Syntheses, and Crystal and Molecular Structures of Tetraethylammonium, and Tetrapropylammonium Tris(thiocyanato)cadmates(II), [R₄N][Cd(SCN)₃], (R=C₂H₅, C₃H₇)

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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The title complexes have been synthesized and their crystal and molecular structures determined by a single crystal X-ray diffraction technique. $[(C_2H_5)_4N][Cd(SCN)_3]$ (**1**) is orthorhombic with a space group of $A2_1am$; $a=10.773(2)$, $b=16.574(4)$, $c=9.871(2)$ Å, and $Z=4$, while $[(C_3H_7)_4N][Cd(SCN)_3]$ (**2**) is triclinic with a space group of $P\bar{1}$; $a=10.297(5)$, $b=11.542(5)$, $c=9.374(3)$ Å, $\alpha=90.10(3)$, $\beta=91.61(4)$, $\gamma=80.94(4)°$, and $Z=2$. In **1**, the metal atom has a $3N,3S$-hexa-coordinated octahedral geometry, and three ligated N atoms take *fac*-configuration. Each pair of a metal atoms are bridged by three thiocyanate (SCN) ions, where two SCN ions are S-coordinated, while the other is N-coordinated to the same side metal atom, forming a linear polymeric form. In **2**, the metal atom is in a $3N,2S$-penta-coordinated trigonal-bipyramidal geometry, where one non-bridging SCN ion is N-coordinated equatorially, while four bridging SCN ions are ligated with two N (axially), and two S atoms (equatorially), respectively. Each pair of metal atoms is bridged by two SCN ions, forming a linear polymeric form. The respective tetraalkylammonium ions in **1** and **2** are not bridged to the complex anions, but are bonded only electrostatically. The final R values obtained are: **1**, 0.042 and **2**, 0.052.

Several reports about the thiocyanato complexes of cadmium, in which the metal atoms are bridged by thiocyanate (SCN) ions, have already been published.[1-9] Many of the complexes are the neutral Lewis base adducts of cadmium(II) thiocyanates,[1-7] but there are some, not many, anionic thiocyanato complexes where the central cadmium atoms are coordinated only to SCN ions.[8,9] These anionic complexes have their own polymeric form, respective types of bridging structures. The M[Cd(SCN)₃] type tris(thiocyanato)-cadmates of rubidium,[9] cesium,[9] and tetramethylammonium[8] are in two-, three-, and one-dimensional polymeric form, respectively. Moreover, in the case of the tetramethylammonium salt, we could obtain another type of thiocyanatocadmate, $[(CH_3)_4N]_2[Cd(SCN)_4]$, which has a different type of polymeric chain.[8] Therefore, it was thought to be very interesting to synthesize and to clarify the structures of the other kinds of tetraalkylammonium thiocyanatocadmates.

From this aspect, we have synthesized the title two new complexes, and their crystal and molecular structures were determined by the single-crystal X-ray diffraction method.

Experimental

Synthesis of Tetraethylammonium and Tetrapropylammonium Tris(thiocyanato)cadmates(II). Cadmium(II) thiocyanate, as well as tetraethyl- and tetrapropylammonium thiocyanates were obtained by metathetical reactions between their chlorides and potassium thiocyanate in methanol, respectively, by the method of Singh.[10]

The tetraethylammonium salt, $[(C_2H_5)_4N][Cd(SCN)_3]$ (**1**), was obtained as follows. Cadmium thiocyanate (0.57 g, 2.5 mmol) was dissolved into 10 cm³ of methanol, and the acetone solution (5 cm³) of tetraethylammonium thiocyanate (0.47 g, 2.5 mmol) was added. The mixture was stirred and was left standing for about 1 h at ambient temperature; the

crystalline product precipitated. Yield: 0.56 g (1.34 mmol, 54%). Found: Cd, 26.88; C, 31.63; H, 4.76: N, 13.29%. Calcd for $CdC_{11}H_{20}N_4S_3$: Cd, 26.96; C, 31.69; H, 4.84; N, 13.44%.

The tetrapropylammonium salt, $[(C_3H_7)_4N][Cd(SCN)_3]$ (**2**), was obtained almost by the same method as that for **1**, using an aqueous solution of cadmium thiocyanate (0.57 g, 2.5 mmol, in 5 cm³ of water) and the acetone solution of tetrapropylammonium thiocyanate (0.61 g, 2.5 mmol, in 7 cm³ of the solvent). Yield: 0.60 g (1.27 mmol, 51%). Found: Cd, 23.83; C, 37.85; H, 5.88; N, 11.85%. Calcd for $CdC_{15}H_{28}N_4S_3$: Cd, 23.76; C, 38.09; H, 5.97; N, 11.84%.

Intensity Data Collection. The crystallographic data as well as various experimental conditions used to obtain the intensity data of both complexes are listed in Table 1. The used crystals of both complexes were colorless. The reflections were collected on a Rigaku AFC-6A automated 4-circle X-ray diffractometer with graphite monochromated Mo $K\alpha$ radiation $(\lambda=0.71073$ Å). The observed intensities were corrected for Lorentz and polarization factors, but not for absorption and extinction.

Structure Determination. The structures were solved by the heavy-atom method. The positions of the metal, sulfur, and some other atoms were deduced from their three-dimensional Patterson maps; the other non-hydrogen atoms were located by means of successively Fourier syntheses. Their positional, isotropic and then anisotropic thermal parameters were refined by means of a block-diagonal least-squares method.

In a crystal of **1**, the ab-plane is a mirror plane, and the cadmium atom as well as one bridging SCN ion, S(2)-C(2)-N(2), are on it, while the other two bridging SCN ions are arranged on both sides of the plane, since one is the mirror image of the other (Fig. 3).

The N(3) atom of the tetraethylammonium ion is also in the mirror plane. Although only one set of its carbon atoms are shown in Fig. 3, another set of carbon atoms also exists at the respective mirror image positions, and the occupancy factors of each pair should be equal, 0.5, except for those of C(4) and C(6), 1.0, which are in the mirror plane.

As the respective electron clouds of the pairs of C(3) and C(3ⁱ), as well as of C(5) and C(5ⁱ), which are on both sides of

Table 1.   Crystallographic Data and Some Experimental Conditions Regarding the Collection of the Intensity Data of Tetraethylammonium and Tetrapropyl-ammonium Tris(thiocyanato)cadmates

Complex	$[(C_2H_5)_4N]$-$[Cd(SCN)_3]$	$[(C_3H_7)_4N]$-$[Cd(SCN)_3]$
F. W.	416.91	473.02
Crystal system	Orthorhombic	Triclinic
Space group	$A2_1am$	$P\bar{1}$
$a(l/Å)$	10.773(2)	10.297(5)
$b(l/Å)$	16.574(4)	11.542(5)
$c(l/Å)$	9.871(2)	9.374(3)
$\alpha(\phi/°)$	90.0	90.10(3)
$\beta(\phi/°)$	90.0	91.61(4)
$\gamma(\phi/°)$	90.0	80.94(4)
$U(v/Å^3)$	1762.5(7)	1099.7(8)
$D_m(d/g\ cm^{-3})$	1.56(3)	1.41(3)
$D_x(d/g\ cm^{-3})$	1.57	1.43
Z	4	2
$\mu(Mo\,K\alpha)(n/cm^{-1})$	15.7	12.7
Number of reflection measured	3640	4111
Reflections used for calculation	1107	2795
Measured range($2\theta/°$)	3—65	3—50
Scan width($\theta/°$)	$1.00+0.5\tan\theta$	$1.06+0.5\tan\theta$
Size of crystal (v/mm^3)	0.03×0.25×0.30	0.13×0.16×0.27
$R\ (R_w)$	0.042(0.050)	0.052(0.067)
$R_r\ (R_{rw})$	0.043(0.051)	
F_w	0.024	0.024

$R=\sum||F_o|-|F_c||/\sum|F_o|$
$R_w=[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2}$, where $w=1/$
$[\{\sigma(|F_o|)\}^2+(F_w\times F_o)^2]$

$R_r\ (R_{rw})$: The R_r and R_{rw} values for the structure of inversed chirality. As these values are higher than the normal ones, they are not adopted. Moreover, as the differences between the corresponding values of the normal and inversed chirality are only a little, any more stereochemical investigations were not attempted.

the mirror plane symmetrically, are hardly separated, they are too large to be regarded as being at one position in the mirror plane. Therefore, in the final step of refinement, as a device to converge their positional parameters, two of their thermal parameters, B_{23} and B_{13}, were fixed to be 0, and were refined as usual. No such problem was found concerning the C(7) and C(9) atoms. An attempt to separate the C(8) atomic position into two was not successful: probably their positions are too close to be distinguished from each other.

All of the calculations were carried out on a HITAC M-682H or M-680H computer at the Computer Center of the University of Tokyo, using the UNICSIII program.[11] The atomic scattering factors were taken from Ref. 12.

Infrared Spectrum Measurement.   The infrared spectra of these complexes were obtained by means of a JASCO 202-A infrared spectrophotometer, using liquid paraffin and hexachloro-1,3-butadiene mull.

Results and Discussion

The final atomic parameters of **1** and **2**, together with their isotropic equivalent temperature factors, are listed in Tables 2 and 3; their bond lengths and bond angles are tabulated in Tables 4 and 5, respectively.[13]

A perspective drawing of the skeletons of complexes **1** and **2**, together with the numbering scheme of the atoms, are shown in Figs. 1 and 2. Projections of the unit cell of **1** and **2** along c-axis are given in Figs. 3 and 4. The numbering scheme of the tetraalkylammonium cations of **1** and **2** are shown in Figs. 3 and 4,

Table 2.   Final Atomic Coordinates ($\times 10^4$) of the Non-Hydrogen Atoms and Their Equivalent Isotropic Temperature Factors of Tetraethylammonium Tris(thiocyanato)cadmate(II) (Estimated Standard Deviations in Parentheses)

Atom	x	y	z	$B_{eq}/Å^2$ [a]
Cd	0	233.4(4)	0	4.0
S(1)	1277(2)	932(1)	2088(3)	5.3
S(2)	3612(3)	−1616(2)	0	6.0
N(1)	3644(6)	368(4)	1546(8)	5.1
N(2)	1327(8)	−817(5)	0	4.8
N(3)	2461(9)	3477(5)	0	3.9
C(1)	2669(6)	598(4)	1754(7)	3.3
C(2)	2280(9)	−1144(6)	0	3.8
C(3)	3425(20)	2977(10)	858(17)	5.3
C(4)	4390(19)	2584(12)	0	8.7
C(5)	3054(17)	4149(9)	−862(17)	4.9
C(6)	3914(18)	4689(8)	0	7.8
C(7)	1657(14)	3899(10)	1094(18)	4.9
C(8)	728(12)	3273(6)	1718(13)	8.3
C(9)	1709(19)	2907(8)	−910(18)	5.3

a) The equivalent isotropic temperature factors were computed by the following expression: $B_{eq}=4/3$ $(B_{11}a^2+B_{22}b^2+B_{33}c^2)$. The B_{ij}'s are defined by: $T=\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hlB_{13}+2klB_{23}+2hkB_{12})]$.

Table 3.   Final Atomic Coordinates ($\times 10^4$) and Their Equivalent Isotropic Temperature Factors of Tetrapropylammonium Tris(thiocyanato)-cadmate(II) (Estimated Standard Deviations in Parentheses)

Atom	x	y	z	$B_{eq}/Å^2$ [a]
Cd	2685.8(5)	4048.3(5)	4201.5(7)	4.0
S(1)	6694(3)	4181(2)	7133(3)	6.4
S(2)	2456(3)	158(3)	2201(4)	8.4
S(3)	2108(2)	4359(2)	6842(2)	4.8
N(1)	4845(6)	3550(8)	5170(8)	5.2
N(2)	2752(7)	2350(6)	3203(9)	6.0
N(3)	−526(6)	5355(6)	6644(8)	5.0
N(4)	2481(6)	8269(5)	7922(6)	3.6
C(1)	5593(7)	3846(6)	5995(9)	4.0
C(2)	2613(8)	1451(8)	2783(9)	4.9
C(3)	542(7)	4927(6)	6689(8)	3.6
C(4)	2019(7)	7820(7)	6481(8)	3.9
C(5)	753(8)	8543(8)	5883(10)	5.7
C(6)	373(10)	7999(8)	4489(10)	6.1
C(7)	1434(8)	8277(8)	9047(8)	4.7
C(8)	1035(11)	7084(9)	9320(10)	6.8
C(9)	−96(12)	7295(13)	10423(12)	9.4
C(10)	3742(7)	7421(7)	8317(8)	4.3
C(11)	4429(9)	7745(8)	9687(9)	5.6
C(12)	5622(9)	6790(9)	9987(10)	6.1
C(13)	2732(8)	9548(6)	7801(9)	4.3
C(14)	3702(9)	9734(7)	6676(11)	5.7
C(15)	3901(11)	11028(8)	6746(13)	7.3

a) See footnote of Table 2.

Table 4. Selected Bond Lengths and Bond Angles of Tetraethylammonium Tris(thiocyanato)cadmate(II), with Their Standard Deviations in Parentheses

Bond length	$(l/\text{Å})$	Bond length	$(l/\text{Å})$
Cd–S(1)	2.753(2)	Cd^{iv}–S(2)	2.736(3)
Cd^{iv}–N(1)	2.336(7)	Cd–N(2)	2.253(8)
S(1)–C(1)	1.633(7)	S(2)–C(2)	1.635(10)
N(1)–C(1)	1.135(9)	N(2)–C(2)	1.160(13)
Cd···Cd^{iv}	5.442(1)		

Bond angle	$(\phi/^\circ)$	Bond angle	$(\phi/^\circ)$
S(1)–Cd–S(1^i)	97.78(7)	S(1)–Cd–N(2)	90.48(15)
S(1)–Cd–N(1^{ii})	170.92(18)	S(1^i)–Cd–N(1^{iii})	90.90(16)
S(1^i)–Cd–S(2^{ii})	85.43(6)	S(2^{ii})–Cd–N(2)	173.8(2)
N(1^{ii})–Cd–N(1^{iii})	81.6(3)	Cd–S(1)–C(1)	99.6(3)
Cd^{iv}–S(2)–C(2)	94.6(4)	Cd^{iv}–N(1)–C(1)	147.1(7)
Cd–N(2)–C(2)	157.2(8)	S(1)–C(1)–N(1)	178.7(7)
S(2)–C(2)–N(2)	179.2(9)		

Key to the symmetry operations: i, x, y, $-z$; ii, $-0.5+x$, $-y$, z; iii, $-0.5+x$, $-y$, $-z$; iv, $0.5+x$, $-y$, z.

Table 5. Selected Bond Lengths and Bond Angles of Tetrapropylammonium Tris(thiocyanato)cadmate(II), with Their Standard Deviations in Parentheses

Bond length	$(l/\text{Å})$	Bond length	$(l/\text{Å})$
Cd–S(1^i)	2.572(2)	Cd–S(3)	2.573(3)
Cd–N(1)	2.363(7)	Cd–N(2)	2.163(7)
Cd–N(3^{ii})	2.338(7)	S(1)–C(1)	1.625(8)
S(2)–C(2)	1.619(9)	S(3)–C(3)	1.644(7)
N(1)–C(1)	1.165(11)	N(2)–C(2)	1.137(12)
N(3)–C(3)	1.132(9)	Cd···Cd^i	5.373(3)
Cd···Cd^{ii}	5.855(3)		

Bond angle	$(\phi/^\circ)$	Bond angle	$(\phi/^\circ)$
N(1)–Cd–N(3^{ii})	176.1(3)	S(1^i)–Cd–S(3)	116.68(9)
N(2)–Cd–S(1^i)	122.0(2)	N(2)–Cd–S(3)	121.2(2)
N(1)–Cd–S(1^i)	91.7(2)	N(1)–Cd–S(3)	82.8(2)
N(1)–Cd–N(2)	92.3(3)	N(3^{ii})–Cd–S(1^i)	87.4(2)
N(3^{ii})–Cd–S(3)	94.2(2)	N(3^{ii})–Cd–N(2)	91.4(3)
Cd–S(1^i)–C(1^i)	98.3(3)	Cd–S(3)–C(3)	100.8(3)
Cd–N(1)–C(1)	143.1(6)	Cd–N(2)–C(2)	169.5(7)
Cd–N(3^{ii})–C(3^{ii})	160.9(6)	S(1)–C(1)–N(1)	171.5(11)
S(2)–C(2)–N(2)	170.6(11)	S(3)–C(3)–N(3)	169.5(11)

Key to the symmetry operations: i, $1.0-x$, $1.0-y$, $1.0-z$; ii, $-x$, $1.0-y$, $1.0-z$.

respectively.

In 1, each cadmium atom, which is in the mirror plane, has a 3N3S-hexa-coordinated octahedral geometry: the nitrogen atoms as well as sulfur atoms are in the *fac*-configuration, respectively. Each pair of cadmium atoms is bridged triply by three SCN ions, where the ions are coordinated to one side of the metal atom with 2N and 1S atoms, while to the other side of the metal atom with 1N and 2S atoms, respectively. This type of triple SCN bridging structure is only found in this complex, 1, and in [(CH$_3$)$_4$N)][Cd(SCN)$_3$] (3);[8] it is never found in any other metal thiocyanato complexes.

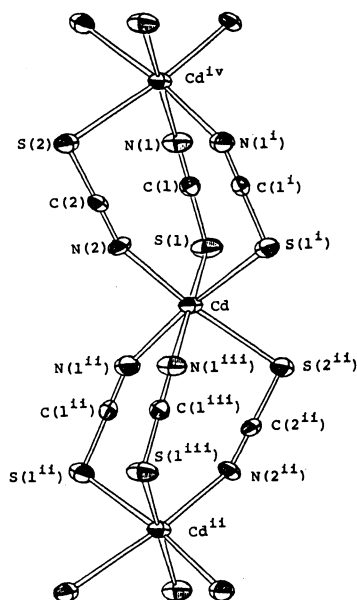The complex is linked approximately linearly along the a-axis. The cadmium atoms lie along the planes

Fig. 1. A perspective drawing of the structure of [(C$_2$H$_5$)$_4$N][Cd(SCN)$_3$] with the numbering scheme. (i, x, y, $-z$; ii, $-0.5+x$, $-y$, z; iii, $-0.5+x$, $-y$, $-z$; iv, $0.5+x$, $-y$, z.)
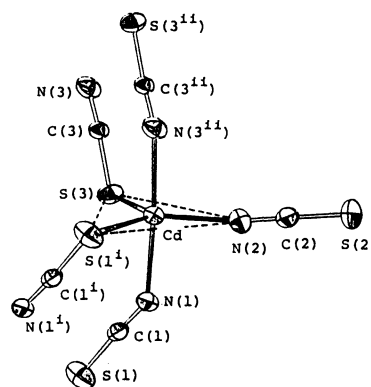
Fig. 2. A perspective drawing of the structure of [(C$_3$H$_7$)$_4$N][Cd(SCN)$_3$] with the numbering scheme. (i, $1.0-x$, $1.0-y$, $1.0-z$; ii, $-x$, $1.0-y$, $1.0-z$.)
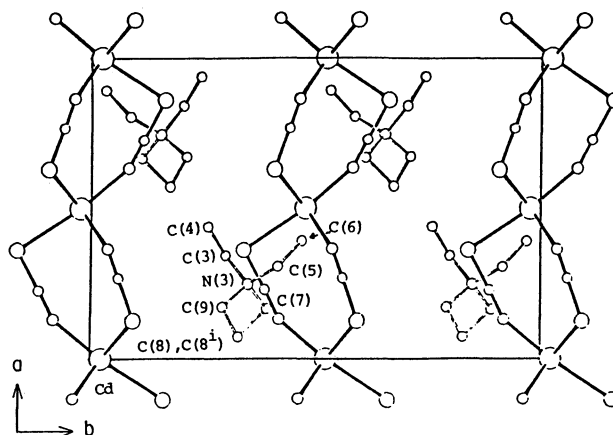
Fig. 3. A projection of the unit cell of [(C$_2$H$_5$)$_4$N][Cd(SCN)$_3$] along c-axis. (i, x, y, $-z$.)
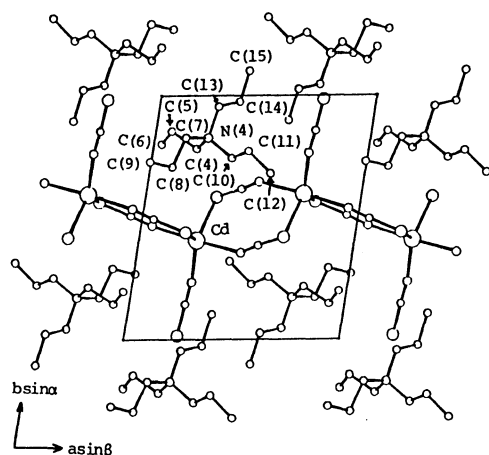
Fig. 4. A projection of the unit cell of [(C$_3$H$_7$)$_4$N]-[Cd(SCN)$_3$] along c-axis.

parallel to the bc-plane, which cross the a-axis at 0 and 0.5.

As shown in Table 4, the average Cd-S and Cd-N bond lengths are shorter than the sum of the Shannon's ionic radii of Cd-S and Cd-N.[14] The average Cd-S and Cd-N bond lengths of 3, 2.720 and 2.334 Å,[8] are not much different from the corresponding ones of 1.

Similar to the Cd-N-C angles of 3 (155.5(7), 145.6(10), and 144.5(11)°),[8] the corresponding bond angles of 1, Cd^{iv}-N(1)-C(1) (iv, 0.5+x, −y, z) and Cd-N(2)-C(2) (147.1(7) and 157.2(8)°), are much smaller than the angles of common thiocyanato complexes, 160—180°.

On the other hand, the Cd-S-C bond angles of 1 are in the range of the common angle of the other cadmium thiocyanato complexes (90—100°).[1-9]

The Cd ⋯ Cd^{iv} distance is 5.442(1) Å, which is not much different from that of 3, 5.373(3) Å, but a little shorter than the values found in the other double-SCN-chain neutral cadmium thiocyanate adducts.[1-7]

However, the chains of complexes 1 and 3 are a little different from each other. As shown in Fig. 3, all complex chains of 1 are exactly parallel, while those of 3 are not, because their neighboring chains are different in their zigzag bending structure from each other. Consequently, their corresponding SCN ions are not exactly parallel.

Complex 1 is less closely packed than 3. Their unit-cell volumes are; 1, 1762.5(7), and 3, 1370(7) Å^3, respectively, where both of them are Z=4, and their respective D$_x$ are: 1, 1.57 and 3, 1.75.

In 2, the cadmium atom is 3N2S-penta-coordinated trigonal bipyramidal geometry: two nitrogen atoms, N(1) and N(3^{ii}), are at the axial positions, while two sulfur, S(1^i) and S(3), and one nitrogen, N(2), atoms are ligated equatorially. The angle N(1)-Cd-N(3^{ii}) is 176.1(3)°, which is approximately a straight line, while the positional deviation of the Cd atom from the plane of N(2), S(3), and S(1^i) atoms is only 0.04 Å.

Since, the complex 2 has a smaller coordination number, 5, than the octahedral ones, the Cd-S as well as the Cd-N bond lengths are expected to be shorter than the latter type complexes. In fact, Shannon's ionic radii of divalent cadmium in coordination number 6 and 5 are 0.95 and 0.87 Å, respectively.[14] Really the Cd-S lengths of 2 (2.573 Å on the average are shorter than those of 1 (2.745 Å on the averge). However, against expectation, the Cd-N length of 2 (2.288 Å on the average) is not much different from those of 1 (2.295 Å on the average). In 2, the axially bridging Cd-N(1), and Cd-N(3^{ii}) bond lengths (2.351 Å on the average) are longer than that of the equatorially coordinated non-bridging SCN ion, Cd-N(2) (2.163(7) Å). This fact is probably due to a steric hindrance caused by packing SCN-bridging complexes in the crystal, which may originate for the same reason, since their Cd-N-C bond angles are abnormally small (143.1(6) and 160.9(6)°), compared with the corresponding angles of any common thiocyanato complexes, 180—160°. The angle of Cd-N(2)-C(2) is 169.5(7)°, which is less deviated from 180°, and which is expected to be less hindered (sterically) in the crystal.

Each pair of cadmium atoms is bridged by two SCN ions, forming a linear polymeric chain laid approximately parallel to the a-axis: Cd ⋯ Cd^i and Cd ⋯ Cd^{ii} are 5.373(3) and 5.855(3) Å, respectively. Two cadmium atoms, the central one and the next one in the line, and the atoms of two SCN ions, which bridge the two metal atoms, form an eight-membered ring. The rings on both sides of a metal atom, are in the respective planes: the deviations of the atomic positions of the rings from the respective mean-square planes are less than 0.1 Å. The dihedral angle between the two planes is 78.1°.

Some temperature factors of propyl carbon atoms of 2 are a little large; however, no clear disorder was found.

This type of penta-coordinated complex is the first example in the anionic thiocyanato complexes of cadmium. Even among the neutral adducts of cadmium-(II) thiocyanates, only one example, bis(thiocyanato)-{tri(m-tolyl)phosphine}cadmium(II) (4), has been reported.[1] In 4, one S and one N atom of SCN ions are ligated to the axial directions, while one each of P(phosphine), S(SCN), and N(SCN) atoms occupy the equatorial positions. The axial Cd-S and Cd-N bond lengths are 2.792(2) and 2.297(6) Å, while the equatorial ones are, 2.595(2) and 2.256(6) Å. Compared with the corresponding bond lengths of 2, in 4, the Cd-S (equatorial) is about the same, while Cd-N (equatorial) is not so short as that of 2. This fact is probably because of the steric hindrance of the large size phosphine ligand, as well as because of the fact that the equatorial SCN ion is a bridging one in 4.

The infrared spectra of 1 and 2 were examined. The ν(CN) band at 2100 cm^{-1} of 1 is approximately a sin-

glet, although some fine structure of the peak was recognized. On the other hand, the band of **2** appeared in two peaks (2100 and 2140 cm^{-1}), other than the additional fine structures of both peaks. The splitting of the band of **2** is probably due to the existence of two types of SCN ions as above mentioned. The ν(CS) (760 cm^{-1}), and δ (SCN) (458 cm^{-1}) bands were found in both spectra of **1** and **2**: both of them are singlets and no clear wavenumber differences were recognized between the corresponding peaks of 1 and 2.

References

1) R. G. Goel, W. P. Henry, M. J. Oliver, and A. L. Beauchamp, *Inorg. Chem.*, **20**, 3924 (1981).

2) M. Cannas, G. Carta, A. Cristini, and G. Marongiu, *Inorg. Chem.*, **16**, 288 (1977).

3) L. Cavalca, M. Nardelli, and G. Fava, *Acta Crystallogr.*, **13**, 125 (1960).

4) M. Taniguchi, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **59**, 2299 (1986).

5) M. Taniguchi and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **60**, 1192 (1987).

6) M. Taniguchi, Y. Sugita, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **60**, 1321 (1987).

7) M. Taniguchi and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **60**, 4172 (1987).

8) Y. Kuniyasu, Y.Suzuki, M. Taniguchi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **60**, 179 (1987).

9) G. Thiele and D. Messer, *Z. Anorg. Allg. Chem.*, **464**, 255 (1980).

10) P. P. Singh and A. K. Gupta, *Inorg. Chem.*, **17**, 1 (1978).

11) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).

12) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp. 72, 150.

13) The final F_o-F_c tables, and some additional data of bond lengths and bond angles of **1** and **2**, are deposited as Document No. 8851 at the Office of the Editor of Bull. Chem. Soc. Jpn.

14) R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976). According to this report, the ionic radii are as follows: Cd(valence, 2+; coordination number, 6), 0.95, (valence, 2+, coordination number, 5), 0.87; S(valence, 2−; coordination number, 6), 1.84 Å; N(valence, 3−; coordination number, 4), 1.46 Å. Therfore, Cd–S and Cd–N in **1** are calculated to be 2.79 and 2.41 Å, while the values of **2**, 2.71 and 2.33 Å, respectively.