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The Crystal and Molecular Structure of Bis(4-methylpyridine)-bis(thiocyanato)cadmium(II) in Polymeric Form, $[Cd(SCN)_2(CH_3C_5H_4N)_2]_n$

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The crystal and molecular structure of the title complex was determined by a single-crystal X-ray diffraction technique. The crystal is triclinic with a space group $P\bar{1}$, a=11.323(4), b=18.383(10), c=9.284(5) Å, α=104.62(4), β=114.26(3), γ=77.71(4)°, Z=4; the final R value obtained was 0.034. All cadmium atoms are lined approximately along the [111] axis and each pair of metal atoms are bridged by two thiocyanate ions (SCN), one of which is *S*-coordinated and the other is *N*-coordinated to the same side metal atom. Also bonded with two nitrogen atoms of 4-methylpyridine (pic) ligands, the metal atom is 4*N*2*S*-hexa-coordinated and is in an octahedral geometry. The cadmium atoms, where the ligated respective pairs of N(SCN), N(pic), and S(SCN) atoms are all in a trans configuration, and the metal atoms where the ligated respective pairs of N(pic) and S(SCN) are in cis, while the pair of the N(SCN) in trans configuration, appear alternatively in the polymer chain.

A variety of polymeric structures of the metal thiocyanates and of their Lewis-base adducts are one of the interesting themes of structural chemistry, and several reports have already been published.[1] According to the soft-hard acid-base theory, cadmium is a rather soft metal, though its softness is less than that of mercury or lead.[2] Therefore, it is expected that the nitrogen as well as the sulfur atoms of a thiocyanate (SCN) ion are able to bond with cadmium easily, and that SCN-bridged polymeric complexes are stable. In fact, the cadmium(II) thiocyanate has a three-dimensional polymeric structure bridged by SCN ions,[3] and some Lewis-base adducts of cadmium(II) thiocyanate are in a variety of linear polymeric forms. For example, in *N,N′*-ethylenethiourea (2-imidazolidinethione) (etu) adduct, $Cd(SCN)_2(etu)_2$(**1**),[4] the 1*H*-1,2,4-triazole (trz) adduct, $Cd(SCN)_2(trz)_2$(**2**),[5] and the tri-*m*-tolylphosphine (tl_3P) adduct, $Cd(SCN)_2(tl_3P)$ (**3**),[6] each pair of the metal atoms, which are lined linearly, are doubly bridged by SCN ions. On the other hand, in the case of bis(2-aminoethyl)amine (ben) adduct, $Cd(SCN)_2(ben)_2$[7] each pair of metal atoms are bridged by one SCN as well as one ben ligand. In the case of 4-*t*-butyl-4*H*-1,2,4-triazole (btrz) adduct, $Cd(SCN)_2(btrz)_2$,[8] metal atoms are bridged by two N-bonded SCN ions and by three btrz ligands (alternatively) on the line.

This paper reports on the crystal and molecular structures of the title complex, $Cd(SCN)_2(pic)_2$ (pic=4-methylpyridine), determined by a single-crystal X-ray diffraction technique.

Experimental

Synthesis of Bis(4-methylpyridine)bis(thiocyanato)cadmium(II). The complex was obtained in almost the same way as that of Ahuja[9] and was recrystallized from methanol. Anal. Found: Cd, 26.99; C, 40.28; H, 3.31; N, 13.45%. Calcd for $CdC_{14}H_{14}N_4S_2$: Cd, 27.10; C, 40.54; H, 3.40; N, 13.51%. The wavenumbers of its infrared spectral bands almost coincide with the respective values of the reference.[9]

Intensity-Data Collection. A crystal with the dimension of 0.3×0.3×0.1 mm³ was used for the measurements. The crystallographic data are: $CdC_{14}H_{14}N_4S_2$, F.W. 414.82, triclinic, space group $P\bar{1}$, a=11.323(4), b=18.383(10), c=9.284(5) Å, α=104.62(4), β=114.26(3), γ=77.71(4)°, Z=4, U=1691.7(15) Å³, D_m=1.62(3), D_x=1.63 Mg m^{-3}, μ(Mo $K\alpha$)= 1.52 mm^{-1}. Reflections within a range of $3° < 2\theta < 50°$ were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer with graphite monochromated Mo $K\alpha$ radiation, the ω—2θ scan technique being employed (scan speed 4° min^{-1} (θ), scan width $(1.10+0.5\tan\theta)°$). The crystal was stable during exposure to X-rays. Of the 5983 reflections measured, 4652 with $|F_o| > 3\sigma(|F_o|)$ were used for the structure determination. The intensities were corrected for the Lorentz and polarization factors, but no correction was made for absorption and extinction.

Structure Determination. 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 anisotropic thermal parameters were refined by a block-diagonal least-squares method. All the hydrogen atoms were at respective calculated positions, assuming their B_{iso}'s to be 8.0 Å², and C–H bond lengths to be 1.08 Å. The final R value obtained was 0.034.[10]

All the calculations were carried out on a HITAC M-280H computer at the Computer Center of the University of Tokyo using a local version of the UNICS program.[11] The atomic scattering factors were taken from Ref. 12.

Results and Discussion

The final atomic parameters of non-hydrogen atoms are listed in Table 1; the selected bond lengths and bond angles are tabulated in Table 2.[13] A perspective drawing of the skeleton of the polymeric chain of the complex, together with the numbering scheme of the atoms, is shown in Fig. 1, the crystal

Table 1. Final Atomic Coordinates ($\times 10^4$) of the Non-Hydrogen Atoms and Their Equivalent Isotropic Temperature Factors of the Complex (Estimated Standard Deviations in Parentheses)

Atom	x	y	z	$B_{eq}/\text{Å}^2$ a)
Cd(1)	0	0	0	3.9_0
Cd(2)	5000	5000	5000	3.8_4
Cd(3)	2500.7(3)	2499.8(2)	316.4(4)	4.0_9
S(1)	2023(1)	−267(1)	−1002(2)	5.1_5
S(2)	605(2)	2730(1)	1529(2)	6.2_6
S(3)	4397(2)	2269(1)	3191(2)	5.8_9
S(4)	2979(1)	5267(1)	2240(1)	4.6_9
N(1)	2669(4)	1195(2)	−255(5)	5.2_7
N(2)	−157(4)	1291(2)	341(5)	5.1_5
N(3)	5162(4)	3707(2)	4207(4)	4.8_8
N(4)	2342(4)	3803(2)	879(4)	4.9_1
C(1)	2391(4)	598(2)	−568(5)	3.8_2
C(2)	165(4)	1881(2)	823(5)	4.1_4
C(3)	4823(4)	3118(2)	3775(5)	4.0_6
C(4)	2616(4)	4398(2)	1446(5)	3.6_7
N(11)	4088(4)	2510(2)	−695(4)	4.7_2
C(11)	5076(5)	1952(3)	−596(6)	4.9_7
C(12)	6039(4)	1946(3)	−1144(6)	4.9_3
C(13)	6022(4)	2545(3)	−1806(5)	4.5_2
C(14)	5009(5)	3114(3)	−1887(7)	6.9_9
C(15)	4072(5)	3082(3)	−1345(7)	6.8_2
C(16)	7087(5)	2582(3)	−2354(7)	6.5_2
N(21)	904(4)	2493(2)	−2295(4)	4.5_0
C(21)	−74(5)	3047(3)	−2624(6)	4.9_6
C(22)	−1038(5)	3052(3)	−4133(5)	4.9_4
C(23)	−1026(4)	2455(3)	−5366(5)	4.5_6
C(24)	0(5)	1879(3)	−5011(6)	5.9_5
C(25)	932(5)	1916(3)	−3503(6)	6.1_3
C(26)	−2077(5)	2420(4)	−7004(6)	6.2_2
N(31)	3497(4)	4940(2)	6124(4)	4.5_3
C(31)	2638(5)	4448(3)	5476(6)	5.0_2
C(32)	1659(5)	4470(3)	6022(6)	5.4_7
C(33)	1555(4)	5024(3)	7310(5)	4.9_7
C(34)	2481(6)	5518(3)	8001(6)	6.3_0
C(35)	3426(5)	5454(3)	7391(6)	6.1_2
C(36)	502(5)	5098(4)	7936(7)	6.6_7
N(41)	1502(4)	61(2)	2691(4)	4.5_5
C(41)	2364(5)	555(3)	3396(6)	5.1_4
C(42)	3341(5)	527(3)	4893(6)	5.3_1
C(43)	3448(4)	−28(3)	5741(5)	4.9_5
C(44)	2522(6)	−517(3)	5007(6)	6.0_4
C(45)	1582(5)	−458(3)	3505(6)	5.8_4
C(46)	4508(5)	−98(4)	7344(6)	6.2_4

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

Table 2. Selected Bond Lengths and Bond Angles of the Complex

Bond length	l/Å	Bond length	l/Å
Cd(1)-S(1)	2.719(2)	Cd(2)-S(4)	2.717(2)
Cd(3)-S(2)	2.722(2)	Cd(3)-S(3)	2.718(2)
Cd(1)-N(2)	2.291(4)	Cd(2)-N(3)	2.295(4)
Cd(3)-N(1)	2.306(4)	Cd(3)-N(4)	2.304(4)
Cd(1)-N(41)	2.365(4)	Cd(2)-N(31)	2.366(5)
Cd(3)-N(11)	2.350(5)	Cd(3)-N(21)	3.353(4)
S(1)-C(1)	1.637(5)	S(2)-C(2)	1.631(5)
S(3)-C(3)	1.625(5)	S(4)-C(4)	1.644(4)
N(1)-C(1)	1.141(6)	N(2)-C(2)	1.141(6)
N(3)-C(3)	1.145(6)	N(4)-C(4)	1.135(5)
Bond angle	ϕ/°	**Bond angle**	ϕ/°
S(1)-Cd(1)-N(2)	94.21(10)	S(1)-Cd(1)-N(41)	89.75(9)
N(2)-Cd(1)-N(41)	89.32(12)	S(4)-Cd(2)-N(3)	94.32(9)
S(4)-Cd(2)-N(31)	89.72(12)	N(3)-Cd(2)-N(31)	89.45(15)
S(2)-Cd(3)-S(3)	91.56(5)	S(2)-Cd(3)-N(1)	96.64(10)
S(2)-Cd(3)-N(4)	83.72(10)	S(2)-Cd(3)-N(21)	90.44(9)
S(3)-Cd(3)-N(1)	83.45(10)	S(3)-Cd(3)-N(4)	96.60(9)
S(3)-Cd(3)-N(11)	90.56(13)	N(1)-Cd(3)-N(11)	92.34(15)
N(1)-Cd(3)-N(21)	87.65(12)	N(4)-Cd(3)-N(11)	87.30(15)
N(4)-Cd(3)-N(21)	92.30(12)	N(11)-Cd(3)-N(21)	88.81(15)
Cd(1)-S(1)-C(1)	99.50(16)	Cd(3)-S(2)-C(2)	96.55(17)
Cd(3)-S(3)-C(3)	96.38(17)	Cd(2)-S(4)-C(4)	99.19(15)
Cd(3)-N(1)-C(1)	160.3(4)	Cd(1)-N(2)-C(2)	158.2(3)
Cd(2)-N(3)-C(3)	157.2(3)	Cd(3)-N(4)-C(4)	160.5(3)
S(1)-C(1)-N(1)	178.9(4)	S(2)-C(2)-N(2)	179.0(4)
S(3)-C(3)-N(3)	177.9(4)	S(4)-C(4)-N(4)	178.6(4)
Cd(3)-N(11)-C(11)	121.4(4)	Cd(3)-N(11)-C(15)	121.7(4)
Cd(3)-N(21)-C(21)	121.6(3)	Cd(3)-N(21)-C(25)	121.1(3)
Cd(2)-N(31)-C(31)	122.9(4)	Cd(2)-N(31)-C(35)	119.7(4)
Cd(1)-N(41)-C(41)	122.8(3)	Cd(1)-N(41)-C(45)	119.7(4)

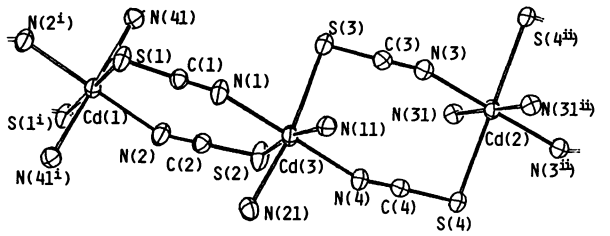

Fig. 1. A perspective drawing of the structure of the title complex with the numbering scheme. The symmetry operations are: i, $-x$, $-y$, $-z$; ii, $1-x$, $1-y$, $1-z$.

packing diagram in Fig. 2, and the numbering scheme of the pic ligand atoms in Fig. 3.

Crystallographically, there are three kinds of cadmium atoms; two of them (Cd(1) and Cd(2)) are located at the centers of symmetry (0,0,0 and 0.5,0.5,0.5), while the other one (Cd(3)) takes a position near their midpoint. All cadmium atoms are lined approximately along the [1 1 1] axis.

Along this direction, neighboring cadmium 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.

As two pic nitrogen atoms are also coordinated to each metal atom, the respective cadmium atoms are totally 4*N*2*S*-hexa-coordinated and are in a slightly deformed octahedral geometry. Around the Cd(1) and Cd(2) atoms, respective pairs of N(SCN), S(SCN), and N(pic) are in trans and their geometries are almost the same. Around Cd(3), respective pairs of

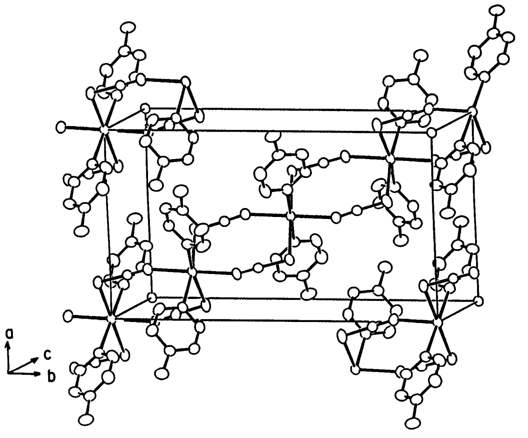

Fig. 2. Crystal packing diagram of the complex.

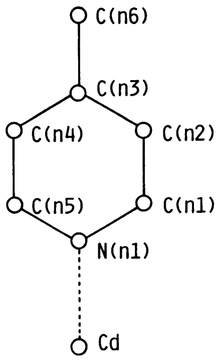

Fig. 3. Schematic presentation of the 4-methylpyridine ligand with the numbering scheme (n=1,2,3, and 4).

S(SCN) and N(pic) are in cis, while the pair of N(SCN) are in a trans configuration. Such a variation of the configuration around the cadmium atoms on the polymer chain has not been found yet for the Lewis-base adducts of cadmium thiocyanate.

The atoms of doubly bridging SCN ios, as well as the cadmium atoms on both sides, make a eight-membered ring.

They are almost on a plane: the average deviations of the atomic positions from the average plane of Cd(1), Cd(3), S(1), C(1), N(1), S(2), C(2), N(2), is 0.111 Å (maximum deviation is to S(2), 0.212 Å), while that from the average plane of Cd(2), Cd(3), S(3), C(3), N(3), S(4), C(4), N(4), is 0.100 Å (maximum deviation is to N(3), 0.244 Å). The dihedral angle between the two planes is 74.3.°.

The Cd-N(SCN) as well as Cd-N(pic) bond lengths around all cadmium atoms are not much different from each other, respectively. However, the bond length Cd-N(SCN) (2.297 Å av.[a]) is significantly shorter than that of Cd-N (pic) (2.361 Å av.). All bond lengths Cd-S are not much different from each other (2.719 Å av.), and the average bond angles of Cd-N-C(SCN) and Cd-S-C(SCN) are 158.6 and 98.4°, respectively.

As the Shannon's ionic radii of cadmium (valence (Val), 2+; and coordination number (CN), 6), sulfur (Val, 2−; CN, 6), nitrogen (Val, 3−; CN, 4) are 0.95, 1.84, and 1.46 Å, respectively, the calculated bond lengths of Cd-S and Cd-N are 2.79 and 2.41 Å.[14] Observed Cd-S lengths are not much different from the calculated one, but the observed Cd-N lengths are shorter than the calculated value. The discrepancy is probably due to the assumed Val of the nitrogen atom, which is not appropriate for atoms where the charge is significantly delocalized; the nitrogen atom in the thiocyanate ion is expected to be less negatively charged, and its ionic radius is likely to be shorter than 1.46 Å.

The bond lengths of Cd-N(SCN) and Cd-S(SCN), as well as the bond angles Cd-N-C(SCN) and Cd-S-C(SCN) in the related other cadmium thiocyanate complexes, are as follows: **1**, 2.53, 2.73 Å; 143, 109.1°; **2** , 2.330, 2.754 Å; 143.4, 96.3°; **3**, 2.28, 2.7 Å; 159, 97°.

For the title complex and **3**, the angles of Cd-N-C(SCN) are approximately 160°, Cd-N(SCN) lengths are relatively short, 2.2—2.3 Å, and Cd-S(SCN) lengths are about 2.69—2.71 Å. On the other hand, for **1** and **2**, the angle is about 140°, and Cd-N(SCN) lengths are longer than 2.3 Å, while the Cd-S(SCN) lengths are a little longer than that of the title complex. The Lewis base of **2** is coordinated to the metal atom by a nitrogen atom as the title complex, and the Cd-N(base) of **2** is shorter than that of the title complex (2.317 vs. 2.361 Å av.). From these data, the SCN bridgings of **3** and the title complex are likely to be stronger than those of **1** and **2**, and the bonding of the Lewis base with the metal atom of the title complex is weaker than that of **2**.

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[a] av. means the average value. In cases of the average of the all Cd-N or S lengths, as each Cd(1 or 2)-N or S bond length shown in the table is equivalent with the one which is trans to it, the value was doubled and added to obtain the sum.

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