The Syntheses and the X-Ray Crystal Structure of Tetramethylammonium Tetrakis- and Tris(thiocyanato)cadmates(II), $[(CH_3)_4N]_2[Cd(SCN)_4]$ and $[(CH_3)_4N][Cd(SCN)_3]$

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The crystal and molecular structure of the two new thiocyanatocadmate(II) complexes indicated in the title were determined by the single-crystal X-ray-diffraction technique. $[(CH_3)_4N]_2[Cd(SCN)_4]$ (**1**) is triclinic, with a space group of $P\bar{1}$; a=7.300(2), b=13.019(4), c=5.8920(9) Å, α=96.32(2), β=93.080(18), γ=104.63(2)°, and Z=1, while $[(CH_3)_4N][Cd(SCN)_3]$ (**2**) is orthorhombic with a space group of $Pna2_1$; a=10.506(3), b=13.797(5), c=9.4506(18) Å, Z=4. In both complexes, the cadmium atom is in an octahedral geometry. In **1**, the metal atom is at the center of symmetry, and respective pairs of side-by-side metal atoms are bridged by two thiocyanate (SCN) ions, where one SCN ion is *S*-coordinated and the other is *N*-coordinated to the same-side metal atom. Also bonded with two nitrogen atoms of unidentate SCN ions, the metal atom is 4*N*2*S*-hexa-coordinated, and they line up along the c-axis in a polymeric form. In **2**, respective pairs of side-by-side metal atoms are bridged by three SCN ions, two of those SCN ions being *S*-coordinated, and one *N*-coordinated, to the same-side metal atom; each metal atom is 3*S*3*N*-hexa-coordinated, and the chain of the polymeric complex lines up along the a-axis. The tetramethylammonium ions bond with the polymeric complex only by the ionic bonding. The final *R* values obtained are **1**=0.039 and **2**=0.050.

It was already known that some thiocyanate complexes of cadmium(II) are in the polymeric form. For example, cadmium(II) thiocyanate itself is in a three-dimensional polymeric form, where each cadmium(II) atom is 4*S*2*N*-hexa-coordinated, being in an octachedral geometry.[1] It is also well-known that some Lewis base adducts of cadmium(II) thiocyanate are in the linear polymeric form, where respective pairs of the side-by-side cadmium(II) atoms are bridged by two thiocyanate (SCN) ions[2—5] or by the base molecules.[6] The cesium salt of tris(thiocyanato)cadmate(II) has a three-dimensional polymeric structure, where the two kinds of cadmium(II) atoms are 6*S*- and 6*N*-hexa-coordinated, while its rubidium salt has a two-dimensional polymeric structure, where the two kinds of cadmium(II) atoms are 4*N*2*S*- and 2*N*4*S*-hexa-coordinated.[7] On the other hand, in $K_2[Cd(SCN)_4]\cdot 2H_2O$, the tetrakis(thiocyanato)cadmate(II) ions are discrete; the cadmium atom is 2*N*4*S*-hexa-coordinated although the octahedron around the metal atom is deformed.[8]

From these results, the bridging structure of the thiocyanatocadmate(II) can be expected to depending on the kind of counter cation. As the rubidium and cesium salts have the respective types of polymeric structures, it can also be expected that, if a different kind of counter cation is introduced, some complex with another type of polymeric structure will be obtained. From this expectation, we started the syntheses of some tetraalkylammonium salts of the thiocyanatocadmate(II), and have thus obtained the title complexes; their crystal and molecular structures were determined by the single-crystal X-ray-diffraction technique.

Experimental

Syntheses of Tetramethylammonium Tetrakis(thiocyanato)cadmate(II) (1), and Tetramethylammonium Tris(thiocyanato)cadmate(II) (2). The cadmium(II) thiocyanate (**3**) and tetramethylammonium thiocyanate (**4**) were obtained by metathetical reactions between the respective chlorides and potassium thiocyanate in a methanol medium, as in cases of the other thiocyanates.[9]

To synthesize Complex **1**, the solutions of **3** and **4** in the mol ratio of 1:2 (**3**, 0.57 g, 2.5 mmol in 20 cm³ of acetone; **4**, 0.66 g, 5.0 mmol in 10 cm³ of acetone) were mixed and left standing overnight at the ambient temperature. Crystals of **1** were thus deposited. Yield, 0.68 g; 1.38 mmol, 58%.

To obtain Complex **2**, aqueous solutions of equimol amounts of **3** and **4** (0.57 g (2.5 mmol) and 0.33 g (2.5 mmol), respectively, in 10 cm³ of water) were mixed and left standing overnight in a silica gel desiccator. Crystals of **2** were thus deposited. Yield, 0.37 g; 1.03 mmol, 41%. An additional lot, which was almost of the same purity, was also obtained from the filtrate.

Intensity Data Collection. The crystallographic data of both complexes are listed in Table 1, while some of the experimental conditions used to obtain the intensity data are tabulated in Table 2. The reflections were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer, with graphite-monochromated Mo $K\alpha$ radiation (the scan speed was 4° min^{-1} (θ), and the ω—2θ scan-technique was employed).

Structure Determination. Their structures were solved by the heavy-atom method. The positions of the metal and sulfur atoms were deduced from the three-dimensional Patterson map; the other non-hydrogen atoms were located by means of successive Fourier syntheses. Their positional, isotropic, and then anisotropic thermal parameters were refined by means of a block-diagonal least-squares method. Eight hydrogen atoms of **1** were found on the difference

Fourier map, while the other hydrogen atoms were situated at their respective positions assuming C–H=1.08 Å and B_{iso}=6.0. In the final cycle, all the hydrogen atoms were fixed. The positions of any hydrogen atoms of **2** were not determined exactly on the difference Fourier map, and so we gave up adding their parameters to the calculation.

All the calculations were carried out on a HITAC M 680H computer at the Computer Center of the University of Tokyo, using a local version of the UNICS program.[10] The atomic scattering factors were taken from Ref. 11.

Infrared Spectrum Measurements. The infrared spectra of the samples were obtained by means of a JASCO 202A grating infrared spectrophotometer, using Nujol and hexachloro-1,3-butadiene mulls.

Results and Discussion

The final atomic parameters of the non-hydrogen atoms of **1** and **2** are listed in Table 3 as 3.1 and 3.2, while the bond lengths and bond angles of **1** and **2** are tabulated in Table 4 and Table 5 respectively.[12] Perspective drawings of the skeleton of the polymeric chains of Complexes **1** and **2**, together with the numbering scheme of the atoms, are shown in Figs, 1 and 3 respectively. The crystal packing diagrams of **1** and **2** are shown in Figs. 2 and 4.

In **1**, the cadmium(II) atom is at the center of symmetry and is 4*N*2*S*-hexa-coordinated, being in a slightly deformed octahedral geometry. Two nitrogen atoms of unidentate SCN ions, two nitrogen atoms, and two sulfur atoms of the respective bridging SCN ions are coordinated. The Cd–N bond lengths of the unidentate SCN (Cd–N(2)=2.357(3) Å) is longer than that of the bridging SCN (Cd–N(1)=2.269(2) Å), but both of them are shorter than the sum of Shannon's ionic radii, 2.41 Å.[13] This is probably because the assumed valence of the nitrogen atom is not appropriate, for the charge on the SCN ion is much delocalized. The observed Cd–S bond length is 2.742(1) Å (Cd–S(1^i)), about the same as the sum of Shannon's ionic radii, 2.79 Å.[13] These values are not much different from the respective values of Lewis base adducts of the cadmium(II) thiocyanate, which have the same type of doubly bridged SCN ions in their polymeric structures.[2–5] The Cd–N(1)–C(1), Cd–N(2)–C(2), and Cd–S(1^i)–C(1^i) angles are 165.8(2), 158.0(2), and 98.65(8)° respectively, while the average

Table 1. Crystallographic Data of the Complexes

Chemical formulae	$[(CH_3)_4N]_2[Cd(SCN)_4]$	$[(CH_3)_4N][Cd(SCN)_3]$
F.W.	493.02	360.79
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	$Pna2_1$
$a(l/\text{Å})$	7.300(2)	10.506(3)
$b(l/\text{Å})$	13.019(4)	13.797(5)
$c(l/\text{Å})$	5.8920(9)	9.4506(18)
$\alpha(\phi/°)$	96.32(2)	90.0
$\beta(\phi/°)$	93.080(18)	90.0
$\gamma(\phi/°)$	104.63(2)	90.0
$U(v/\text{Å}^3)$	536.5(3)	1370.0(7)
$D_m(d/\text{Mg m}^{-3})$	1.51(3)	1.73(3)
$D_x(d/\text{Mg m}^{-3})$	1.52	1.75
μ(Mo $K\alpha$) (n/mm^{-1})	1.39	2.00
Z	1	4

Table 2. Some Experimental Conditions Used to Obtain the Reflection Intensities

Chemical formulae	$[(CH_3)_4N]_2[Cd(SCN)_4]$	$[(CH_3)_4N][Cd(SCN)_3]$
Number of reflections Measured	5104	2850
Reflections used for the calculation$^{a)}$	4258	1551
Measured range $(2\theta/°)$	3—72	3—65
$R^{b)}$	0.039	0.050
$R_{weight}{}^{b)}$	0.042	0.058
Size of the crystal (v/mm^3)	0.30×0.20×0.25	0.30×0.25×0.27
Scan width $(\theta/°)$	$1.02+0.5\tan\theta$	$1.11+0.5\tan\theta$
$S^{c)}$	1.38	1.88

a) Reflections with $|F_o|>3\sigma(|F_o|)$ were used. b) $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_{weight}=[\Sigma(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$, where $w=1/[\{\Sigma(|F_o|)\}^2+(F_{weight}\times F_o)^2]$, F_{weight}=0.015. c) $S=[\Sigma w(|F_o|-|F_c|)^2/(N_o-N_p)]^{1/2}$, where N_o=number of reflections and N_p=number of parameters.

of the S–C–N angle of the SCN ions is 178.6°. Both of the Cd–N–C angles can be said to be almost in the normal range, because in other thiocyante complexes, the M–N–C (SCN) bond angles have been shown to be 160—180°.[14]

The respective pairs of the neighboring cadmium(II) atoms are bridged by two SCN ions; one of them is *S*-coordinated, and the other is *N*-coordinated, to the same-side metal atom, thus forming a polymeric linear chain structure along the [001] axis. Thus, it has been shown that the tetrakis(thiocyanato)cadmate ion in its tetramethylammonium salt takes a linear

Table 3. Final Non-Hydrogen Atomic Coordinates ($\times 10^4$) of $[(CH_3)_4N]_2[Cd(SCN)_4]$ (3.1) and $[(CH_3)_4N][Cd(SCN)_3]$ (3.2) Together with Their Equivalent Isotropic Temperature Factors (Estimated Standard Deviations are Shown in Parentheses)

3.1 $[(CH_3)_4N]_2[Cd(SCN)_4]$

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$ d)
Cd	0.0	0.0	0.0	2.7_4
S (1)	3302 (1)	361 (1)	7852 (1)	3.3_7
S (2)	2092 (1)	4011 (1)	453 (2)	5.2_8
C (1)	2385 (3)	220 (2)	5208 (3)	2.8_6
C (2)	1111 (3)	2753 (2)	522 (4)	3.4_3
N (1)	1798 (3)	116 (2)	3327 (3)	4.6_0
N (2)	404 (4)	1867 (2)	581 (5)	5.1_3
N (3)	6503 (3)	3072 (2)	4438 (3)	3.3_3
C (3)	4902 (4)	3214 (2)	5804 (5)	5.0_1
C (4)	5742 (4)	2275 (2)	2384 (5)	4.7_6
C (5)	7413 (5)	4109 (9)	3626 (7)	6.1_7
C (6)	7865 (6)	2698 (4)	5839 (7)	7.6_3

3.2 $[(CH_3)_4N][Cd(SCN)_3]$

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$ d)
Cd	734.3 (5)	2091.0 (5)	0.0	3.5_8
S (1)	2248 (2)	471 (2)	−9 (11)	4.9_1
S (2)	4370 (3)	3848 (2)	−1978 (4)	4.5_9
S (3)	4445 (3)	3655 (3)	2255 (4)	4.6_6
C (1)	3567 (7)	1117 (6)	68 (27)	3.2_2
N (1)	4494 (6)	1554 (6)	−57 (23)	4.2_4
C (2)	3050 (10)	3215 (8)	−1853 (13)	3.8_2
N (2)	2049 (8)	2870 (7)	−1650 (12)	4.4_5
C (3)	3019 (10)	3213 (8)	1799 (13)	3.6_7
N (3)	2116 (9)	2839 (7)	1668 (13)	4.6_9
N (4)	3524 (8)	1066 (5)	5014 (25)	4.4_7
C (5)	2500 (16)	1801 (12)	4810 (30)	8.4_5
C (6)	4567 (18)	1398 (20)	5885 (30)	$13._6$
C (7)	3002 (22)	262 (14)	5873 (30)	$13._3$
C (8)	3904 (19)	678 (15)	3677 (20)	9.3_1

d) The equivalent isotropic temperature factors were computed using the following expression: $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cos\alpha)$ for (3.1), and $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2)$ for (3.2). The B_{ij}'s are defined by: $T=\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hkB_{12}+2hlB_{13})]$.

Table 4. Bond Lengths and Bond Angles of $[(CH_3)_4N]_2[Cd(SCN)_4]$

Bond Length	(*l*/Å)	Bond Length	(*l*/Å)
Cd–N (1)	2.269 (2)	Cd–N (2)	2.357 (3)
Cd–S (1$^{\mathrm{i}}$)	2.742 (1)	S (1)–C (1)	1.634 (2)
C (1)–N (1)	1.148 (3)	S (2)–C (2)	1.619 (2)
C (2)–N (2)	1.144 (3)	N (3)–C (3)	1.492 (4)
N (3)–C (4)	1.487 (3)	N (3)–C (5)	1.488 (4)
N (3)–C (6)	1.467 (5)		
Bond Angle	**(*ϕ*/°)**	**Bond Angle**	**(*ϕ*/°)**
N(1)–Cd–N(2)	89.76 (8)	N(2)–Cd–S(1$^{\mathrm{i}}$)	91.79 (6)
N(1)–Cd–(S$^{\mathrm{i}}$)	92.40 (6)	Cd–N(1)–C(1)	165.8 (2)
Cd–N(2)–C(2)	158.0 (2)	Cd–S(1$^{\mathrm{i}}$)–C(1$^{\mathrm{i}}$)	98.65 (8)
N(1)–C(1)–S(1)	177.7 (2)	N(2)–C(2)–S(2)	179.4 (2)
C(3)–N(3)–C(4)	109.3 (2)	C(3)–N(3)–C(5)	108.8 (2)
C(3)–N(3)–C(6)	109.8 (3)	C(4)–N(3)–C(5)	107.7 (2)
C(4)–N(3)–C(6)	109.7 (3)	C(5)–N(3)–C(6)	111.6 (3)

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

Table 5. Bond Lengths and Bond Angles of $[(CH_3)_4N][Cd(SCN)_3]$

Bond Length	(*l*/Å)	Bond Length	(*l*/Å)
Cd–S (1)	2.743 (3)	Cd–S (2$^{\mathrm{ii}}$)	2.689 (4)
Cd–S (3$^{\mathrm{ii}}$)	2.727 (4)	Cd–N (1$^{\mathrm{ii}}$)	2.280 (7)
Cd–N (2)	2.344 (11)	Cd–N (3)	2.378 (12)
S (1)–C (1)	1.649 (8)	C (1)–N (1)	1.151 (11)
S (2)–C (2)	1.643 (11)	C (2)–N (2)	1.170 (14)
S (3)–C (3)	1.673 (11)	C (3)–N (3)	1.087 (14)
N (4)–C (5)	1.491 (19)	N (4)–C (6)	1.44 (3)
N (4)–C (7)	1.48 (3)	N (4)–C (8)	1.43 (3)
Cd···Cd$^{\mathrm{i}}$	5.373 (3)		
Bond Angle	**(*ϕ*/°)**	**Bond Angle**	**(*ϕ*/°)**
S(1)–Cd–S(2$^{\mathrm{ii}}$)	85.08 (10)	S(1)–Cd–S(3$^{\mathrm{ii}}$)	89.02 (10)
S(2$^{\mathrm{ii}}$)–Cd–S(3$^{\mathrm{ii}}$)	95.54 (12)	S(1)–Cd–N(3)	90.1 (3)
S(1)–Cd–N(2)	91.7 (3)	S(2$^{\mathrm{ii}}$)–Cd–N(1$^{\mathrm{ii}}$)	94.3 (2)
S(2$^{\mathrm{ii}}$)–Cd–N(2)	94.2 (3)	S(3$^{\mathrm{ii}}$)–Cd–N(1$^{\mathrm{ii}}$)	92.5 (2)
S(3$^{\mathrm{ii}}$)–Cd–N(3)	87.1 (3)	N(1$^{\mathrm{ii}}$)–Cd–N(3)	90.5 (3)
N(1$^{\mathrm{ii}}$)–Cd–N(2)	86.9 (3)	N(3)–Cd–N(2)	83.2 (4)
S(1)–Cd–N(1$^{\mathrm{ii}}$)	178.36 (19)	S(2$^{\mathrm{ii}}$)–Cd–N(3)	174.5 (3)
S(3$^{\mathrm{ii}}$)–Cd–N(2)	170.3 (3)		
Cd$^{\mathrm{i}}$–N(1)–C(1)	155.5 (7)	Cd–N(2)–C(2)	145.6 (10)
Cd–N(3)–C(3)	144.5 (11)	Cd–S(1)–C(1)	92.7 (3)
Cd$^{\mathrm{i}}$–S(2)–C(2)	98.3 (4)	Cd$^{\mathrm{i}}$–S(3)–C(3)	96.1 (4)
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)	C(5)–N(4)–C(6)	114.0 (14)
C(5)–N(4)–C(7)	108.2 (14)	C(5)–N(4)–C(8)	110.0 (18)
C(6)–N(4)–C(7)	101.9 (19)	C(6)–N(4)–C(8)	114.3 (15)
C(7)–N(4)–C(8)	107.9 (14)		

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

polymeric chain structure, while its potassium salt has discrete anions, although the latter is in a dihydrate form.[8]

In **2**, the cadmium(II) atom is 3*N*3*S*-hexacoordinated, being in a slightly deformed octahedral geometry, where three nitrogen atoms and, accordingly three sulfur atoms, also- are in the *fac*-configuration; around one metal atom, each sulfur atom is at the *trans*-position of a nitrogen atom. The average Cd-S and Cd-N bond lengths are 2.720 and 2.334 Å respectively. Therefore, the average values are not very different from the respective values of **1** or from the Lewis base adducts of cadmium(II) thiocyanate, although as is shown in Table 5, the respective Cd-N bond lengths as well as Cd-S bond lengths of **2** are a little different from each other. However, all of them are shorter than the respective sums of Shannon's ionic radii; 2.41 and 2.79 Å.[13] The average bond angles of Cd-N-C, Cd-S-C, and S-C-N are 148.5, 95.7, and 170.4° respectively. Although the angles of the latter two are not much different from the corresponding values of **1**, nor from those of the Lewis base adducts of cadmium(II) thiocyanate,[2-5] the Cd-N-C angles of **2**, especially Cd-N(2)-C(2) and Cd-N(3)-C(3), are much smaller than the normal value.[14] This structural deformation is probably caused by the mutual steric interaction of the

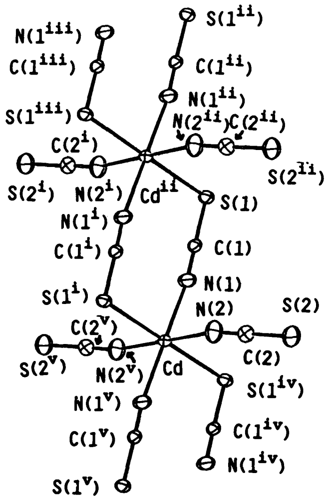

Fig. 1. A perspective drawing of the structure of $[(CH_3)_4N]_2[Cd(SCN)_4]$, with the numbering scheme of the atoms. Key to the symmetry operations: i, $-x$, $-y$, $1-z$; ii, x, y, $1+z$; iii, $-x$, $-y$, $2-z$; iv, x, y, $-1+z$; *v*, $-x$, $-y$, $-z$.

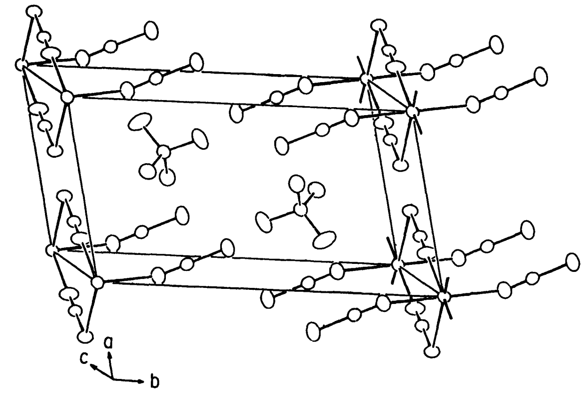

Fig. 2. Crystal packing diagram of $[(CH_3)_4]_2[Cd(SCN)_4]$.

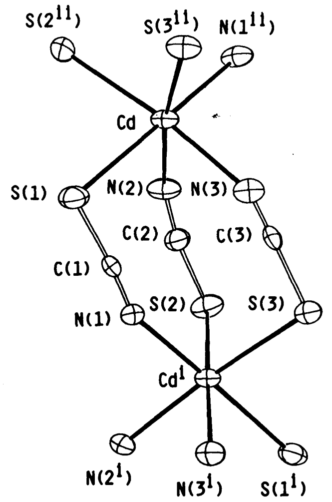

Fig. 3. A perspective drawing of the structure of $[(CH_3)_4N][Cd(SCN)_3]$, with the numbering scheme of the atoms. Key to the symmetry operations: i, $0.5+x$, $0.5-y$, z; ii, $-0.5+x$, $0.5-y$, z.

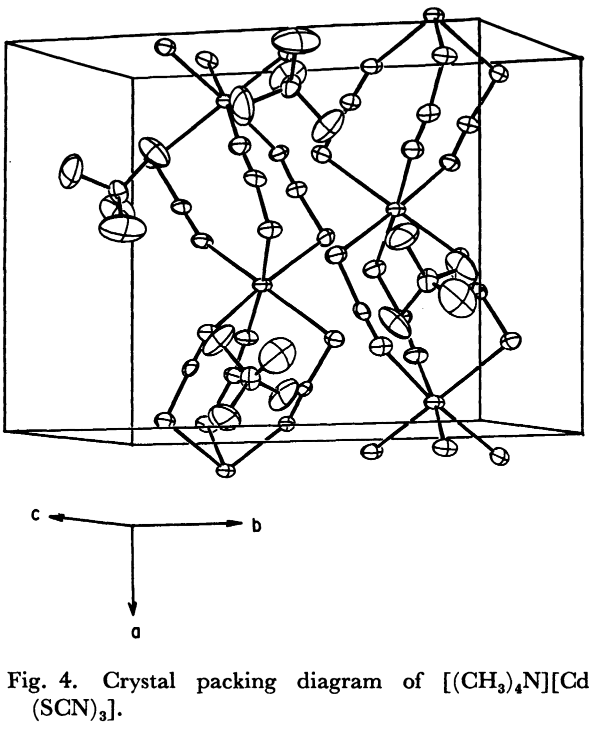

Fig. 4. Crystal packing diagram of $[(CH_3)_4N][Cd(SCN)_3]$.

respective SCN ions in a limited packing space of the crystal, thus forming such a type of triple chain.

The respective pairs of the neighboring cadmium(II) atoms are bridged by three SCN ions, where one of them is *N*-coordinated, and the other two are *S*-coordinated to a one-side metal atom. Thus, in **2**, the side-by-side metal atoms are triply bridged by three SCN ions, thus forming a polymeric linear chain structure along the [100] axis, although in a zig-zag way.

Although many kinds of bridging structures have been found in cadmium(II) thiocyanate complexes, no such triply bridged one has yet been found; this is a new type of polymeric chain of the thiocyanate ions.

The tetramethylammonium ions in **1** and **2** are not bridged, but are isolated from the complex chain; only mutual electrostatic interaction is expected.

In the infrared spectrum of **1**, the ν(CN) and δ(SCN) bands appear as doublets: the maximum wavenumbers are 2070, 2105(s), and 453, 464(m) cm^{-1} respectively, although the ν(CS) band at 768(w) cm^{-1} is found to be a singlet. On the. other hand, in the spectrum of **2**, the ν(CN), δ(SCN), and ν(CS) bands are all singlet; their maximum wave numbers are 2100(s), 460(m), and 758(w) cm^{-1} respectively. These facts may be due to the existence of two kinds of SCN ions in **1**, as has been shown by the structure analysis, while the bond strengths of the three SCN ions in **2** are not very different from each other. The absorption bands of the tetramethylammonium ion are found at 1480(s), 1378(s), and 941(s) cm^{-1}; they are about the same in the spectra of **1** and **2**.

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12) The positions and isotropic temperature factors of the hydrogen atoms in **1**, the anisotropic thermal parameters of the non-hydrogen atoms of **1** and **2**, and the final F_o—F_c tables of both complexes are deposited as Document No. 8713 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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