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The Crystal and Molecular Structure of Bis(dibenzylamine)bis(thiocyanato)cadmium(II), $Cd(SCN)_2\{(C_6H_5CH_2)_2NH\}_2$

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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 technique. A crystal of $CdC_{30}H_{30}N_4S_2$, F. W.=623.13, is triclinic, with a space group $P\bar{1}$, a=11.284(2), b=11.404(2), c=5.974(1) Å, α=93.31(2), β=98.37(1), γ=71.84(1)°, U=722.6(2) Å^3, Z=1, D_m=1.42(3) D_x=1.43 Mg m^{-3}, and μ(Mo $K\alpha$)=9.17 cm^{-1}. The cadmium(II) atom is hexacoordinated, being ligated with two thiocyanato(SCN) sulfur atoms as well as two SCN and two dibenzylamine nitrogen atoms, where the respective pairs of the same kinds of atoms are all in a *trans*-configuration. All cadmium(II) atoms are lined along the c-axis and the side-by-side metal atoms are doubly bridged by SCN ions.

It has already been found that many Lewis base(L) adducts of cadmium(II) thiocyanate, $Cd(SCN)_2L_2$ have chain structures in which respective side-by-side metal atoms are bridged by two thiocyanate (SCN) ions. Among them, in the cases of 2-imidazolinethione,1) 1*H*-1,2,4-triazole,2) and 3-methylpyridine adducts,3) the planes of the side-by-side eight-membered rings by two cadmium(II) and six atoms of two SCN ions between them in the chain are parallel. On the other hand, in the cases of 2-methylpyridine,3) 4-methylpyridine,4) and tri(*p*-tolyl)phosphine adducts,5) two kinds of planes in different directions appear alternately. Moreover, the coordination positions of the respective ligating atoms around the cadmium(II) atoms are not the same in respective complexes, although all of them, except the tri(*p*-tolyl)phosphine adduct, are in octahedral geometry. In cases of the thiocyanatocadmates(II), it was found that the chain structures bridged by SCN ions change, depending on the kinds of the counter cations. Especially in cases of salts of relatively large cations (such as rubidium and cesium) they are in complicated network structures.6) Therefore, some special structure complexes may be found if some massive ligands are used as the additional Lewis base. From such an expectation, this time we synthesized the dibenzylamine adduct; its crystal and molecular structures were determined by the single-crystal X-ray diffraction method.

Experimental

Synthesis of Bis(dibenzylamine)bis(thiocyanato)cadmium(II). Cadmium(II) thiocyanate (1.14 g, 5 mmol) was dissolved into 10 cm^3 of methanol; dibenzylamine (dba) (1.97 g, 10 mmol) dissolved into 10 cm^3 of ethanol was added to it. When the mixed solution was left standing for about one hour at ambient temperature, colorless needle-like crystals were deposited. Yield: 1.7 g (55%). The larger crystals deposited from a more diluted mixed solution (which was left standing several days) were used for an X-ray structure analysis. Anal. Found: Cd, 18.04; C, 57.41; H, 4.84; N, 8.96%. Calcd for ($CdC_{30}H_{30}N_4S_2$), Cd, 18.04; C, 57.82; H, 4.85; N, 8.99%.

Single-Crystal X-Ray Analysis. The crystal used for a structure determination was about 0.3×0.3×0.2 mm^3 in size and was used without shaping. The reflections in the range $3° < 2\theta < 60°$ (2θ) were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer using graphite-monochromated Mo $K\alpha$ radiation, by means of a ω—2θ scan technique (scan speed 4° min^{-1}; scan width 1.10+0.5 tanθ° (θ)). The intensities were corrected for Lorentz and polarization factors, but no corrections were made for absorption and extinction. Of 4596 independent reflections collected, 3565 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.7) The scattering factors were taken from Ref. 8.

The structure was solved by the heavy-atom method. The positions of the cadmium and some sulfur atoms were deduced from a three-dimensional Patterson map; other non-hydrogen atoms were located by means of successive Fourier syntheses. Their positional, isotropic and then anisotropic thermal parameters were refined by a block-diagonal least-squares method. The positions of all hydrogen atoms were obtained by a calculation which assumed C-H bond lengths to be 1.08 Å. They were added to the refinement cycles fixing their positional parameters. The final R value9) obtained was 0.033.

Results and Discussion

The bond lengths and bond angles are shown in Table 1.10) A perspective drawing of the complex, together with the numbering scheme of the non-

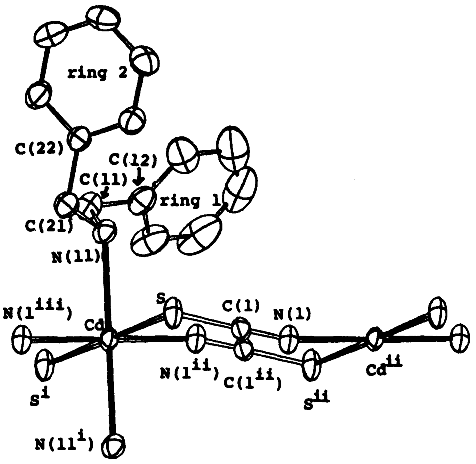

Fig. 1. A perspective drawing of the structure of the title complex with the numbering scheme of the atoms. The key to the symmetry operations; i, $-x$, $-y$, $-z$; ii, $-x$, $-y$, $1-z$; iii, x, y, $-1+z$.

hydrogen atoms, is shown in Fig. 1.[11] Projections of the unit cell along b- and c-axes are shown in Figs. 2 and 3, respectively.

The cadmium(II) atom is at the center of symmetry; it is hexa-coordinated and is in an octahedral geometry. As shown in Fig. 2, the cadmium(II) atoms are lined along the c-axis and the respective pairs of side-by-side metal atoms are bridged by two SCN ions; one of them is *S*-coordinated and the other one is *N*-coordinated to the same side metal atom, thus forming a polymeric linear chain structure.

Around one cadmium(II) atom, two SCN sulfur, two SCN nitrogen, and two dibenzylamine nitrogen atoms are coordinated, where each pair of the same kinds of the ligating atoms are all in a *trans*-configuration. The bond lengths are: Cd-N(SCN), 2.307(3) and Cd-S(SCN), 2.7576(10) Å. Bond angles are: Cd-S-C(1), 99.93(11) and Cd-N(1$^{\mathrm{ii}}$)-C(1$^{\mathrm{ii}}$), 161.0(2)°. These values are all not much different from those of the double SCN ion-bridging type cadmium complexes. The Cd-N(11) (Lewis base) bond length is 2.396(2) Å, longer than that of Cd-N(1$^{\mathrm{ii}}$) (SCN). Moreover, this Cd-N (base) bond length is a little longer than those of the 3- and 4-methylpyridine adducts;[3,4] however, still longer Cd-N (base) bonds were found in 2-methylpyridine and bis(2-aminomethyl) amine adducts.[3,12]

An eight-membered ring, consisting of a pair of side-by-side cadmium(II) atoms and in total six atoms of a pair of SCN ions bridging them, is formed in this complex as in cases of the other cadmium(II) thiocyanate adducts.[1-3] Different from the planes of

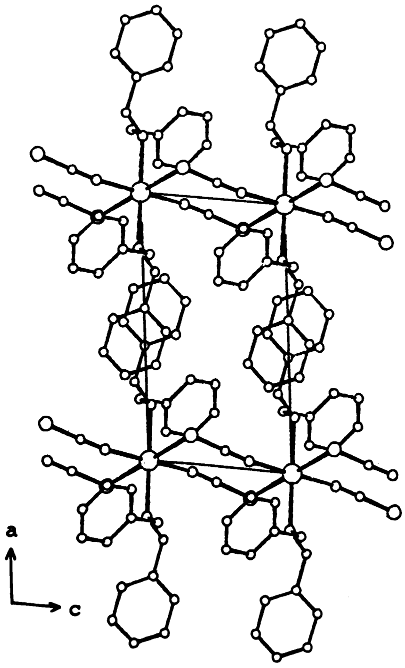

Fig. 2. The projection of the unit-cell along b-axis.

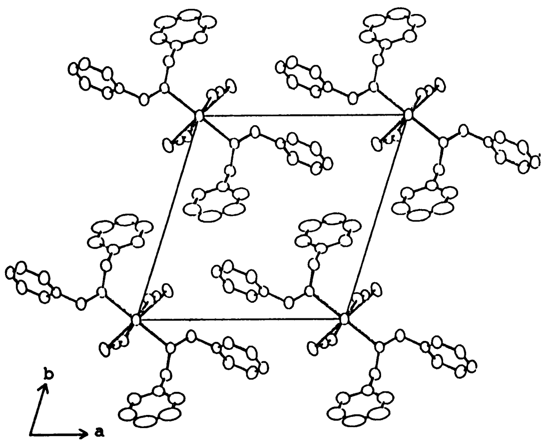

Fig. 3. The projection of the unit-cell along c-axis.

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	2.7576(10)	Cd$^{\mathrm{ii}}$-N(1)	2.307(3)	Cd-N(11)	2.396(2)
S-C(1)	1.641(3)	C(1)-N(1)	1.142(4)	N(11)-C(11)	1.487(4)
N(11)-C(21)	1.500(5)	C(11)-C(12)	1.491(5)	C(12)-C(13)	1.382(7)
C(13)-C(14)	1.391(9)	C(14)-C(15)	1.365(8)	C(15)-C(16)	1.362(11)
C(16)-C(17)	1·412(8)	C(17)-C(12)	1.373(5)	C(21)-C(22)	1.507(4)
C(22)-C(23)	1.385(4)	C(23)-C(24)	1.377(5)	C(24)-C(25)	1.372(5)
C(25)-C(26)	1.365(6)	C(26)-C(27)	1.396(5)	C(27)-C(22)	1.376(4)
Bond angle	**(ϕ/°)**	**Bond angle**	**(ϕ/°)**	**Bond angle**	**(ϕ/°)**
S-Cd-N(1$^{\mathrm{ii}}$)	90.09(7)	S-Cd-N(11)	83.81(6)	N(1$^{\mathrm{ii}}$)-Cd-N(11)	91.41(9)
Cd-S-C(1)	99.93(11)	Cd-N(1$^{\mathrm{ii}}$)-C(1$^{\mathrm{ii}}$)	161.0(2)	S-C(1)-N(1)	178.3(3)
Cd-N(11)-C(11)	118.18(19)	Cd-N(11)-C(21)	110.24(16)	N(11)-C(11)-C(12)	112.1(3)
C(11)-C(12)-C(13)	120.1(3)	C(11)-C(12)-C(17)	119.8(4)	C(12)-C(13)-C(14)	120.0(4)
C(13)-C(14)-C(15)	119.4(6)	C(14)-C(15)-C(16)	121.8(6)	C(15)-C(16)-C(17)	119.0(5)
C(16)-C(17)-C(12)	119.7(5)	N(11)-C(21)-C(22)	113.0(3)	C(21)-C(22)-C(23)	119.9(3)
C(21)-C(22)-C(27)	121.7(3)	C(22)-C(23)-C(24)	121.0(3)	C(23)-C(24)-C(25)	120.1(3)
C(24)-C(25)-C(26)	120.0(3)	C(25)-C(26)-C(27)	120.0(3)	C(26)-C(27)-C(22)	120.5(3)

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

the 2-, 3-, and 4-methylpyridine adducts, which are almost in a real plane,[3,4] the ring of this complex is in a chair form; both cadmium(II) atoms are deviated up- and downwards by about 0.5 Å from the average plane of the six atoms of two SCN ions (average deviation of the six atoms from the average plane is 0.003 Å).

As shown in Figs. 2 and 3, the phenyl ring 2 of the dibenzylamine ligand is parallel to the same type ring of the next complex along the a-axis; the distance between the approaching ring planes is about 3.64 Å, and about 13% of the area overlaps each other.[13] On the other hand, as shown in Fig. 3, ring 1 of the ligand takes a position in the wide space between the side-by-side complexes along the b-axis; such an overlapping of rings was not found. This fact should be the cause of the relatively large temperature factors of ring 1 carbon atoms.

The next chains to the a- and b-axis directions are separated by 11.28 and 11.40 Å; these are the respective axis lengths. These values are far longer than those of the other Lewis base adducts of the same type: for example, in the case of 3-methylpyridine adduct, they are 8.77 and 8.33 Å (the latter value is a half of its b-axis length),[3] and the 1*H*-1,2,4-triazol adduct, 7.57 and 7.68 Å.[5] In spite of such a large separation between the polymeric chains, no fundamental discrepancies in the bridging structure were found compared with the other same type complexes, except for the above-mentioned minor differences.

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9) $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.

10) The positions of hydrogen atoms, the final thermal parameters, and the final F_o-F_c table are deposited as Document No. 8723 at the Office of the Editor of the Bull. Chem. Soc. Jpn.

11) The numbering of the phenyl carbon atoms are as follows: In the ring 1, the carbon atoms are numbered successively from C(12) to C(17) and the C(17) atom is bonded to C(12) atom. In the ring 2, they are numbered from C(22) to C(27) in the same manner.

12) M. Cannas, G. Carta, A. Cristini, and G. Marongiu, *Inorg. Chem.*, **16**, 228 (1977).

13) Here, the overlapping area was the one between one ring and the projection of the other ring to the former ring plane; the value is shown by the percentage of the overlapping area to one ring area.