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The Crystal and Molecular Structures of Bis(2-methylpyridine)-, and Bis(3-methylpyridine)bis(thiocyanato)cadmium(II) in Polymeric Forms, $[Cd(SCN)_2(CH_3C_5H_4N)_2]_n$

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The crystal and molecular structures of the title complexes were determined by the single-crystal X-ray diffraction method. Both of them are triclinic, with the space group $P\bar{1}$. The crystallographic data: 2-methylpyridine (α-pic) adduct, $a=11.076(3)$, $b=18.478(8)$, $c=9.299(3)$ Å, $\alpha=104.60(3)$, $\beta=114.84(2)$, $\gamma=81.12(3)°$, $Z=4$, final R value is 0.037; 3-methylpyridine (β-pic) adduct, $a=8.7667(16)$, $b=16.655(4)$, $c=5.8447(10)$ Å, $\alpha=91.406(18)$, $\beta=100.571(14)$, $\gamma=92.525(18)°$, $Z=2$, final R value is 0.041. In both complexes, all cadmium atoms are in 4*N*2*S*-hexa-coordination, being in an octahedral geometry; they are oriented as any pair of side-by-side metal atoms being bridged by two thiocyanate ions. In the α-pic adduct, the chain is oriented approximately along the [111] axis. In the chain, the metal atoms in two kinds of orientations appear alternately: Around one kind of the metal atoms three kinds of ligating atoms are all in *trans*-configurations, and around the other kind of the metal atoms the respective pairs of N(base) and S(SCN) atoms are in *cis* and the pair of the N(SCN) atoms in a *trans*-configuration. In the β-pic adduct, the chain is along the [001] axis and pairs of three kinds of ligating atoms are all in *trans*-configurations.

The structures of cadmium(II) thiocyanate and several kinds of its Lewis base adducts have already been elucidated.[1-8] Many of them are in a linear polymeric form having double thiocyanate (SCN) ion bridgings between any pair of adjacent metal atoms.[5-8] Previously, we determined the structure of bis(4-methylpyridine)bis(thiocyanato)cadmium(II), $Cd(SCN)_2(\gamma\text{-pic})_2$ (where γ-pic=γ-picoline=4-methylpyridine).[8] In this complex, there are three kinds of crystallographically independent cadmium atoms. They are oriented approximately along the [111] axis; side-by-side metal atoms are bridged by two SCN ions. This type of the chain structure had not yet been found in the other Lewis base adducts of cadmium(II) thiocyanate. Therefore, it is interesting to make a comparative study of a variety of chain structures caused by differences in the additional Lewis base, especially when the structure of the base molecules are not much different from each other. For this purpose, we determined the structures of the title complexes, $Cd(SCN)_2(\alpha\text{-pic})_2$ (α-pic=α-picoline=2-methylpyridine), and $Cd(SCN)_2(\beta\text{-pic})_2$ (β-pic=β-picoline=3-methylpyridine), by a single-crystal X-ray diffraction method.

Experimental

Synthesis of Bis(2-methylpyridine)bis(thiocyanato)cadmium(II) and Bis(3-methylpyridine)bis(thiocyanato)cadmium(II). These complexes were obtained in almost the same way as that of Ahuja.[9] The crystal used for the X-ray analysis was obtained as follows: crystals of the α-pic adduct were deposited from a mixture of $Cd(SCN)_2$ (0.57 g, 2.5 mmol) in 15 cm^3 of ethanol-water (1 : 1=v/v) and 2-methylpyridine (0.47 g, 5.0 mmol) in 10 cm^3 of ethanol after being left standing at ambient temperature for several hours. The crystals of the β-pic adduct were obtained from a mixed solution of $Cd(SCN)_2$ (0.57 g, 2.5 mmol) and 3-methylpyridine (0.47 g, 5.0 mmol) in 20 and 10 cm^3 methanol, respectively, after being left standing for several hours at ambient temperature. Anal. (for both complexes), ($CdC_{14}H_{14}N_4S_2$), Cd, C, H, N. The wavenumbers of their infrared spectral bands almost coincide with the respective values of the references.[9]

X-Ray Structure Analysis. The crystallographic data, the size of the used crystal, and some experimental conditions to determine intensity data are listed in Table 1. Reflections 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)). The intensities were corrected for Lorentz and polarization factors, but no correction was made for absorption and extinction.

Structure Determination. Their structures were 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 successive Fourier syntheses. Their positional, isotropic and then anisotropic thermal parameters were refined by a block-diagonal least-squares method. All the hydrogen atoms of the pyridine rings were at respective calculated positions, assuming their B_{iso}'s to be 8.0 Å^2, and C-H bond lengths to be 1.08 Å. 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.

Results and Discussion

The final atomic parameters of the non-hydrogen atoms of the complexes are listed in Tables 2 and 3; their selected bond lengths and bond angles are tabulated in Tables 4 and 5.[12] A perspective drawing of the skeleton of the polymeric chain of the α-pic adduct, as well as that around a metal atom of the β-pic complex, together with their numbering scheme of the atoms, are shown in Figs. 1 and 2. Their crystal packing diagrams are given in Figs. 3 and 4.

In the α-pic complex, the arrangement of the cadmium atoms, the coordination geometries of the respective metal atoms, and the bridging modes of the SCN ions resemble those of the γ-pic complex.[8]

There are crystallographically three kinds of cad-

Table 1. Crystallographic Data and Some Experimental Conditions to Obtain the Reflection Intensities of the Complexes; $Cd(SCN)_2(\alpha\text{-pic})_2$ and $Cd(SCN)_2(\beta\text{-pic})_2$

Lewis Base	2-Methylpyridine	3-Methylpyridine
F.W.	414.82	414.82
Crystal System	Triclinic	Triclinic
Space Group	$P\bar{1}$	$P\bar{1}$
$a(l/\text{Å})$	11.076(3)	8.7667(16)
$b(l/\text{Å})$	18.478(8)	16.655(4)
$c(l/\text{Å})$	9.299(3)	5.8447(10)
$\alpha(\phi/°)$	104.60(3)	91.406(18)
$\beta(\phi/°)$	114.84(2)	100.571(14)
$\gamma(\phi/°)$	81.12(3)	92.525(18)
$U(v/\text{Å}^3)$	1668.6(10)	837.6(3)
$D_m(d/\text{Mg m}^{-3})$	1.64(3)	1.65(3)
$D_x(d/\text{Mg m}^{-3})$	1.65	1.65
Z	4	2
$\mu(\text{Mo}\,K\alpha)(n/\text{mm}^{-1})$	1.54	1.53
Number of Reflections Measured	6233	4920
Reflections used for the Calculation[a)]	4413	2756
Measured Range $(2\theta/°)$	3—50	3—60
R[b)]	0.037	0.041
R_{weight}[b)]	0.048	0.048
S[c)]	1.434	1.206
Size of Crystal (v/mm^3)	0.2X0.3X0.1	0.2X0.3X0.1
Scan Width $(\theta/°)$	1.04+0.5tanθ	1.08+0.5tanθ

a) Reflections with $|F_o|>3\sigma(|F_o|)$ were used. b) $R=\sum||F_o|-|F_c||/\sum|F_o|$; $R_{\text{weight}}=[\sum(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2}$, were $w=1/[\{\sigma(|F_o|)\}^2+(F_{\text{weight}}\times F_o)^2]$, $F_{\text{weight}}=0.020$. c) $S=[\sum w(|F_o|-|F_c|)^2/(N_o-N_p)]^{1/2}$, where N_o=number of reflections, N_p=number of parameters.

Table 2. Final Non-Hydrogen Atomic Coordinates (X10⁴) of $Cd(SCN)_2 1(\alpha\text{-pic})_2$ Together with the Equivalent Isotropic Temperature Factors; Estimated Standard Deviations of Them are Shown in Parentheses

Atom	x	y	z	$B_{eq}/\text{Å}^2$[d)]	Atom	x	y	z	$B_{eq}/\text{Å}^2$[d)]
Cd(1)	0.0	0.0	0.0	3.3_3	N(21)	3562(4)	1666(3)	7039(6)	3.9_8
Cd(2)	5000.0	5000.0	5000.0	3.3_8	C(21)	4869(6)	1487(4)	7305(8)	5.3_1
Cd(3)	2500.4(4)	2499.9(2)	5243.9(5)	3.6_3	C(22)	5681(7)	1041(4)	8328(10)	6.6_6
S(1)	−1216(2)	744(1)	2017(2)	4.2_7	C(23)	5157(7)	753(5)	9137(11)	8.6_0
S(2)	3765(2)	1670(2)	3270(3)	8.4_7	C(24)	3831(7)	917(4)	8885(9)	6.5_8
S(3)	1228(2)	3335(1)	2839(2)	8.1_3	C(25)	3048(6)	1376(3)	7829(7)	4.2_4
S(4)	6216(2)	4256(1)	7491(2)	4.1_7	C(26)	1624(7)	1561(4)	7603(9)	6.3_8
N(1)	578(5)	1854(3)	3828(6)	4.3_8	N(31)	6032(4)	4019(3)	3365(5)	3.5_8
N(2)	1829(5)	673(3)	1219(6)	4.3_0	C(31)	5758(6)	3315(3)	3293(7)	3.9_2
N(3)	3171(5)	4330(3)	3716(6)	4.2_7	C(32)	6202(7)	2683(3)	2467(7)	4.6_9
N(4)	4414(5)	3142(3)	6394(6)	4.3_1	C(33)	6952(7)	2762(4)	1668(8)	5.3_2
C(1)	−157(5)	1400(3)	3091(6)	3.2_9	C(34)	7246(7)	3462(4)	1728(8)	5.1_4
C(2)	2623(5)	1082(3)	2078(6)	3.8_3	C(35)	6778(6)	4089(3)	2579(7)	4.1_7
C(3)	2371(5)	3920(3)	3363(6)	3.7_6	C(36)	7100(8)	4858(4)	2652(10)	7.1_7
C(4)	5158(5)	3599(3)	6849(6)	3.4_3	N(41)	−1039(4)	984(3)	−1689(5)	3.7_5
N(11)	1440(5)	3338(3)	6810(5)	3.7_1	C(41)	−758(6)	1677(3)	−781(7)	4.3_0
C(11)	151(6)	3511(4)	5947(7)	4.4_3	C(42)	−1206(7)	2313(4)	−1429(8)	5.2_3
C(12)	−664(7)	3961(4)	6601(8)	5.9_0	C(43)	−1952(7)	2235(4)	−3051(9)	5.5_4
C(13)	−153(7)	4236(5)	8227(9)	7.3_9	C(44)	−2239(6)	1528(4)	−3976(8)	5.0_3
C(14)	1166(7)	4082(4)	9132(8)	5.7_6	C(45)	−1772(6)	912(3)	−3291(7)	4.0_4
C(15)	1940(6)	3625(3)	8403(6)	3.9_1	C(46)	−2108(8)	142(4)	−4317(8)	6.1_0
C(16)	3367(6)	3432(4)	9406(7)	5.2_1					

d) The equivalent isotropic temperature factors were computed using the following expression;

$$B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cos\alpha).$$

The B_{ij}'s are defined by;

$$T=\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB^{12}+2hlB_{13}+2klB_{23})].$$

Table 3. Final Non-Hydrogen Atomic Coordinates ($\times 10^4$) of $Cd(SCN)_2(\beta\text{-pic})_2$ Together with the Equivalent Isotropic Temperature Factors; Estimated Standard Deviations of Them are Shown in Parentheses

Atom	x	y	z	$B_{eq}/Å^{2}$ d)
Cd	1984.8(5)	2543.9(3)	3864.0(6)	3.1_0
S(1)	955(2)	3829(1)	1288(2)	3.7_8
S(2)	2822(2)	1220(1)	6467(3)	4.5_5
N(1)	1148(6)	3170(3)	−3065(7)	4.0_5
N(2)	2893(5)	1913(3)	10881(7)	3.7_5
C(1)	1087(6)	3440(3)	−1267(9)	3.2_1
C(2)	2853(6)	1633(3)	9046(8)	2.9_9
N(11)	4463(5)	3213(3)	5089(8)	3.5_0
C(11)	5023(6)	3761(4)	3788(9)	3.6_3
C(12)	6422(6)	4190(3)	4442(10)	3.7_8
C(13)	7302(7)	4019(4)	6620(11)	4.5_9
C(14)	6752(7)	3448(4)	7948(10)	4.5_3
C(15)	5339(7)	3059(4)	7145(10)	4.1_1
C(16)	6981(8)	4829(4)	2933(12)	5.2_9
N(21)	−485(5)	1897(3)	2565(8)	3.9_0
C(21)	−759(7)	1370(4)	798(10)	4.3_4
C(22)	−2177(7)	960(4)	−7(11)	4.3_6
C(23)	−3340(7)	1127(4)	1156(14)	5.5_7
C(24)	−3093(8)	1689(5)	2969(15)	6.6_2
C(25)	−1645(7)	2053(4)	3639(12)	5.0_8
C(26)	−2379(10)	337(5)	−2012(14)	6.7_3

d) See below Table 2.

mium atoms; two of them, Cd(1) and Cd(2), are at the centers of symmetry, 0, 0, 0 and 0.5, 0.5, 0.5, while the Cd(3) atom is situated between them. Any pair of adjacent cadmium atoms are bridged by two SCN ions, where one SCN ion is *S*-coordinated, and the other SCN ion is *N*-coordinated to the same side metal atom. The polymeric chain lines approximately along the [111] axis, in the order ···Cd(1)···Cd(3)···Cd(2)···Cd(3^{ii})···(Key to the symmetry operation: see Fig. 1, caption). All cadmium atoms are 4*N*2*S*-hexa-coordinated, being in an octahedral geometry. Around the Cd(1) and Cd(2) atoms all N(SCN), S(SCN), and N(α-pic) atoms are in *trans*-configurations, while around the Cd(3) atom, N(SCN) atoms are in *trans*; however, the other two kinds of atoms are in *cis*-configurations. Between Cd(1) and Cd(3), as well as Cd(3) and Cd(2) atoms, there are eight-membered rings consisting of the two metal and two SCN ion atoms bridging them. The average positional deviation of the atoms from the average planes of the rings are 0.047 and 0.051 Å, respectively.

On the other hand, there are some differences between the structures of the α-pic and γ-pic adducts, as follows.

The interatomic distances, Cd(1)···Cd(3) and Cd(3)···Cd(2), in the α-pic adduct are 5.834(3) and 5.836(2)

Table 4. Interatomic Distances and Bond Angles of $Cd(SCN)_2(\alpha\text{-pic})_2$ with the Standard Deviations in Parentheses

Bond Length	(l/Å)	Bond Length	(l/Å)
Cd(1)···Cd(3)	5.834(3)	Cd(2)···Cd(3)	5.836(2)
Cd(1)-S(1)	2.734(2)	Cd(2)-S(4)	2.735(2)
Cd(3)-S(2)	2.786(3)	Cd(3)-S(3)	2.792(3)
Cd(1)-N(2)	2.252(5)	Cd(2)-N(3)	2.249(5)
Cd(3)-N(1)	2.308(5)	Cd(3)-N(4)	2.297(5)
Cd(1)-N(41)	2.524(5)	Cd(2)-N(31)	2.517(5)
Cd(3)-N(11)	2.374(5)	Cd(3)-N(21)	2.373(5)
S(1)-C(1)	1.639(5)	S(2)-C(2)	1.627(6)
S(3)-C(3)	1.627(7)	S(4)-C(4)	1.641(6)
N(1)-C(1)	1.135(7)	N(2)-C(2)	1.138(7)
N(3)-C(3)	1.142(8)	N(4)-C(4)	1.145(8)
Bond Angle	**(ϕ/°)**	**Bond Angle**	**(ϕ/°)**
S(1)-Cd(1)-N(2)	96.13(13)	S(1)-Cd(1)-N(41)	88.44(12)
N(2)-Cd(1)-N(41)	86.44(17)	S(4)-Cd(2)-N(3)	96.21(13)
S(4)-Cd(2)-N(31)	88.58(12)	N(3)-Cd(2)-N(31)	86.44(17)
S(2)-Cd(3)-S(3)	86.24(8)	S(2)-Cd(3)-N(1)	93.73(13)
S(2)-Cd(3)-N(4)	81.82(14)	S(2)-Cd(3)-N(21)	88.35(14)
S(3)-Cd(3)-N(1)	81.85(13)	S(3)-Cd(3)-N(4)	93.77(14)
S(3)-Cd(3)-N(11)	87.96(14)	N(1)-Cd(3)-N(11)	89.49(18)
N(1)-Cd(3)-N(21)	94.59(18)	N(4)-Cd(3)-N(11)	94.49(18)
N(4)-Cd(3)-N(21)	89.34(18)	N(11)-Cd(3)-N(21)	97.70(18)
Cd(1)-S(1)-C(1)	98.7(2)	Cd(3)-S(2)-C(2)	99.4(2)
Cd(3)-S(3)-C(3)	99.6(2)	Cd(2)-S(4)-C(4)	98.8(2)
Cd(3)-N(1)-C(1)	163.7(5)	Cd(1)-N(2)-C(2)	164.4(5)
Cd(2)-N(3)-C(3)	164.6(5)	Cd(3)-N(4)-C(4)	163.8(5)
S(1)-C(1)-N(1)	179.6(5)	S(2)-C(2)-N(2)	178.6(5)
S(3)-C(3)-N(3)	179.4(6)	S(4)-C(4)-N(4)	179.6(6)
Cd(3)-N(11)-C(11)	113.6(4)	Cd(3)-N(11)-C(15)	128.7(4)
Cd(3)-N(21)-C(21)	114.1(5)	Cd(3)-N(21)-C(25)	128.3(4)
Cd(2)-N(31)-C(31)	111.9(4)	Cd(2)-N(31)-C(35)	130.5(4)
Cd(1)-N(41)-C(41)	111.4(4)	Cd(1)-N(41)-C(45)	130.4(4)

Table 5. Bond Lengths and Bond Angles of $Cd(SCN)_2(\beta\text{-pic})_2$, with the Standard Deviations in Parentheses

Bond Length	(l/Å)	Bond Length	(l/Å)
Cd-S(1)	2.737(2)	Cd-S(2)	2.759(2)
Cd-N(1^{ii})	2.304(5)	Cd-N(2^{i})	2.296(5)
Cd-N(11)	2.377(4)	Cd-N(21)	2.361(4)
S(1)-C(1)	1.638(6)	S(2)-C(2)	1.637(5)
C(1)-N(1)	1.144(7)	C(2)-N(2)	1.153(7)
Cd···Cd^{i}	5.845(1)		
Bond Angle	**(ϕ/°)**	**Bond Angle**	**(ϕ/°)**
S(1)-Cd-S(2)	176.25(5)	N(11)-Cd-N(21)	178.61(15)
N(1^{ii})-Cd-N(2^{i})	178.15(18)	S(1)-Cd-N(11)	90.82(11)
S(1)-Cd-N(21)	87.95(11)	S(2)-Cd-N(11)	92.64(11)
S(2)-Cd-N(21)	88.60(11)	S(1)-Cd-N(1^{ii})	86.89(13)
S(1)-Cd-N(2^{i})	94.33(13)	S(2)-Cd-N(1^{ii})	91.73(13)
S(2)-Cd-N(2^{i})	87.14(13)	N(11)-Cd-N(1^{ii})	88.92(16)
N(11)-Cd-N(2^{i})	89.68(16)	N(21)-Cd-N(1^{ii})	91.65(17)
N(21)-Cd-N(2^{i})	89.78(16)	Cd-S(1)-C(1)	97.2(2)
Cd-S(2)-C(2)	97.9(2)	Cd-N(1^{ii})-C(1^{ii})	163.3(5)
Cd-N(2^{i})-C(2^{i})	157.4(5)	Cd-N(11)-C(11)	121.8(4)
Cd-N(11)-C(15)	120.6(4)	Cd-N(21)-C(21)	122.4(4)
Cd-N(21)-C(25)	119.8(4)	S(1)-C(1)-N(1)	178.7(5)
S(2)-C(2)-N(2)	178.7(5)		

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

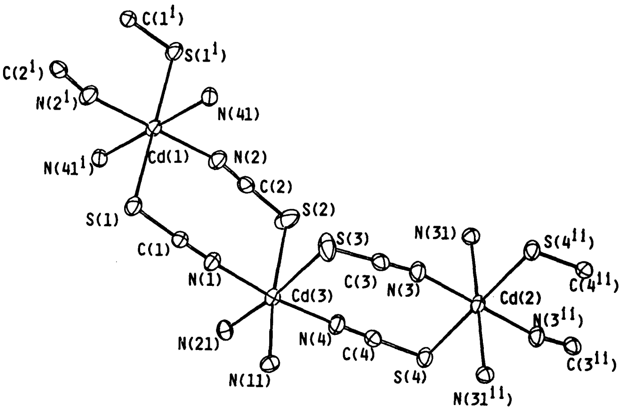

Fig. 1. A perspective drawing of the structure of $Cd(SCN)_2(\alpha\text{-pic})_2$ with the numbering scheme. (Key to the symmetry operation: i, $-x$, $-y$, $-z$; ii, $1-x$, $1-y$, $1-z$.)

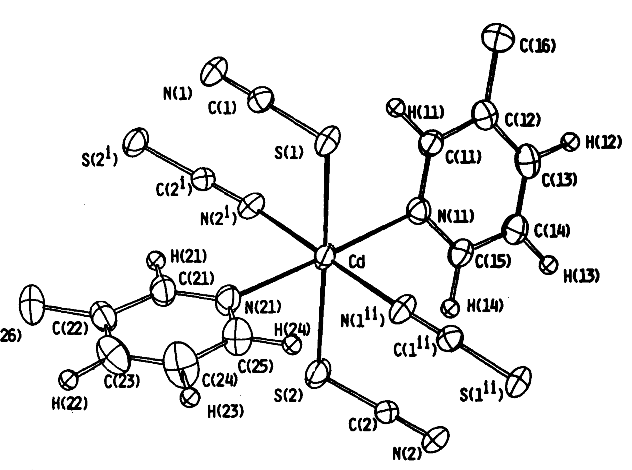

Fig. 2. A perspective drawing of $Cd(SCN)_2(\beta\text{-pic})_2$ around the cadmium atom with the numbering scheme. (Key to the symmetry operation: i, x, y, $1+z$; ii, x, y, $-1+z$.)

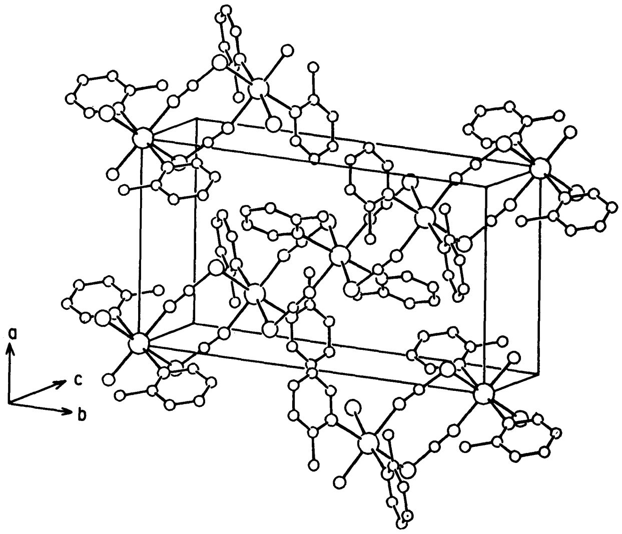

Fig. 3. Crystal packing diagram of $Cd(SCN)_2(\alpha\text{-pic})_2$.

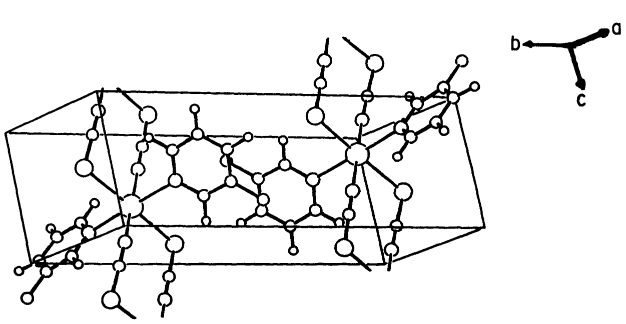

Fig. 4. Crystal packing diagram of $Cd(SCN)_2(\beta\text{-pic})_2$.

Å, respectively, while the corresponding bond lengths in the γ-pic adduct are on the average 5.778 Å. Moreover, the Cd-N(base) bond length of the former, especially those around the Cd(1) and Cd(2) atoms, are longer than the corresponding lengths of the latter complex. These differences are likely caused by a steric effect of the substituted methyl groups on the pyridine rings of the ligands. In the α-pic adduct the methyl groups approach the Cd⋯Cd chain and prevent the next cadmium, as well as the ligating α-pic nitrogen atoms, from approaching the central metal atom.

The directions of the coordinating ligands in the α- and γ-pic complexes are not the same. As shown in Fig. 3, in the α-pic adduct, the 4-carbon atoms of the pyridine rings of the ligands are directed rather in the c-axis direction, while in the γ-pic adduct, they are directed approximately in the a-axis direction.[8] As a result, the a-axis length of the α-pic adduct (11.076(3) Å) is shorter than that of the γ-pic adduct (11.323(4) Å). This is because in the latter adduct the methyl group of the ligand is directed along the a-axis direction. On the other hand, the b- and c-axis lengths of the α-pic adduct are longer than the respective lengths of the γ-pic adduct; in total, the cell volume of the α-pic adduct (1668.6(10) Å^3) is a little smaller than that of the γ-pic one (1691.7(15) Å^3): the α-pic adduct is a little more closely packed in the crystal.

The crystal structure of the β-pic adduct is drastically different from those of the α- and γ-pic adducts, though the difference between their molecules is only the substituted positions of a methyl group on the Lewis base ligand. In the β-pic adduct, crystallographically, there is only one kind of cadmium atom: 4*N*2*S*-hexa-coordinated with an octahedral geometry, where the respective pairs of N(SCN), S(SCN), and N(β-pic) atoms are ligated in *trans*-configurations. Any pair of adjucent metal atoms is bridged by two SCN ions as in cases of the α- and γ-pic complexes and line along [001] axis. As the intermetallic distance along the line, which is the same as the c-axis length, is 5.8447(10) Å, it is longer than that of the γ-pic adduct; however, it is not much different from that of the α-pic one. The volume per one metal atom is also not much different from those of the α- and γ-pic adducts.

The planarity of the eight-membered ring, comprising two bridging SCN ion atoms and two metal atoms, is not so good as those of the α- and γ-pic adducts; the average deviation of the atoms from the average plane is about twice (0.120 Å) as much. However, the puckering of the ring is not as large as the other complex ones where all eight-membered rings in the chain are parallel.[5,6]

It is interesting to consider the reason why the β-pic adduct takes a different structure. Although an exact quantitative explanation is difficult at this stage (because of the scarcity of available reference data), some considerations will be presentaed from a comparison between the structures of the adducts $Cd(SCN)_2L_2$ (L=Lewis base) where the metal atoms are doubly bridged by SCN ions. In addition to the β-pic adduct, complexes of 1*H*-1,2,4-triazol (trz),[6] dibenzylamine,[14] and imidazolinethione (etu)[5] possess the same type of structure: all have eight-membered rings comprizing the bridging of two SCN ions and two metal atoms. They are parallel in the chain and, crystallographically, only one kind of cadmium atom is in the chain. The anion of the $[(CH_3)_4N]_2[Cd(SCN)_4]$[15] also has the same type of bridge. Therefore, the twisted chains of the α- and γ-pic adducts are rather thought to be exceptional, although the pyridine (py) adduct, $Cd(SCN)_2py_2$, is expected to have a different type of long-period chain.[16]

The volume of the Lewis base is probably not the only factor to determine the type of structure since the massive dibenzylamine as well as the smaller trz adduct have the same type crystal structure as the β-pic adduct.

One probable explanation is that when some interaction between the ligand molecules is dominant, they are regularly laid on a line or accumulated with their planar molecules in parallel. This is because their respective eight-membered rings of the double SCN bridges are in parallel as is found in the β-pic adduct type chain. However, here the interaction means a long-distance type which may be weak in strength.

In trz and etu adducts, the existence of such an interaction between ligands was reported[5,6] and in the dibenzylamine adduct, half of the ligand benzene rings were reported to partially overlap.[14] Also, the unidentate SCN ions in the anion of the $[(CH_3)_4N]_2$-$[Cd(SCN)_4]$ salt have been shown to be electrostatically connected via the cations.[15]

In the case of the α-pic adduct, as the directions of the respective methyl groups of the ligands are quite limited and prevent them from excessively approaching the SCN chain, it is difficult to place the pyridine planes of the ligand in parallel in order to have them overlap in the crystal. In the case of the γ-pic adduct, as the ligand pyridine ring has a methyl group at the 4-position, the next ligand pyridine ring cannot approach or sufficiently overlap, even though they are oriented almost parallel in the crystal.[8] On the other hand, in the case of the β-pic adduct, such obstacles do not exist.

There is another possible explanation regarding the stronger interaction between the pyridine rings of the β-pic adduct. Although the density of the delocalized electrons of the non-substituted pyridine ring is poor, when some electron donating group, such as a methyl group, is introduced as in the case of the β-pic ligand, the electron density of the ring is much increased. It can, thus, form a stronger interaction with the parallel ring of the next ligand than that of the non-substituted pyridine complex. In cases of the α- and γ-pic ligands, although the electrons are similarly supplied from the methyl group, they are absorbed by the ring nitrogen and/or the ligating metal atom since the methyl group takes the 2- and 4-position of the ring; the increase of the ring electron density is not much. Thus, the interaction of the β-pic ligand is stronger than those of the α- and γ-pic as well as of the py ones.

When such an inter-ligand force is minor, some other type of the chain can be adopted to achieve a closest packing in the crystal. The α- and γ-pic adducts have such twisted chain structures, and they are slightly different from each other and can pack the respective molecules in the most effective way.

As the structure of some methylpyridine adducts of the polymeric metal thiocyanates (Ag(SCN)L (L=α- and β-pic),[17] and $Cu(SCN)L_2$ (L=α-, β-, and γ-pic))[18] were already elucidated, we can refer to their results and compare them with the results concerning cadmium complexes.

In the case of the Ag(SCN)L type complex,[17] both of the α- and β-pic adducts are in the two-dimensional polymeric structure, where each metal atom is *2S2N*-tetra-coordinated, and the side-by-side metal atoms are bridged by one SCN ion. Although their space group, as well as their *Z* numbers, are different from each other, the main structural difference between them is some deformation of the Ag(SCN) network. Their best packings are attained mainly by a change in the polymeric network of the complex. As the ligands around the metal atom are not very closely packed, the steric effect of the 2-methyl group of the ligand is not very strong, although the 2,6-dimethylpyridine adduct has a very different skeleton due to the stronger steric effect of the methyl groups.

In cases of the $Cu(SCN)L_2$ type complex,[18] all of the α-, β-, and γ-pic adducts have one-dimensional polymeric structures, where each metal atom is tetra-coordinated and each pair of the metal atoms are bridged by one SCN ion. Their space groups and the *Z* numbers are different from each other. The polymeric chain of the α-pic adduct is in a zig-zag form, while the chains of the β- and γ-pic adducts have a quasi-mirror plane parallel to the chain line; the structures of the latter two resemble each other. As was discussed by the authors,[18] the steric hindrance of the 2-methyl group is important and, consequently, only the α-pic adduct has a very different type of structure. As the single SCN chain of the type of adduct is easily deformed, the most closely packed, as well as energetically the most stable arrangement, is attained mainly by the deformation of the chain.

On the other hand, in cadmium thiocyanate adducts, the double SCN ion chain is very rigid and is always oriented approximately along one direction. To attain the closest packed and the most stable arrangement, only a deviation of the ligand molecule direction and/or a twisting of the chain are allowed. Therefore, the effect of the interaction between the ligands is rather likely to be dominant, as mentioned in the former part of this paper. The steric effect of the 2-methyl group is not the strongest one, though there is some; this is because the stable double SCN chain is not able to be deformed by the approach of a methyl group.

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