Three-Dimensional Metal Complex Host with Alternating Arrangement of the Occupied and Vacant Channels. The Crystal Structure of Cd$(NH_2CH(CH_3)CH_2NH_2)Ni(CN)_4\cdot 0.25G$ ($G=CH_3C_6H_5$, p-$(CH_3)_2C_6H_4$)

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Received June 19, 1996

Crystal structure of two inclusion compounds $Cd(pn)Ni(CN)_4\cdot 0.25G$ (G = toluene and p-xylene, pn = 1,2-diaminopropane) have been determined from single-crystal X-ray diffraction data; toluene clathrate: monoclinic $P2_1/n$, $a=13.838(6)$, $b=26.893(5)$, $c=7.543(5)$ Å, $\gamma=90.92(3)°$, $Z=4$, $R=0.0616$; p-xylene clathrate: monoclinic $P2_1/n$, $a=13.895(2)$, $b=26.900(3)$, $c=7.613(1)$ Å, $\gamma=91.06(1)°$, $Z=4$, $R=0.0486$. The host structures determined for toluene- and p-xylene-guest clathrates are substantially identical to the U-type structures observed for the straight chain aliphatic-guest clathrates. However, the alternating arrangement of occupied channels with the guest molecules and vacant channels appears in the host structure. The non-centrosymmetric toluene molecules are distributed about the inversion center to give an image like p-xylene molecule. The guests, toluene and p-xylene, prefer the U-type channel, favoring the interaction between the π-electrons of the aromatic ring and the pn-amino groups to hold the aromatic ring vertical to the cyanometallate meshes.

Introduction

As has been reported previously,[1] the three-dimensional framework of *catena*-[(1,2-diaminopropane)cadmium(II) tetra-μ-cyanonickelate(II)] provides the host structures having two kinds of channel cavities according to the shape of aliphatic guest molecules. One is a snake-like channel cavity, called U-type for the straight chain aliphatic guest molecules, analogous to that observed in urea-host inclusion compounds.[2] The other is a nodal one, called T-type, for the branched aliphatic guest molecules, similar to that in the thiourea-host inclusion compounds.[2] Whereas non-substituted small aromatic molecules such as pyrrole, thiophene, and benzene lead the host structure to the Hofmann-pn-type clathrate, $Cd(pn)Ni(CN)_4\cdot 1.5G$ with the same host composition.[3] The structure of the Hofmann-pn-type host is substantially similar to that of Hofmann's benzene clathrate $Ni(NH_3)_2Ni(CN)_4\cdot 2C_6H_6$,[4,5] as has been demonstrated for the pyrrole clathrate.[3] The two-dimensionally extended $CdNi(CN)_4$ networks are stacked with pillars of the ambidentate pn between the Cd atoms. However, when the aromatic guest has a substituent such as methyl, or nitro group, the host turns into the channel structure like U- or T-type described above. Toluene and p-xylene are accommodated in a snake-like channel U-type, and nitrobenzene in a nodal T-type. The report on nitrobenzene guest clathrate was already contributed.[6] This paper describes the crystal structure of toluene and p-xylene guest clathrates of the metal complex host $Cd(pn)Ni(CN)_4$.

Experimental

Preparations of single crystals were examined for toluene and p-xylene molecules under the conditions similar to those applied to the Hofmann-pn-type,[3] but the pH of the aqueous solution containing the host moieties was adjusted to 8.0 using citric acid. Yellow plate-like crystals of the clathrates $Cd(NH_2CH(CH_3)CH_2NH_2)Ni(CN)_4\cdot 0.25G$ ($G=CH_3C_6H_5$, **1**, and p-$(CH_3)_2C_6H_4$, **2**) were obtained at the interface between the aqueous and organic phases by standing in a refrigerator for a few minutes. Anal. for **1**. Found: C, 27.20; H, 3.40; N, 21.99%. Calcd. for $C_{8.75}H_{12}N_6CdNi$: C, 28.33; H, 3.25; N, 22.57%. Anal. for **2**. Found: C, 27.98; H, 3.53; N, 21.68%. Calcd. for $C_9H_{12.5}N_6CdNi$: C, 28.76; H, 3.35; N, 22.36%. The densities were measured by the flotation technique in carbon tetrachloride-bromoform mixture. The presence of the guest in the product was ascertained by infrared spectroscopy. The value of 0.25 for guest compounds will be interpreted later in terms of the solved crystal structures.

The single crystals subjected to the X-ray experiments were coated with acrylate resin in order to avoid spontaneous decomposition under ambient conditions. During the intensity data collection for each crystal, three standard reflections were monitored after every 200 for **1** and after every 150 for **2**: no significant decay was observed. Crystal data and conditions of intensity data collection and structure analysis are summarized in Table 1.

The Cd and Ni atom positions were determined from the heavy-atom method. All non-hydrogen atoms were found in electron density maps and were refined with isotropic thermal parameters by block-diagonal least-squares calculations. The unit weight scheme was applied to all the refinements. Lorentz, polarization and absorption corrections was applied to all the diffraction data.

The calculations were carried out using the programs in UNICS III[7] on a HITAC M680/682H at the Computer Center of the University of Tokyo; atomic scattering factors for neutral atoms were taken from those in the International Tables including real dispersion corrections.[8] Crystallographic diagrams were obtained using the program of ORTEP-PC version.[9]

Table 1. Summary of Crystal Data, Data Collection and Structure Analysis

General formula	$Cd(NH_2CH(CH_3)CH_2NH_2)Ni(CN)_4 \cdot 0.25G$	
Crystal system	monoclinic	
Space group	$P2_1/n$	
G	$CH_3C_6H_5$	p-$(CH_3)_2C_6H_4$
Formula weight	372.61	376.36
a/Å	13.838(6)	13.895(2)
b/Å	26.893(5)	26.900(3)
c/Å	7.543(5)	7.613(1)
γ/°	90.92(3)	91.06(1)
V/Å^3	2807(2)	2844.9(7)
Z	4	4
D_m, D_x/g cm^{-3}	1.75(1), 1.76	1.75(1), 1.76
F(000)	1462	1480
Crystal size/mm	0.20×0.10×0.30	0.20×0.10×0.30
Diffractometer	Rigaku-AFC5R^a	Rigaku-AFC5S^b
μ(Mo K_α)/cm^{-1}	28.475	28.100
Scan mode	ω	2θ-ω
Scan range	$4° \leq 2\theta \leq 60°$	$4° \leq 2\theta \leq 60°$
No. of reflections measured	5877	5275
No. of reflections used in refinement, $(F_o > 3\sigma(F_o))$	5823	5229
No. of parameter	308	308
Applied matrix for hkl	1 0 0 0 0 1 0 −1 0	1 0 0 0 0 1 0 −1 0
R^c	0.0616	0.0486
$R_w{}^d$	0.0678	0.0536
G.O.F.^{e}	4.4516	3.8863

^{a}Radiation: rotating Mo K_α (λ=0.70926 Å); monochromator: graphite; temperature: ambient. ^{b}Radiation: rotating Mo K_α (λ=0.71069 Å); monochromator: graphite; temperature: ambient. $^c R=\Sigma(||F_o|-|F_o||)/\Sigma|F_o|$. $^d R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w(F_o)^2]^{1/2}$, $w=1$. ^{e}G.O.F.$=[(\Sigma w(|F_o-F_c|)^2/(N_{data}-N_{par})]^{1/2}$

Results and Discussion

The host structures determined for toluene and p-xylene guest clathrates are substantially identical to the U-type structures observed for the straight chain aliphatic guest clathrates.[1] The unit cell parameters, $a=ca.$ 13.8-13.9, $b=ca.$ 26.9, c=7.5-7.6 Å, $\gamma=ca.$ 91°, are similar to those observed for the straight chain aliphatic-guest series in the coordinates setting selected for the sake of structure comparison. However, the crystal symmetries are lowered for U-type structure of the aromatic-guest compounds. The monoclinic lattice turns to the primitive $P2_1/n$ from the base-centered $A2/a$ for the aliphatic-guest ones.

The solved structures are shown in Figure 1 and 2. The refined atomic parameters for toluene- and p-xylene-guest clathrates are listed in Table 2 and 3, respectively. Selected bond distances and bond angles for both clathrates are summarized in Table 4; no unusual bond distances and angles have been observed.

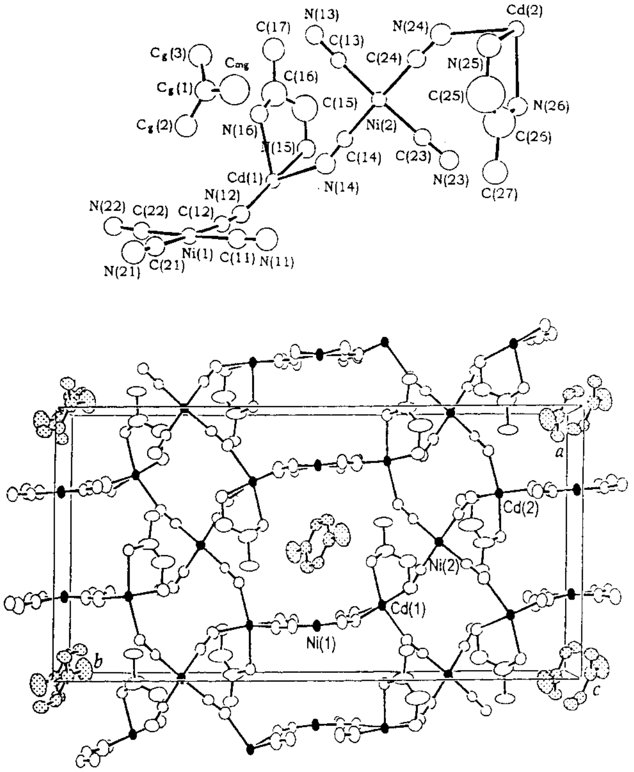

Figure 1. Structure of $Cd(NH_2CH(CH_3)CH_2NH_2)Ni(CN)_4 \cdot 0.25p$-$(CH_3)_2C_6H_4$. Top: Asymmetric unit with atomic notations; bottom: projection along the c-axis. The Cd and Ni atoms are shown as solid ellipsoids and the guest atoms are dotted.

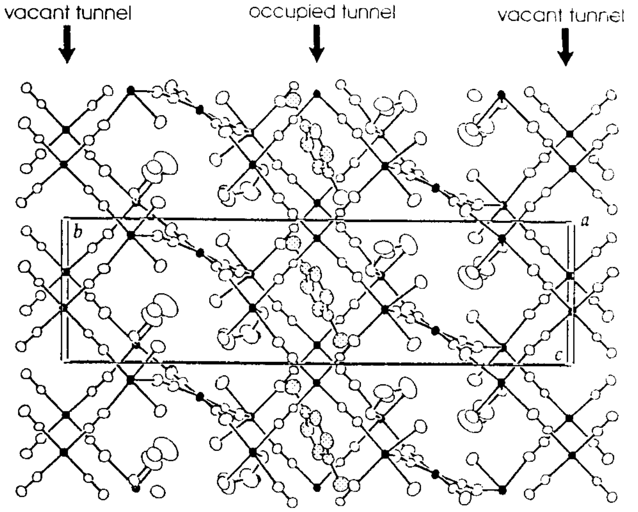

Figure 2. Structure of $Cd(NH_2CH(CH_3)CH_2NH_2)Ni(CN)_4 \cdot 0.25p$-$(CH_3)_2C_6H_4$. along the a-axis in the range of $ca.$ 0.7a, 1.2b and 3c. The Cd and Ni atoms are shown as solid ellipsoids and the guest atoms are dotted.

The topology of the host framework is essentially similar to that of the straight chain aliphatic-guest clathrate. There are two kinds of tetracyanonickelate(II) moieties: one consists of the ceiling or the floor of the channel by taking a double-1D extension with Cd atoms along the c-axis of crys-

Table 2. Final Coordinates and Equivalent Isotropic Thermal Parameters for $Cd(NH_2CH(CH_3)CH_2NH_2)Ni(CN)_4 \cdot 0.25G$ (Estimated Standard Deviations in Parentheses)

Atom	x/a	y/b	z/c	$B_{eq}{}^a$	x/a	y/b	z/c	$B_{eq}{}^a$
G	$CH_3C_6H_5$				p-$(CH_3)_2C_6H_4$			
Cd(1)	0.26592(5)	0.36960(2)	−0.62048(9)	2.24(1)	0.26681(4)	0.36989(2)	−0.61713(8)	2.09(1)
Cd(2)	0.69154(5)	0.13703(2)	0.12063(9)	2.19(1)	0.69060(4)	0.13635(2)	0.12103(7)	2.04(1)
Ni(1)	0.19669(9)	0.50006(3)	−0.1277(2)	1.40(2)	0.19723(7)	0.49967(3)	−0.1272(1)	2.16(2)
Ni(2)	0.50410(8)	0.26394(4)	−0.2396(2)	2.16(2)	0.50402(7)	0.26370(3)	−0.2336(1)	2.01(2)
N(11)	0.2220(8)	0.4215(3)	0.148(1)	4.3(3)	0.2265(7)	0.4221(3)	0.149(1)	4.0(2)
N(12)	0.2097(7)	0.4227(3)	−0.413(1)	3.3(2)	0.2106(5)	0.4227(2)	−0.4132(9)	2.9(2)
N(13)	0.3698(6)	0.1816(3)	−0.128(1)	3.4(2)	0.3698(5)	0.1806(3)	−0.120(1)	3.2(2)
N(14)	0.3342(6)	0.3162(3)	−0.398(1)	4.0(2)	0.3346(5)	0.3162(3)	−0.388(1)	3.9(2)
N(15)	0.3266(7)	0.3139(3)	−0.843(1)	4.0(2)	0.3246(6)	0.3117(3)	−0.830(1)	3.6(2)
N(16)	0.4288(7)	0.3924(3)	−0.662(1)	3.6(2)	0.4307(5)	0.3907(3)	−0.653(1)	3.2(2)
N(21)	0.2052(7)	0.5757(3)	0.163(1)	3.8(2)	0.2034(7)	0.5752(3)	0.162(1)	4.1(2)
N(22)	0.1861(7)	0.5821(3)	−0.396(1)	3.5(2)	0.1865(5)	0.5816(2)	−0.395(1)	3.1(2)
N(23)	0.6466(6)	0.3421(3)	−0.370(1)	3.1(2)	0.6463(5)	0.3416(2)	−0.360(1)	3.0(2)
N(24)	0.6679(7)	0.2070(3)	−0.080(1)	4.0(2)	0.6663(6)	0.2062(3)	−0.073(1)	3.7(2)
N(25)	0.6687(7)	0.1944(3)	0.356(1)	4.2(2)	0.6693(5)	0.1929(3)	0.360(1)	3.9(2)
N(26)	0.5238(6)	0.1346(3)	0.174(1)	3.1(2)	0.5225(5)	0.1343(2)	0.1774(9)	2.9(2)
C(11)	0.2116(9)	0.4506(3)	0.044(1)	3.5(3)	0.2137(7)	0.4509(3)	0.043(1)	3.0(2)
C(12)	0.2010(8)	0.4519(3)	−0.306(1)	2.8(2)	0.2010(6)	0.4520(3)	−0.304(1)	2.3(2)
C(13)	0.4211(6)	0.2131(3)	−0.167(1)	2.6(2)	0.4205(6)	0.2122(3)	−0.162(1)	2.5(2)
C(14)	0.3992(7)	0.2969(3)	−0.336(1)	2.8(2)	0.4004(6)	0.2972(3)	−0.329(1)	2.4(2)
C(21)	0.2006(8)	0.5477(3)	0.051(1)	3.1(2)	0.1996(7)	0.5470(3)	0.052(1)	2.9(2)
C(22)	0.1883(7)	0.5510(3)	−0.296(1)	2.7(2)	0.1878(6)	0.5507(3)	−0.295(1)	2.6(2)
C(23)	0.5903(6)	0.3132(3)	−0.319(1)	2.4(2)	0.5910(5)	0.3127(3)	−0.312(1)	2.2(2)
C(24)	0.6060(7)	0.2291(3)	−0.142(1)	2.8(2)	0.6067(6)	0.2286(3)	−0.138(1)	2.7(2)
C(15)	0.429(1)	0.3212(6)	−0.852(3)	7.7(5)	0.4294(9)	0.3166(5)	−0.836(2)	7.4(5)
C(16)	0.470(1)	0.3668(7)	−0.811(3)	8.2(6)	0.4703(8)	0.3627(5)	−0.800(2)	6.9(4)
C(17)	0.580(1)	0.3730(6)	−0.833(2)	6.4(5)	0.5814(7)	0.3659(5)	−0.812(2)	5.1(3)
C(25)	0.568(1)	0.1971(8)	0.386(3)	10.8(8)	0.5680(9)	0.1961(7)	0.394(3)	10.1(6)
C(26)	0.4991(9)	0.1698(7)	0.313(2)	7.7(5)	0.4998(8)	0.1693(5)	0.314(2)	7.2(4)
C(27)	0.3944(8)	0.1761(5)	0.353(2)	4.5(3)	0.3957(6)	0.1749(4)	0.360(2)	4.3(3)
$C_g(1)^b$	0.513(2)	0.4826(6)	−0.365(4)	12(1)	0.5156(8)	0.4771(3)	−0.338(1)	3.9(3)
$C_g(2)^b$	0.427(1)	0.4989(7)	−0.391(5)	16(1)	0.4278(7)	0.4976(3)	−0.378(2)	4.2(3)
$C_g(3)^b$	0.601(2)	0.4862(9)	−0.480(6)	18(2)	0.5886(7)	0.4800(4)	−0.463(2)	4.7(3)
$C_{mg}{}^c$	0.542(2)	0.4663(8)	−0.230(4)	12(1)	0.533(1)	0.4513(5)	−0.162(2)	7.7(5)

${}^aB_{eq}=4(\Sigma_{ij}\beta_{ij}a_ia_j)/3$, Å². ${}^bC_g$: Carbon atom of guest benzene ring. ${}^cC_{mg}$: Methyl carbon atom of guest toluene or p-xylene.

tal, and the other spans between the Cd atoms on the ceiling and the floor also by taking another double-1D along the *a*-axis. The term 'double-1D' refers to a one-dimensional infinite structure involved with the square-planar tetracyanometallate such as $Ni(CN)_4$ and other M metals which are alternately linked at the N atoms to form a double cyanide bridges like $>Ni<(CN\text{-}M\text{-}NC)_2>Ni<$ extension.[10] The pn chelates bound to the Cd atoms, are located point-symmetrically as shown in Figure 2. However, two kinds of crystallographically independent Cd atoms and pn chelates occur due to the lowering of crystal symmetries for toluene- and *p*-xylene-clathrates.

In case of aromatic-guest clathrates, every other channel is collapsed as shown in Figure 1. There is a remarkable difference between the aromatic- and the aliphatic-guest clathrates with the U-type structure. The channel accommodating the guest is expanded along the *a*-axis. That is, the heights of the channel in order to hold the aromatic plane of the guest almost parallel to the *a*-axis, which expansion leads to the shrinkage of neighboring channels along the *a*-axis: the heights of expanded and shrunken channels along the *a*-axis are *ca.* 8.5 and 5.5 Å, respectively. This is why aromatic-guest is not accommodated in this shrunken channel. Thus the number of guest molecules in the unit formula decreases to 0.25 from 0.5 which is required in the fully-occupied structure. The alternating arrangement of occupied and vacant channels lowers the crystal symmetry from the base-centered monoclinic A2/*a* which is common for the straight chain aliphatic-guest compounds. Except for the alternating expansion and shrinkage of the channel height, there are no substantial differences in the host structure between the aromatic- and aliphatic-guest clathrates.

Table 3. Interatomic Distances and Selected Angles in $Cd(NH_2CH(CH_3)CH_2NH_2)Ni(CN)_4 \cdot 0.25CH_3C_6H_5$

Distances (d/Å)

Cd(1)-N(11)^{*1}	2.322(9);	Cd(1)-N(12)	2.266(9);	Cd(1)-N(13)^{*2}	2.311(8);
Cd(1)-N(14)	2.41(1);	Cd(1)-N(15)	2.41(1);	Cd(1)-N(16)	2.347(9);
Cd(2)-N(21)^{*3}	2.331(8);	Cd(2)-N(22)^{*4}	2.251(8);	Cd(2)-N(23)^{*5}	2.301(8);
Cd(2)-N(24)	2.44(1);	Cd(2)-N(25)	2.38(1);	Cd(2)-N(26)	2.356(9);
Ni(1)-C(11)	1.87(1);	Ni(1)-C(12)	1.87(1);	Ni(1)-C(21)	1.86(1);
Ni(1)-C(22)	1.87(1);	Ni(2)-C(13)	1.853(9);	Ni(2)-C(14)	1.861(9);
Ni(2)-C(23)	1.865(9);	Ni(2)-C(24)	1.86(1);	N(11)-C(11)	1.12(2);
N(12)-C(12)	1.13(1);	N(13)-C(13)	1.14(1);	N(14)-C(14)	1.14(1);
N(15)-C(15)	1.43(2);	N(16)-C(16)	1.44(2);	C(15)-C(16)	1.38(3);
C(16)-C(17)	1.54(3);	N(21)-C(21)	1.13(2);	N(22)-C(22)	1.13(1);
N(23)-C(23)	1.16(1);	N(24)-C(24)	1.15(1);	N(25)-C(25)	1.42(3);
N(26)-C(26)	1.46(2);	C(25)-C(26)	1.31(3);	C(26)-C(27)	1.49(2);
$C_g(1)$-$C_g(2)$	1.29(5);	$C_g(1)$-$C_g(3)$	1.50(5);	$C_g(1)$-C_{mg}	1.19(4);

Angles (δ/deg)

N(11)^{*1}-Cd(1)-N(12)	92.6(3);	N(11)^{*1}-Cd(1)-N(13)^{*2}	97.0(3);
N(11)^{*1}-Cd(1)-N(14)	171.9(3);	N(11)^{*1}-Cd(1)-N(15)	87.0(3);
N(11)^{*1}-Cd(1)-N(16)	90.2(3);	N(12)-Cd(1)-N(13)^{*2}	96.3(3);
N(12)-Cd(1)-N(14)	92.0(3);	N(12)-Cd(1)-N(15)	179.4(3);
N(12)-Cd(1)-N(16)	105.3(3);	N(13)^{*2}-Cd(1)-N(14)	89.1(3);
N(13)^{*2}-Cd(1)-N(15)	84.3(3);	N(13)^{*2}-Cd(1)-N(16)	156.9(3);
N(14)-Cd(1)-N(15)	88.4(3);	N(14)-Cd(1)-N(16)	82.2(3);
N(15)-Cd(1)-N(16)	74.2(3);	N(21)^{*3}-Cd(2)-N(22)^{*4}	93.7(3);
N(21)^{*3}-Cd(2)-N(23)^{*5}	93.5(3);	N(21)^{*3}-Cd(2)-N(24)	173.4(3);
N(21)^{*3}-Cd(2)-N(25)	87.1(3);	N(21)^{*3}-Cd(2)-N(26)	87.2(3);
N(22)^{*4}-Cd(2)-N(23)^{*5}	101.9(3);	N(22)^{*4}-Cd(2)-N(24)	92.1(3);
N(22)^{*4}-Cd(2)-N(25)	170.4(3);	N(22)^{*4}-Cd(2)-N(26)	95.1(3);
N(23)^{*5}-Cd(2)-N(24)	88.5(3);	N(23)^{*5}-Cd(2)-N(25)	87.5(3);
N(23)^{*5}-Cd(2)-N(26)	162.9(3);	N(24)-Cd(2)-N(25)	86.6(4);
N(24)-Cd(2)-N(26)	89.1(3);	N(25)-Cd(2)-N(26)	75.5(3);
Cd(1)-N(11)^{*1}-C(11)^{*1}	170.2(8);	Cd(1)-N(12)-C(12)	165.9(9);
Cd(1)-N(13)^{*2}-C(13)^{*2}	160.6(8);	Cd(1)-N(14)-C(14)	150.6(9);
Cd(1)-N(15)-C(15)	107.7(9);	Cd(1)-N(16)-C(16)	111.1(9);
Cd(2)-N(21)^{*3}-C(21)^{*3}	171.3(8);	Cd(2)-N(22)^{*4}-C(22)^{*4}	172.1(8);
Cd(2)-N(23)^{*5}-C(23)^{*5}	144.8(7);	Cd(2)-N(24)-C(24)	139.6(9);
Cd(2)-N(25)-C(25)	107(1);	Cd(2)-N(26)-C(26)	110.2(8);
C(11)-Ni(1)-C(12)	90.1(5);	C(11)-Ni(1)-C(21)	89.1(5);
C(11)-Ni(1)-C(22)	176.9(5);	C(12)-Ni(1)-C(21)	176.5(5);
C(12)-Ni(1)-C(22)	91.2(5);	C(21)-Ni(1)-C(22)	89.5(5);
C(13)-Ni(2)-C(14)	89.3(4);	C(13)-Ni(2)-C(23)	177.6(4);
C(13)-Ni(2)-C(24)	88.7(4);	C(14)-Ni(2)-C(23)	91.8(4);
C(14)-Ni(2)-C(24)	178.0(4);	C(23)-Ni(2)-C(24)	90.1(4);
Ni(1)-C(11)-N(11)	179(1);	Ni(1)-C(12)-N(12)	176(1);
Ni(1)-C(21)-N(21)	178(1);	Ni(1)-C(22)-N(22)	178(1);
Ni(2)-C(13)-N(13)	177.9(9);	Ni(2)-C(14)-N(14)	178.3(9);
Ni(2)-C(23)-N(23)	176.9(9);	Ni(2)-C(24)-N(24)	179(1);
N(15)-C(15)-C(16)	120(2);	N(16)-C(16)-C(15)	117(2);
N(16)-C(16)-C(17)	115(1);	C(15)-C(16)-C(17)	117(2);
N(25)-C(25)-C(26)	127(2);	N(26)-C(26)-C(25)	119(2);
N(26)-C(26)-C(27)	117(1);	C(25)-C(26)-C(27)	123(2);
$C_g(2)$-$C_g(1)$-$C_g(3)$	130(3);	$C_g(2)$-$C_g(1)$-C_{mg}	126(3);
$C_g(3)$-$C_g(1)$-C_{mg}	104(3).		

Key to symmetry operations:

*1: $x, y, z-1$; *2: $1/2-x, 1/2-y, (z+1/2)-1$; *3: $x+1/2, (y+1/2)-1, 1/2-z$; *4: $x+1/2, (y+1/2)-1, (1/2-z)-1$; *5: $(1/2-x)+1, 1/2-y, 1/2+z$

Table 4. Interatomic Distances and Selected Angles in Cd(NH$_2$CH(CH$_3$)CH$_2$NH$_2$)Ni(CN)$_4$·0.25p-(CH$_3$)$_2$C$_6$H$_4$

Distances (d/Å)					
Cd(1)-N(11)^{*1}	2.342(8);	Cd(1)-N(12)	2.253(7);	Cd(1)-N(13)^{*2}	2.313(7);
Cd(1)-N(14)	2.463(9);	Cd(1)-N(15)	2.403(8);	Cd(1)-N(16)	2.350(8);
Cd(2)-N(21)^{*3}	2.340(8);	Cd(2)-N(22)^{*4}	2.266(7);	Cd(2)-N(23)^{*5}	2.336(7);
Cd(2)-N(24)	2.419(8);	Cd(2)-N(25)	2.391(9);	Cd(2)-N(26)	2.374(7);
Ni(1)-C(11)	1.862(9);	Ni(1)-C(12)	1.860(8);	Ni(1)-C(21)	1.865(9);
Ni(1)-C(22)	1.881(8);	Ni(2)-C(13)	1.873(8);	Ni(2)-C(14)	1.859(8);
Ni(2)-C(23)	1.871(8);	Ni(2)-C(24)	1.874(8);	N(11)-C(11)	1.13(1);
N(12)-C(12)	1.16(1);	N(13)-C(13)	1.14(1);	N(14)-C(14)	1.15(1);
N(15)-C(15)	1.46(2);	N(16)-C(16)	1.46(2);	C(15)-C(16)	1.38(2);
C(16)-C(17)	1.55(2);	N(21)-C(21)	1.13(1);	N(22)-C(22)	1.13(1);
N(23)-C(23)	1.14(1);	N(24)-C(24)	1.14(1);	N(25)-C(25)	1.44(2);
N(26)-C(26)	1.44(2);	C(25)-C(26)	1.33(2);	C(26)-C(27)	1.50(2);
C$_g$(1)-C$_g$(2)	1.38(2);	C$_g$(1)-C$_g$(3)	1.40(2);	C$_g$(1)-C$_{mg}$	1.53(2);
Angles (δ/deg)					
N(26)-C(26)-C(27)	117(1);	C(25)-C(26)-C(27)	123(2);		
N(11)^{*1}-Cd(1)-N(12)	93.2(3);	N(11)^{*1}-Cd(1)-N(13)^{*2}	98.1(3);		
N(11)^{*1}-Cd(1)-N(14)	171.2(3);	N(11)^{*1}-Cd(1)-N(15)	87.9(3);		
N(11)^{*1}-Cd(1)-N(16)	90.6(3);	N(12)-Cd(1)-N(13)^{*2}	95.0(2);		
N(12)-Cd(1)-N(14)	91.3(3);	N(12)-Cd(1)-N(15)	178.4(3);		
N(12)-Cd(1)-N(16)	106.0(3);	N(13)^{*2}-Cd(1)-N(14)	89.0(3);		
N(13)^{*2}-Cd(1)-N(15)	83.7(3);	N(13)^{*2}-Cd(1)-N(16)	156.8(2);		
N(14)-Cd(1)-N(15)	87.7(3);	N(14)-Cd(1)-N(16)	81.0(3);		
N(15)-Cd(1)-N(16)	95.1(3);	N(21)^{*3}-Cd(2)-N(22)^{*4}	94.7(3);		
N(21)^{*3}-Cd(2)-N(23)^{*5}	92.8(3);	N(21)^{*3}-Cd(2)-N(24)	172.2(3);		
N(21)^{*3}-Cd(2)-N(25)	85.6(3);	N(21)^{*3}-Cd(2)-N(26)	86.7(3);		
N(22)^{*4}-Cd(2)-N(23)^{*5}	102.9(2);	N(22)^{*4}-Cd(2)-N(24)	92.1(3);		
N(22)^{*4}-Cd(2)-N(25)	171.5(3);	N(22)^{*4}-Cd(2)-N(26)	96.3(2);		
N(23)^{*5}-Cd(2)-N(24)	89.4(2);	N(23)^{*5}-Cd(2)-N(25)	85.6(3);		
N(23)^{*5}-Cd(2)-N(26)	160.8(2);	N(24)-Cd(2)-N(25)	87.1(3);		
N(24)-Cd(2)-N(26)	88.7(3);	N(25)-Cd(2)-N(26)	75.2(3);		
Cd(1)-N(11)^{*1}-C(11)^{*1}	172.7(7);	Cd(1)-N(12)-C(12)	166.3(7);		
Cd(1)-N(13)^{*2}-C(13)^{*2}	158.7(6);	Cd(1)-N(14)-C(14)	148.9(7);		
Cd(1)-N(15)-C(15)	107.7(8);	Cd(1)-N(16)-C(16)	109.9(7);		
Cd(2)-N(21)^{*3}-C(21)^{*3}	172.4(7);	Cd(2)-N(22)^{*4}-C(22)^{*4}	172.7(7);		
Cd(2)-N(23)^{*5}-C(23)^{*5}	146.0(6);	Cd(2)-N(24)-C(24)	141.6(7);		
Cd(2)-N(25)-C(25)	108.1(9);	Cd(2)-N(26)-C(26)	110.0(7);		
C(11)-Ni(1)-C(12)	90.7(4);	C(11)-Ni(1)-C(21)	88.4(4);		
C(11)-Ni(1)-C(22)	176.5(4);	C(12)-Ni(1)-C(21)	177.3(4);		
C(12)-Ni(1)-C(22)	91.0(4);	C(21)-Ni(1)-C(22)	89.8(4);		
C(13)-Ni(2)-C(14)	89.8(3);	C(13)-Ni(2)-C(23)	177.0(3);		
C(13)-Ni(2)-C(24)	88.9(4);	C(14)-Ni(2)-C(23)	91.7(3);		
C(14)-Ni(2)-C(24)	178.7(4);	C(23)-Ni(2)-C(24)	89.6(3);		
Ni(1)-C(11)-N(11)	177.6(9);	Ni(1)-C(12)-N(12)	175.0(7);		
Ni(1)-C(21)-N(21)	178.1(9);	Ni(1)-C(22)-N(22)	176.9(8);		
Ni(2)-C(13)-N(13)	178.9(8);	Ni(2)-C(14)-N(14)	177.4(8);		
Ni(2)-C(23)-N(23)	177.9(7);	Ni(2)-C(24)-N(24)	176.7(8);		
N(15)-C(15)-C(16)	118(1);	N(16)-C(16)-C(15)	117(1);		
N(16)-C(16)-C(17)	114(1);	C(15)-C(16)-C(17)	116(1);		
N(25)-C(25)-C(26)	125(2);	N(26)-C(26)-C(25)	122(1);		
N(26)-C(26)-C(27)	117(1);	C(25)-C(26)-C(27)	121(1);		
C$_g$(2)-C$_g$(1)-C$_g$(3)	118(1);	C$_g$(2)-C$_g$(1)-C$_{mg}$	121(1);		
C$_g$(3)-C$_g$(1)-C$_{mg}$	121(1).				

Key to symmetry operations:

*1: x, y, $z-1$; *2: $1/2-x$, $1/2-y$, $(z+1/2)-1$; *3: $x+1/2$, $(y+1/2)-1$, $1/2-z$; *4: $x+1/2$, $(y+1/2)-1$, $(1/2-z)-1$; *5: $(1/2-x)+1$, $1/2-y$, $1/2+z$

The tetracyanonickelate(II) moieties, both for Ni(1) and Ni(2), are little distorted from a square-planar structure. The coordination sphere is considerably distorted from the regular one about both the octahedral Cd(1) and Cd(2) atoms as listed in Table 4. However, these distortions are less than those of the clathrates accommodating aliphatic guests described before.[1]

The guests, toluene and *p*-xylene, are centered at the inversion center of the $P2_1/n$ unit cell so that the non-centrosymmetric toluene molecules are distributed about the inversion center to give an image like the *p*-xylene molecule. Hence the ORTEP diagram of toluene-guest clathrate is very similar to that of the *p*-xylene-guest one. Only the ORTEP diagrams of *p*-xylene-guest clathrate are shown in this paper. The thermal parameters are comparatively smaller for the *p*-xylene than the toluene, although that for the methyl-C, C_{mg}, of the former is considerably larger than those for the skeletal C. Since *p*-xylene has a six-atomic skeletal sequence, the molecule appears to be commensurate with the unit length of the channel like hexane molecule in the U-type structure.[1]

The aromatic ring is vertically sandwiched between the mesh-openings of the ceiling and floor of the channel, whose arrangement is similar to those observed for the aromatic guests in the Hofmann-type and related metal-complex host clathrates.[10] The relative orientation between the aromatic plane and the amino group of the pn is also similar to the case of the Hofmann-type and analogous clathrates.[10] The lipophilic methyl group of the pn is located rather far from the aromatic ring which appears to be clipped by the amino groups with the distance of 3.29 Å; a hydrogen-bond interaction is suggested between the π-electrons and the amino-hydrogens.[11]

In this work, the crystal structures have been determined in detail for the p-xylene-guest clathrate of U-type without disorder. It is due to the characteristic feature of the metal complex host built of the square-planar tetracyanonickelate (II) moieties and the pn-chelated Cd atoms. The guests, toluene and *p*-xylene, prefer U-type channel which favors the interaction between the π-electrons of the aromatic ring and the pn-amino groups to hold the aromatic ring vertical to the cyanometallate meshes.

It is reported that nitrobenzene-guest molecule leads the host framework, $Cd(pn)Ni(CN)_4$, to the T-type.[6] In summary, toluene and p-xylene are accommodated in a snake-like channel, U-type, and nitrobenzene in a nodal T-type. Therefore, the selectivity of the guest for the host structure, rather than that of the host structure for the guest, is exhibited in the aromatic-guest inclusion compounds of U- and T-types.

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