric ratio in methanolic medium was always a mixture of **1** and **2**. Although the crystals of **2** were almost insoluble in methanol and ethanol after once precipitated, while the solubility of the crystals of **1** was also very low, the yield of **1** after recrystallization from methanol was poor. The process to obtain **1**, found empirically, is as follows.

Cadmium(II) thiocyanate (0.9 g, 4 mmol) and benzylamine (0.9 g, 8.4 mmol) were dissolved into 30 and 10 cm^3 of methanol–ethanol mixture (2:1=v/v), separately (the mixing of ethanol lowers the solubility of deposited **2**). They were warmed to about 80 °C and mixed. After the mixture was refluxed about 2 h, it was filtered off while hot in order to remove **2** (a part of **1** was also removed). The filtrate was slowly cooled to 6 °C, and deposited crystals of **1** were separated, washed with a little portion of the ethanol–methanol mixture, and dried in open air. Yield: 0.80 g, 1.8 mmol, 45%. Found: Cd, 25.30; C, 42.99; H, 4.00; N, 12.55%. Calcd for $(CdC_{16}H_{18}N_4S_2)$ Cd, 25.38; C, 43.39; H, 4.10; N, 12.65%.

On the other hand, the precipitated crystals were almost pure **2**, when being added benzylamine a little less than the calculated quantity, using methanol–water mixture as the solvent (98:2=v/v) to increase the solubility of **1**, and being left standing the mixed solution overnight at room temperature. Yield: 0.48 g, 1.1 mmol (59%) from 2 mmol of $Cd(SCN)_2$ and 3.7 mmol of benzylamine in 40 cm^3 of the solvent.

Although both crystals of **1** and **2** appear commonly in a spatula-like plate form (as shown in Fig. 1**A**) relatively large crystals of **1** and **2** appear in the forms shown by Figs. 1**B** and 1**C**, respectively: this is the best simple method for distinguishing both types of the crystals. From an X-ray photographic study, the respective unit-cell axes of **1** and **2** are found to be in the directions shown in the figure captions.

Single Crystal X-Ray Structure Analysis. The crystal used for the structural analysis was colorless, and parallelepiped in shape (0.3×0.3×0.15 mm^3). The intensities in the range of $3<2\theta<67°$ (2θ) were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer using graphite monochromated Mo $K\alpha$ radiation (λ=0.71073 Å) by means of $\omega-2\theta$ scan technique (scan speed 4° min^{-1}; scan width 1.25+0.5 tanθ (°/θ)). The intensities were corrected for Lorentz and polarization factors, but not for absorption and extinction. Of 3891 independent intensities collected, 2457 reflections with $|F_o|>3\sigma(|F_o|)$ were used for the structure determination.

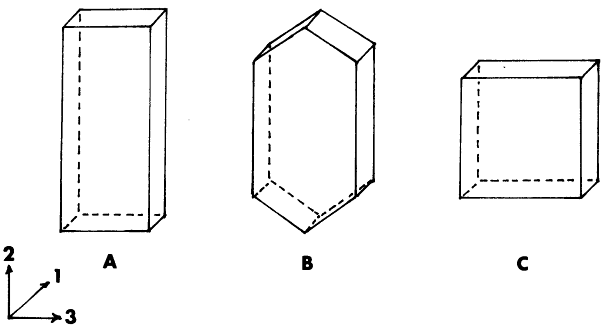

Fig. 1. The apparent features of the complexes **1** and **2** crystals. The directions of the unit-cell axes of **1** and **2** are as follows, respectively. **1**: 1, a; 2, b; 3, c. **2**: 1, a; 2, −c; 3, b.

All the calculations were carried out on a HITAC M-682H computer at the Computer Center of the University of Tokyo, using a local version of the UNICS program.[11] The scattering factors were taken from Ref. 12.

The structure was solved by the heavy-atom method (positional, and thermal parameters were refined by a block diagonal least-squares method). The final *R* value applying an anisotropic temperature factors was 0.057 (all the hydrogen atoms were not included into the structure factor calculations).

Results and Discussion

The selected bond lengths and bond angles are shown in Table 1. A perspective drawing of the complex including the four SCN ions bridging to the neighboring four metal atoms, together with the numbering scheme of the atoms, is shown in Fig. 2, and a packing diagram of a unit cell in Fig. 3.[13] Each cadmium atom is at the center of symmetry (0,0,0 and 0,0.5,0.5), and is bridged to four neighboring metal atoms with a SCN ion, respectively, and the two-dimensional network of the complex is expanded on the bc-plane. This type of the planar-polymeric structure is the first example found in a Lewis base adduct of cadmium(II) thiocyanates.

Table 1. Selected Bond Lengths and Bond Angles of the Complex **1**

Bond length	(l/Å)	Bond length	(l/Å)
Cd-S$^{\mathrm{iii}}$	2.753(2)	Cd-N(1)	2.339(8)
Cd-N(2)	2.322(5)	S-C(1)	1.637(10)
N(1)-C(1)	1.157(13)	N(2)-C(2)	1.477(7)
Cd···Cd$^{\mathrm{ii}}$	6.416(1)		
Bond angle	**(ϕ/°)**	**Bond angle**	**(ϕ/°)**
N(1)-Cd-N(2)	86.8(2)	N(1)-Cd-S$^{\mathrm{iii}}$	90.8(2)
N(2)-Cd-S$^{\mathrm{iii}}$	89.20(14)	Cd-N(1)-C(1)	146.3(7)
Cd$^{\mathrm{ii}}$-S-C(1)	98.39(16)	S-C(1)-N(1)	179.3(9)
Cd-N(2)-C(2)	117.0(4)	N(2)-C(2)-C(3)	113.9(6)

Key to the symmetry operations: ii, *x*, 0.5−*y*, 0.5+*z*; iii, −*x*, −0.5+*y*, 0.5−*z*.

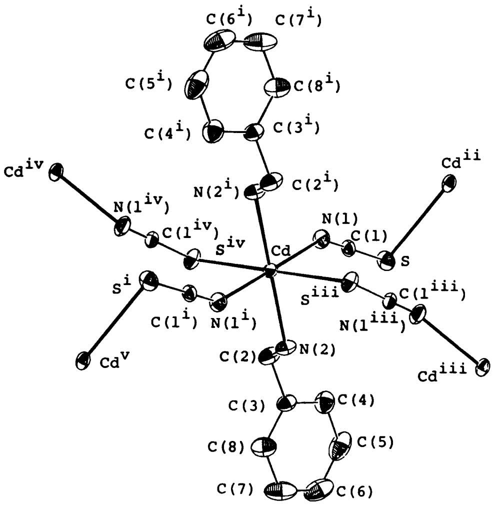

Fig. 2. The perspective drawing of the complex **1** around the central metal atom and thiocyanate ion bridgings: the numbering scheme of the atoms are shown in the figure. The key to the symmetry operations: i, −*x*, −*y*, −*z*; ii, *x*, 0.5−*y*, 0.5+*z*; iii, −*x*, −0.5+*y*, 0.5−*z*; iv, *x*, 0.5−*y*, −0.5+*z*; v, *x*, −0.5−*y*, −0.5+*z*.

As shown in Fig. 2, around a cadmium(II) atom, two SCN sulfur, two SCN nitrogen, and two benzylamine nitrogen atoms are coordinated, where each pair of the same kind of the ligating atoms are in a trans-configuration. The configuration of the complex, as well as the respective bond lengths around the metal atom (Cd-S(SCN), 2.753(2); Cd-N(SCN), 2.339(8); Cd-N(benzylamine), 2.322(5) Å) are not much different from those of **2**. The Cd-N-C(SCN) angle of **1**, 146.3(7)°, is much smaller than the other common thiocyanato complexes (160—180°), while the angles Cd-S-C (98.39(16)°) and S-C-N (179.3(4)°) are in the common range of the other

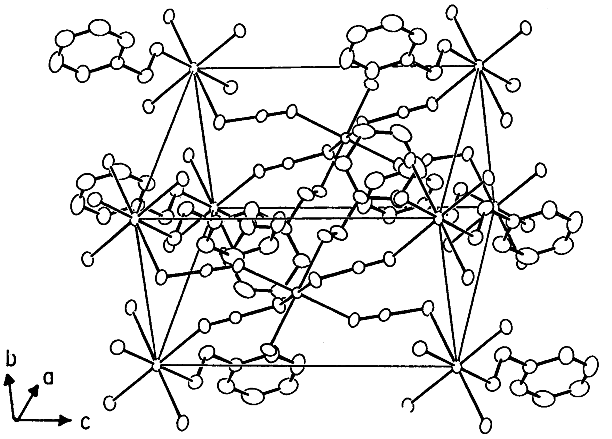

Fig. 3. Crystal packing diagram of the complex **1**.

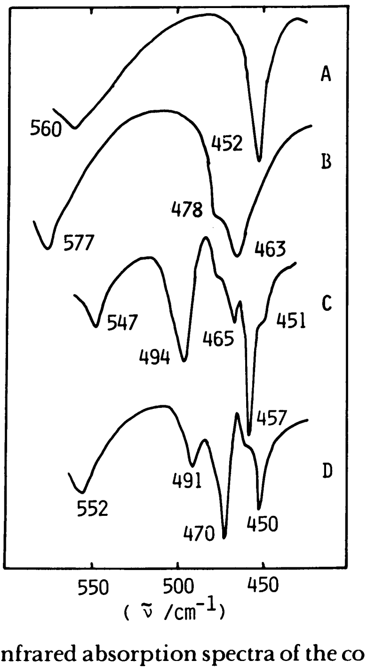

Fig. 4. Infrared absorption spectra of the complexes **1** and **2** near their δ(SCN) peak together with the spectra of some related compounds. (A) Benzylamine, (B) cadmium thiocyanate, (C) complexes **2**, (D) complexes **1**.

cadmium thiocyante complexes.[7–10] These data are the same for the cases of **2**. The inter-bridging-metal-atomic-distance of **1**, 6.416(1) Å, is much longer than that of **2**, 5.873(1) Å.

The infrared absorption spectra of **1** and **2** were found to be aproximately the same: ν(CN), 2080; ν(CS), 752(s), and 720(sh) cm^{-1}. However, as shown in Fig. 4, the features of the δ(SCN) bands of **1** and **2** are a little different from each other: the former peak is more clearly separated. This is another way to distinguish crystals of **1** and **2**.

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13) The final atomic positional and thermal parameters, the final $F_o - F_c$ table, and some additional bond length and bond angle data are deposited as Document No. 8821, at the Editor of the Office of Bull. Chem. Soc. Jpn.