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Crystal and Molecular Structure of Bis(benzylamine)bis(thiocyanato)cadmium(II), [$Cd(SCN)_2(C_6H_5CH_2NH_2)_2$]

Masahiro Taniguchi* and Akira Ouchi
Department of Chemistry, College of Arts and Sciences, The University of Tokyo,
Komaba, Meguro-ku, Tokyo 153

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Synopsis. The crystal and molecular structure of the title complex was determined by means of a single-crystal X-ray diffraction method. A crystal of $CdC_{16}H_{18}N_4S_2$, F. W. 442.8, is monoclinic, with the space group of $P2_1/n$, a=27.390(19), b=5.7709(8), c=5.8733(9) Å, β=90.35(3)°, U=928.3(7) Å^3, Z=2, D_m=1.57(3), D_x=1.58 Mg m^{-3}, and μ(Mo $K\alpha$)=1.59 mm^{-1}. The cadmium(II) atom is hexa-coordinated being ligated with two thiocyanato (SCN) sulfur atoms, as well as with two SCN and two benzylamine nitrogen atoms, where the respective pairs of the same kinds of atoms are all in trans-configuration. Each cadmium atom is at the center of symmetry, and the coordination structure around the atom is symmetric. The metal atoms are lined along c-axis, and the pair of the neighboring metal atoms are doubly bridged by SCN ions, although the bridges are a little weaker than the other same type adducts.

There are already several structural reports about the Lewis-base (L) adducts of cadmium(II) thiocyanate, $Cd(SCN)_2L_2$, where L is 1-, 2-, or 3-methylpyridine,[1,2] dibenzylamine,[3] 2-imidazolidinethione,[4] or $1H$-1,2,4-triazole.[5] In all of them, the octahedrally coordinated cadmium(II) complex cores are laid linearly, and each pair of the neighboring metal atoms are doubly bridged by the thiocyanate (SCN) ions.

This time, we could obtain the same type adduct of benzylamine (bza), $Cd(SCN)_2(bza)_2$, and it was thought to be interesting to clarify its structure due to the reasons as follows. First, how is the direction of the benzene rings of the ligands in the crystal? Although their benzene rings can rotate around the methylene-carbon atom, even in the complex molecule, they must be laid regularly in the crystal to attain the closest packing in it. Therefore, what kind of the arrangement of the rings is adopted there, or whether the π-electron interaction due to the overlapping of the benzene rings exists or not, are interesting problems. Secondly, a preliminary test has shown that the crystal has a unit cell in which only the a-axis is very long, while the other two axes are short; why such long and short periodicities in the crystal take place? Thirdly, to better clarify the character of this type of the double SCN bridging, it is necessary to add more data about the complexes with the bridge.

From these points of view, we determined its crystal and molecular structures by the single-crystal X-ray diffraction method.

Experimental

Synthesis of Bis(benzylamine)bis(thiocyanato)cadmium(II). Cadmium(II) thiocyanate (0.57 g, 2.5 mmol) was dissolved into 20 cm^3 of methanol; benzylamine (0.53 g, 5 mmol) dissolved into 10 cm^3 of methanol was added to it, and mixed. The mixed solution gradually became turbid and precipitation started soon. After being left standing about 30 min at ambient temperature, the deposited crystals were filtered off, washed with acetone, and dried in open air. Yield, 1.0 g (90%). Found; Cd, 25.37; C, 43.07; H, 4.03; N, 12.57%. Calcd for ($CdC_{16}H_{18}N_4S_2$) Cd, 25.38; C, 43.39; H, 4.10; N, 12.65%.

Single Crystal X-Ray Structure Analysis. The colorless crystal used for the structure determination was 0.3×0.3×0.15 mm^3 in size, and was used without shaping. The intensities in the range of $3<2\theta<60°$ (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 ω-scan technique (scan speed 4° min^{-1}; scan width 1.08° (θ)). The intensities were corrected for Lorentz and polarization factors, but no corrections were made for absorption and extinction. Of 3667 independent intensities collected, 2273 with $|F_o|>3\sigma(|F_o|)$ were used for the structure determination.

All the calculations were carried out on a HITAC M-680H computer at the Computer Center of the University of Tokyo, using UNICS III.[6] The scattering factors were taken from Ref. 7.

The structure was solved by the heavy-atom method. The positions of the metal and some sulfur atoms were deduced from a three dimensional Patterson map: other non-hydrogen atoms were succesively located by means of the Fourier syntheses. The positional, isotropic and then anisotropic thermal parameters were refined by a block-diagonal least-squares method. At the final step, all hydrogen atoms were added in the refinement, fixing at the calculated positions (C–H=1.08 Å for the benzene-ring hydrogen atoms, and 1.09 Å for the methylene ones, β_{iso}=8.0 Å^2 being given). The final R and R_w values[8] thus obtained were 0.042 and 0.052, respectively.

Results and Discussion

The selected bond lengths and bond angles are shown in Table 1. A perspective drawing of the complex together with the numbering scheme of the atoms, except the benzene rings of the ligands, is shown in Fig. 1.[9] The projections of the unit cell along b- and c-axes are shown in Figs. 2 and 3, respectively.[10]

The cadmium atoms are lined along c-axis and the respective pair of the side-by-side metal atoms are bridged by two SCN ions as in the case of the other $Cd(SCN)_2L_2$ type adducts.[1–5]

As shown in Fig. 1, around one cadmium(II) atom, two SCN sulfur, two SCN nitrogen, and two bza nitrogen atoms are coordinated, where each pair of the same kinds of the ligating atoms are in trans-configurations. The bond lengths are; Cd-S is 2.7540(15), Cd-N(SCN) is 2.372(3), and Cd-N(bza) is 2.294(3) Å, respectively. The Cd-N(bza) bond length is shorter than, and the Cd-N(SCN) length is longer than, the corresponding bonds of the other Cd-

Table 1. Bond Lengths and Bond Angles of the Title Complex with Estimated Standard Deviations in Parentheses

Bond length	(l/Å)	Bond length	(l/Å)	Bond length	(l/Å)
Cd-S	2.7540(15)	Cd-N(1^{ii})	2.372(3)	Cd-N(2)	2.294(3)
S-C(1)	1.652(4)	N(1)-C(1)	1.143(5)	N(2)-C(2)	1.482(6)
C(2)-C(3)	1.496(6)				
Bond angle	**(ϕ/°)**	**Bond angle**	**(ϕ)/°**	**Bond angle**	**(ϕ/°)**
S-Cd-N(1^{ii})	90.52(9)	S-Cd-N(2)	87.69(9)	N(1^{ii})-Cd-N(2)	88.17(12)
Cd-S-C(1)	99.15(14)	Cd-N(1^{ii})-C(1^{ii})	145.2(3)	S(1)-C(1)-N(1)	177.3(4)
Cd-N(2)-C(2)	118.7(3)	N(2)-C(2)-C(3)	112.8(4)	C(2)-C(3)-C(4)	120.4(4)
C(2)-C(3)-C(8)	120.8(4)	C(4)-C(3)-C(8)	118.8(4)		

Key to the symmetry operation: ii, $-x$, $-y$, $1-z$.

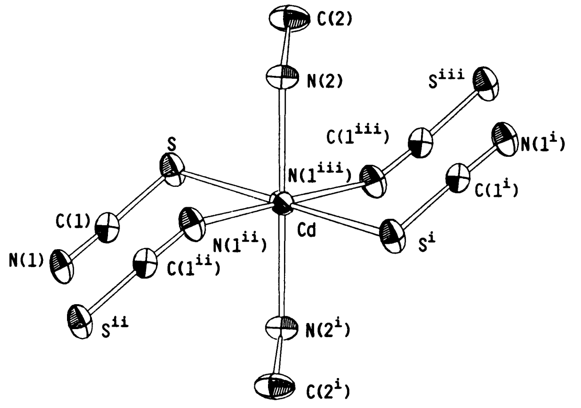

Fig. 1 A perspective drawing of the title complex around the central metal atom with the numbering scheme of the ligating atoms. The key to the symmetry operation: i, $-x$, $-y$, $-z$; ii, $-x$, $-y$, $1-z$; iii, x, y, $-1+z$.

(SCN)$_2$L$_2$ type Lewis base adducts, although their Cd-S(SCN) bond lengths are not much different from each other.[1–5] It is noteworthy that the Cd–N(base) bonds are stronger than the Cd-N(SCN) bonds in this complex; reverse to the other base adducts.

The Cd-N-C(SCN) angle, 145.2(3)°, is much smaller than the other thiocyanato complexes: commonly in the range of 180—160°.[11] However, S-C-N angle, 177.3(4)°, as well as Cd-S-C, 99.15(14)°, are not much different from the corresponding values of the type of cadmium(II) thiocyanate adducts (Cd(SCN)$_2$L$_2$).[1–5]

An eight-membered ring consisting of the two metal atoms and two SCN ions bridging them is in the chair form. The metal atom deviates 1.063 Å from the least-squares plane by six atoms of the two SCN ions (the average deviation of the six atoms are 0.010 Å); the deviation is much larger than the other adducts of this type.[1–5]

From these data, we deduce that the ring is quite deformed and the bridging of the double SCN chains in this complex is weaker than those in the other complexes of this type: The Cd···Cd distance, 5.8733(9) Å (the same as the c-axis length) is longer than the corresponding distances of the latters.[1–5]

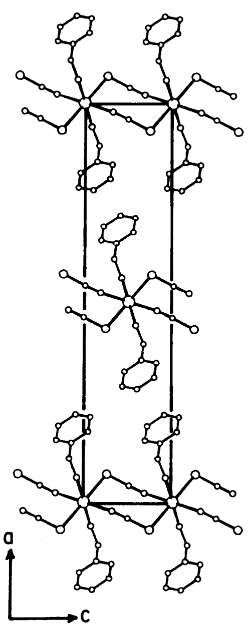

Fig. 2. The projection of the unit cell along b-axis.

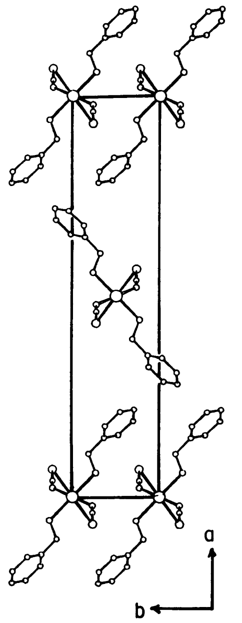

Fig. 3. The projection of the unit cell along c-axis.

As shown in Figs. 2 and 3, no bridgings are found between the complex chains. Respective chains are parallel to the bc-plane. They are intercalated by the parallel hydrophobic layers consisting of the ligand benzene-rings of both side complexes; the rings from both side complexes are not interposed with each other, and the rings from one side metal complexes are not parallel with those of the other side metal complexes. There is no overlapping between the neighboring parallel benzene-ring planes,[12] and no π-electron interaction between the benzene rings are expected. However, such short structural periodicities found in the directions of the b- and c-axes are probably due to the quite regular and closely packed arrangement of the benzene rings in the crystal as above mentioned.

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8) $R=\Sigma||F_\mathrm{o}|-|F_\mathrm{c}||/\Sigma|F_\mathrm{o}|$;
$R_\mathrm{w}=\{\Sigma w(|F_\mathrm{o}|-|F_\mathrm{c}|)^2/\Sigma w|F_\mathrm{o}|^2\}^{1/2}$ where
$w=1/[\{\sigma(|F_\mathrm{o}|)\}^2+(0.0006|F_\mathrm{o}|)^2]$

9) The numbering of the benzene-ring carbon atoms are as follows. The stem methylene carbon atom, C(2), is bonded with the ring carbon atom C(3), and the ring carbon atoms are numbered successively from C(3) to C(8) where the C(3) and C(8) atoms are bonded.

10) The positions of the hydrogen atoms, the final anisotropic temperature factors of non-hydrogen atoms, the final $F_\mathrm{o}-F_\mathrm{c}$ table, and some additional data of bond lengths and bond angles are deposited as Document No. 8762, at the Office of the Editor of Bull. Chem. Soc. Jpn.

11) A. F. Wells, "Structural Inorganic Chemistry," fifth ed, Clarendon, Oxford, U. K. (1984), p. 935.

12) It was examined that when one ring is projected to the other ring plane, whether the projection and the latter ring was overlapping or not.