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Variations in Catenation Behavior in Aromatic Guest Clathrates Containing Rigid Host Entities *p*-Xylylenediamine (*p*-xda) and Tetracyanonickelate(II) Linking Octahedral Cadmium(II) in [Cd(*p*-xda)$_n$Ni(CN)$_4$] Host (n = 1, 1.5, or 2) and the Related Complex [Cd($C_6H_5NH_2$)$_2$(*p*-xda)Ni(CN)$_4$]

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A number of *catena*-μ-linkage modes have been observed for the *p*-xylylenediamine (*p*-xda) and Ni(CN)$_4$ linking octahedral Cd atoms in the X-ray single crystal structures of five inclusion compounds with aromatic guests and a three-dimensional (3D) complex salt: [Cd(*p*-xda)Ni(CN)$_4$]·*o*-$CH_3C_6H_4NH_2$ (**1**), [Cd(*p*-xda)$_2$Ni(CN)$_4$]·*m*-$CH_3C_6H_4NH_2$ (**2**), [Cd(*p*-xda)$_2$Ni(CN)$_4$]·C_6H_5OH·H_2O (**3a**), [Cd(*p*-xda)$_2$Ni(CN)$_4$]·C_9H_7N (**3b**), [Cd$_2$(*p*-xda)$_3${Ni(CN)$_4$}$_2$]·2C_4H_5N (**4**), and [Cd($C_6H_5NH_2$)$_2$(*p*-xda)Ni(CN)$_4$] (**5**). Clathrate **1** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 6.960(2)$ Å, $b = 7.718(2)$ Å, $c = 9.693(2)$ Å, $\alpha = 90.61(2)°$, $\beta = 91.72(2)°$, $\gamma = 90.17(2)°$, $Z = 1$, and $R = 0.0298$ for 2751 reflections; clathrate **2** crystallizes in the triclinic system, $P\bar{1}$, with $a = 8.149(2)$ Å, $b = 9.577(1)$ Å, $c = 9.865(2)$ Å, $\alpha = 81.03(1)°$, $\beta = 94.08(2)°$, $\gamma = 106.08(1)°$, $Z = 1$, and $R = 0.0490$ for 3285 reflections; clathrate **3a** crystallizes in the monoclinic system, $P2_1/m$, with $a = 8.615(3)$ Å, $b = 17.568(2)$ Å, $c = 9.950(2)$ Å, $\beta = 105.30(2)°$, $Z = 2$, and $R = 0.0519$ for 2792 reflections; clathrate **3b** crystallizes in the monoclinic system, $P2_1/m$, with $a = 8.505(1)$ Å, $b = 17.737(1)$ Å, $c = 10.106(1)$ Å, $\beta = 102.64(1)°$, $Z = 2$, and $R = 0.0422$ for 3480 reflections; clathrate **4** crystallize in the monoclinic system, $C2/c$, with $a = 19.820(2)$ Å, $b = 7.738(2)$ Å, $c = 31.213(1)$ Å, $\beta = 109.138(5)°$, $Z = 4$, and $R = 0.0480$ for 4092 reflections; complex **5** crystallize in the monoclinic system, $C2/c$, with $a = 22.240(1)$ Å, $b = 9.254(1)$ Å, $c = 16.241(1)$ Å, $\beta = 130.668(3)°$, $Z = 4$, and $R = 0.0389$ for 2810 reflections. The puckered two-dimensional (2D) network of [CdNi(CN)$_4$]$_\infty$ in **1** is successively spanned by *p*-xda at every Cd atom to form a 3D host for the *o*-toluidine. The 2D network in **2** is broken at a couple of CN groups in *trans* positions of each Ni(CN)$_4$; instead, the bridge of *p*-xda is doubled to span the Cd atoms in the host accommodating *m*-toluidine. The breaking is at *cis* positions in the hosts of **3a** and **3b**, enclathrating hydrated phenol and quinoline, respectively. The complicated 3D host structure of pyrrole clathrate **4** is constructed of three single spans of *p*-xda from one Cd to three other Cd atoms, the respective Cd atoms being interconnected by *cis*-[−NC−Ni(CN)$_2$−CN−] and four-handed Ni(CN)$_4$ moieties. The bis(aniline)-ligated Cd complex **5** has a 3D structure built from the −[Cd−*p*-xda−]$_\infty$ and −[(*cis*-)NC−Ni(CN)$_2$−CN−Cd−]$_\infty$ catenations. These structural variations are interpreted in terms of rigidity of *p*-xda and Ni(CN)$_4$ skeletons, partial flexibility of the −CH_2NH_2 substituents in *p*-xda, flexible utilization of N-ends of Ni(CN)$_4$ in the catenation, hydrogen bond interactions among the host entities, and host−guest interactions through hydrogen bonds; no strong $\pi-\pi$ interactions were observed between the guest and the π-rich host entities.

Introduction

As for the supramolecular systems constructed of multidimensional cyanometallate complex hosts and organic guest molecules, the Hofmann-type clathrates and their analogues appear to be one of the best known families of inclusion compounds stimulating theoretical chemists to calculate the host−guest interactions in detail.[1] Among them, the Hofmann-diam-type series [Cd(diam)Ni(CN)$_4$]·xG (x = 0.5−2; G = aromatic guest) have the 3D metal complex host structures topologically the same to one another in spite of the variation in the number of methylene units n for the diam $NH_2(CH_2)_nNH_2$ from n = 2 to 9;[2] the two-dimensional (2D) network of [Ni−(CN−Cd$_{1/4}$−)$_4$]$_\infty$ (close-2D network)[3] is successively spanned to adjacent networks at every Cd atom by the one-dimensional (1D) catenation of −[Cd−diam−]$_\infty$ (single-1D catenation). The 3D hosts are built of flat network and vertical diam pillar for n = 2 (Hofmann en- and pn-types). Although the host frameworks are more or less distorted for $n \geq 3$ with puckered networks and slant pillars, the host topology is preserved owing to the aliphatic diam skeleton flexible enough to match the cavity dimensions to the geometry of the guest molecule. The *o*-toluidine clathrates have been obtained for the hosts with

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Table 1. Crystallographic and Experimental Data for **1**−**5**[a]

	1	**2**	**3a**	**3b**	**4**	**5**
formula	$C_{19}H_{21}CdN_7Ni$	$C_{27}H_{33}CdN_9Ni$	$C_{26}H_{32}CdN_8NiO_2$	$C_{29}H_{31}CdN_9Ni$	$C_{40}H_{46}Cd_2N_{16}Ni_2$	$C_{24}H_{26}CdN_8Ni$
fw	518.53	654.72	659.70	676.73	1093.12	597.63
crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/m$ (No. 11)	$P2_1/m$ (No. 11)	$C2/c$ (No. 15)	$C2/c$ (No. 15)
a, Å	6.960(2)	8.149(2)	8.615(3)	8.505(1)	19.820(2)	22.240(1)
b, Å	7.718(2)	9.577(1)	17.568(2)	17.737(1)	7.738(2)	9.254(1)
c, Å	9.693(2)	9.865(2)	9.950(2)	10.106(1)	31.213(1)	16.241(1)
α, deg	90.61(2)	81.03(1)	90	90	90	90
β, deg	91.72(2)	94.08(2)	105.30(2)	102.64(1)	109.138(5)	130.668(3)
γ, deg	90.17(2)	106.08(1)	90	90	90	90
V, Å^3	520.4(2)	730.4(2)	1452.6(5)	1487.5(3)	4522(1)	2545.5(4)
Z	1	1	2	2	4	4
ρ_{obs}, ρ_{calc}, g cm^{-3}	1.64(1), 1.62	1.47(1), 1.49	1.50(1), 1.51	1.50(1), 1.51	1.60(1), 1.63	1.54(1), 1.56
μ(Mo Kα), cm^{-1}	19.46	14.04	14.16	13.81	17.96	16.03
R, R_w	0.0298, 0.0480	0.0490, 0.0567	0.0519, 0.0520	0.0422, 0.0474	0.0480, 0.0508	0.0389, 0.0444

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

n = 3, 4, 5, 6, and 8. Pyrrole, aniline, *o*-toluidine, *N*,*N*-dimethylaniline, and 2,3-xylidine are respectively accommodated in the Hofmann diaminobutane-type (n = 4) host, although the degree of distortion varies compound by compound for the hosts in the same topology.[2,3]

Our aim in this paper is to investigate what inclusion structures are possible for *p*-xylylenediamine [*p*-xda: *p*-$C_6H_4(CH_2NH_2)_2$] in place of the aliphatic diam in the Hofmann diam-type. As a bridging ligand *p*-xda may behave differently from the aliphatic diam with flexible methylene chains owing to its rigid aromatic ring; partial flexibility is allowed for the $-CH_2NH_2$ substituents at *para*-positions favorable for bridging between 2D networks. Eventually we obtained four types of the *p*-xda-bridged host clathrates that differ in the catenation behavior of *p*-xda and $Ni(CN)_4$; one type is topologically the same as the Hofmann diam-type, while the three other types are different. A bis(aniline)cadmium(II) complex involving catenations of *p*-xda and $Ni(CN)_4$ was also obtained. Their single-crystal structures are described in detail to discuss the catenation behavior of the *p*-xda and $Ni(CN)_4$ moieties interacting with each other and with the guests *o*- and *m*-toluidine, hydrated phenol, quinoline, and pyrrole.

Experimental Section

Preparation. The procedure to prepare single crystals was similar to that applied for the Hofmann diam-type clathrates.[2] The pH of the aqueous solution of $CdCl_2$, $K_2[Ni(CN)_4]$, and *p*-xda in a 1:1:2 molar ratio was adjusted to 9.5 by adding citric acid and 2-aminoethanol; in the final solution the concentration of each metal species was adjusted to 0.1 mol dm^{-3}. The aqueous solution covered by the organic phase of relevant guest species was left standing for a few months at room temperature; yellow crystals were obtained.[4] As for the examined organic species as guests, aniline gave an aniline-ligated Cd complex instead of aniline clathrate; from the aqueous phase covered by toluene an onium salt (*p*-$xdaH_2$)$[Ni(CN)_4]$ was obtained.[5]

Their chemical formula, morphology and elemental analyses are as follows. Anal. Found (calcd) for $[Cd(p\text{-xda})Ni(CN)_4]\cdot o\text{-}CH_3C_6H_4NH_2$ (**1**) (block-like): C, 47.5 (44.0); H, 4.37 (4.08); N, 18.1 (18.9). Anal. Found (calcd) for $[Cd(p\text{-xda})_2Ni(CN)_4]\cdot m\text{-}CH_3C_6H_4NH_2$ (**2**) (flaky): C, 47.2 (49.5); H, 5.09 (5.08); N, 18.3 (19.3). Anal. Found (calcd) for $[Cd(p\text{-xda})_2Ni(CN)_4]\cdot C_6H_5OH\cdot H_2O$ (**3a**) (platelike): C, 47.5 (47.3); H, 4.95 (4.89); N, 17.2 (17.0). Anal. Found (calcd) for $[Cd(p\text{-xda})_2Ni(CN)_4]\cdot C_9H_7N$ (**3b**) (platelike): C, 50.8 (51.5); H, 4.59 (4.62); N, 17.9 (18.6). Anal. Found (calcd) for $[Cd_2(p\text{-xda})_3\{Ni(CN)_4\}_2]\cdot 2C_4H_5N$ (**4**) (flaky): C, 43.6 (44.0); H, 4.37 (4.24); N, 20.2 (20.5). Anal. Found (calcd) for $[Cd(C_6H_5NH_2)_2(p\text{-xda})Ni(CN)_4]$ (**5**), (blocklike): C, 44.3 (48.2); H, 4.55 (4.39); N, 18.1 (18.7). Specimens subjected to the analyses appeared to suffer partial decomposition or to be contaminated with unidentified fine powders; finally, the compositions were estimated as above from the results of the single-crystal structure determinations.

Crystallography. The crystallographic and selected experimental data for **1**−**5** are listed in Table 1. Single-crystal X-ray measurements were carried out for epoxy-resin coated specimens at room temperature on a Rigaku AFC-5R four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.709 26 Å) from a rotating Mo anticathode. The cell dimensions were refined using 25 each reflections (25° $\leq 2\theta \leq$ 35°). Three standard reflections were monitored after every 200; no significant decay was observed. *Lp* correction was applied but no extinction; an empirical absorption correction[6] was applied only for **5**.

Positions of Cd and Ni atoms were located from Patterson syntheses. All non-H atoms found in the subsequent Fourier and Fourier-difference syntheses were refined anisotropically through the full-matrix least-squares procedures. H atoms located at calculated positions were not refined further but included in the final F_c calculations except for those of the disordered guest molecules in **1** and **2** and those of the water molecule in **3a**. All calculations were performed using SHELX 76[7] on a HITAC M-680H computer in the Computer Center of the Institute for Molecular Science, Okazaki. Atomic scattering factors were taken from ref 8 for Cd and Ni and from SHELX 76 for C, H, N, and O.

Results and Discussion

ORTEP[9] views of the structures are shown in Figures 1 and 2 for **1** and **2**, Figure 3 for **3a** and **3b**, Figure 4 for **4**, and Figure 5 for **5** with atomic notations. Selected interatomic distances and angles are summarized in Table 2 for **1**−**5**.

Structure of *o*-Toluidine Clathrate 1. As shown in Figure 1, the topology of the host framework is the same to that of the Hofmann diam-type: the 3D framework is constructed of puckered close-2D networks of $[Ni-(CN-Cd_{1/4}-)_4]_\infty$ and *p*-xda pillars between the networks. According to our classification,[3b] this structure may be called the Hofmann *p*-xda-type. The unit cell dimensions and contents, the puckered close-2D network,

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(4) Reproducible results were obtained for the crystals grown from 5 to 10 aliquots of each compound in preliminary crystallographic observations on the diffractometer.

(5) The salt of the composition (*p*-$xdaH_2$)$[Ni(CN)_4]$ (**6**) determined by the elemental analyses gave the crystal data as follows: $C_{12}H_{14}N_6Ni$ = 300.98, triclinic, $P\bar{1}$, a = 7.392(3) Å, b = 7.921(2) Å, c = 6.247(1) Å, α = 90.89(2)°, β = 101.49(2)°, γ = 70.92(2)°, Z = 1, R = 0.039 for 2792 reflections. Further details of the crystallographic data of **6** compound of discrete (*p*-$xdaH_2$)$^{2+}$ and $[Ni(CN)_4]^{2-}$ have been included in Supporting Information. Although the following species were examined as probable guests, no suitable crystals for the X-ray structure analysis were obtained: C_6H_6, $C_6H_5CH_3$, $C_6H_4(CH_3)_2$ isomers, C_6H_5X (X = F, Cl, Br), C_6H_5OH, $C_6H_5CH(CH_3)OH$, $C_6H_5NO_2$, *p*-$CH_3C_6H_4NH_2$, $C_6H_3(CH_3)_2NH_2$ isomers, $C_6H_5CH{=}CHC_6H_5$, *n*-C_xH_{2x+2} (x = 5−7), and *n*-$C_xH_{2x+1}OH$ (x = 1−5).

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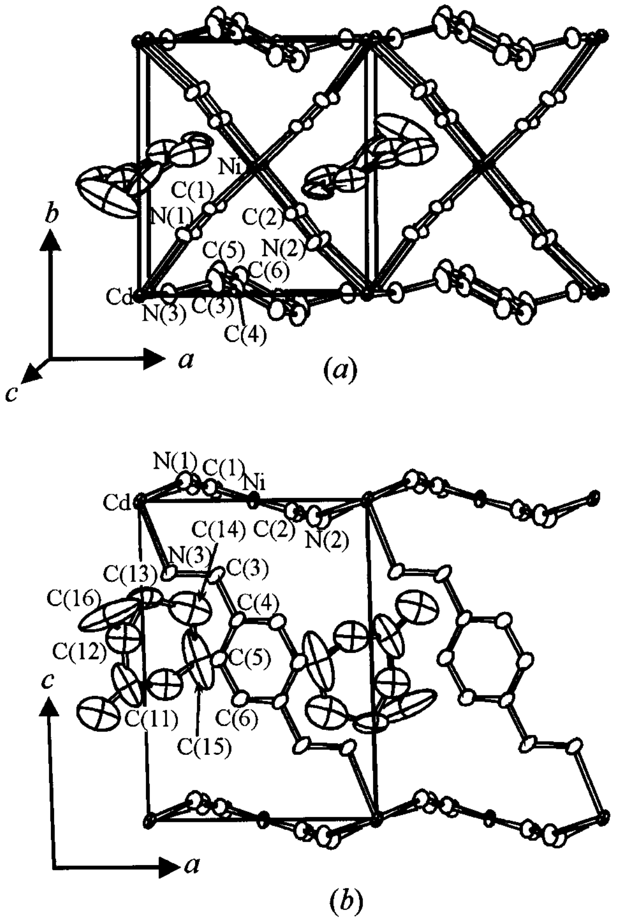

Figure 1. Structure of **1** showing 30% probability thermal ellipsoids: (a) projection to the (001) plane and (b) projection along the *b* axis. The guest *o*-$CH_3C_6H_4NH_2$ molecule in disorder is shown for each of the orientations distributed statistically about the inversion center 0, $^1/_2$, $^1/_2$ (see text).

the slant single-1D pillar, and the disordered guest are all similar to those observed for the Hofmann diaminohexane- (dahxn-) type *o*-$CH_3C_6H_4NH_2$ clathrate (the space group *P*2/*m*),[2c] but **1** ($P\bar{1}$) has no mirror symmetries. Although each skeleton of the guest *o*-$CH_3C_6H_4NH_2$ and the dahxn pillar are on the mirror plane in the Hofmann dahxn-type, both aromatic rings of the guest and the *p*-xda in **1** are arranged alternately with a dihedral angle of 56.0° in the interlayer space similarly to the C_6H_6 molecules in the Hofmann type $[Cd(NH_3)_2Ni(CN)_4]\cdot 2C_6H_6$.[3] The *o*-$CH_3C_6H_4NH_2$ molecule is in disorder with extremely large thermal ellipsoids. The observed peaks of electronic density have been tentatively assigned to a couple of the orientations, though the molecular shape is much distorted, distributed with an equal probability about the inversion center at 0, $^1/_2$, $^1/_2$, on which the center of gravity of the molecule is approximately located. C(12) and C(14) are shared by the couple; discrimination between methyl-C and amino-N was impossible.

Structure of *m*-Toluidine Clathrate 2. The close-2D network of $[Ni{-}(CN{-}Cd_{1/4}{-})_4]_\infty$ in **1** is broken into 1D chains in **2** leaving the CN groups at the *trans* positions of the Ni(CN)$_4$ moiety unbridged. The resulting 1D chain $-[(trans\text{-})\text{-}NC{-}Ni(CN)_2{-}CN{-}Cd\text{-}]_\infty$ (*trans*-1D) runs along the [110] direction of the unit cell (Figure 2). The *trans*-1D catenation has been found in a number of ethylenediamine (1,2-diaminoethane: en) complexes: $[Ni(en)_2Pd(CN)_4]$,[10] $[M(en)_2Ni(CN)_4]$ (M = Ni, Cu, and Zn),[11] and $[M(en)_2Ni(CN)_4]\cdot 2C_6H_5NH_2$ (M = Ni, Cu, Zn, and Cd).[12] The *p*-xda ligands bridge in pair between the Cd atoms of the adjacent *trans*-1D chains along

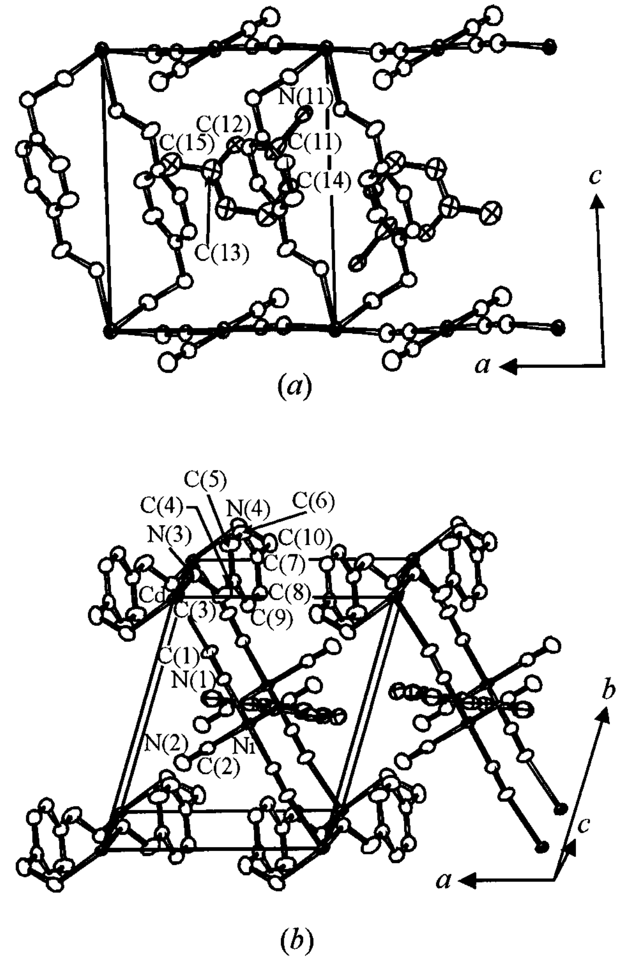

Figure 2. Structure of **2** showing 30% probability thermal ellipsoids: (a) projection to the (010) plane and (b) perspective view of the unit cell along the *c* axis. The guest *m*-$CH_3C_6H_4NH_2$ is shown for each of the orientations distributed statistically about the inversion center $^1/_2$, $^1/_2$, $^1/_2$ (see text).

the *c* axis successively with their aromatic planes in parallel to each other within the pair and between the pairs. The catenation structure of $\rangle[Cd\langle(p\text{-xda})\rangle]_\infty$ may be called double-1D. In the double ligation of the *p*-xda ligands at every Cd, one NH_2 ligates from the apical direction and the other from the equatorial; the $Cd{-}NH_2{-}CH_2$ angle is more distorted for the latter in the *gauche* form than the former in the *trans* form with respect to the N−C bond. This ligation mode makes the aromatic planes overlap along the *a* axis in such a way that the ipso-C of one ring locates on the center of the other like the stacking mode in graphite; however, the interplane distances approximated to *a*/2 (>4 Å) are greater than the van der Waals contact.

Hydrogen bonds are suggested between the unbridged CN in the *trans*-1D Ni(CN)$_4$ and the NH_2 group of the *p*-xda: N(2)···N(3) 3.362(9) Å, N(2)···H(1) 2.47 Å, N(2)···H(1)-N(3) 148.5°; N(2)···N(4) 3.093(10) Å, N(2)···H(12) 2.10 Å, N(2)···H(12)-N(4) 170.6°. The guest *m*-$CH_3C_6H_4NH_2$ molecule is observed in such a disorder in the cavity that a couple of the molecules are distributed with an equal probability at the two positions related by the inversion center $^1/_2$, $^1/_2$, $^1/_2$, which is located at the middle point between C(13) and its equivalent,

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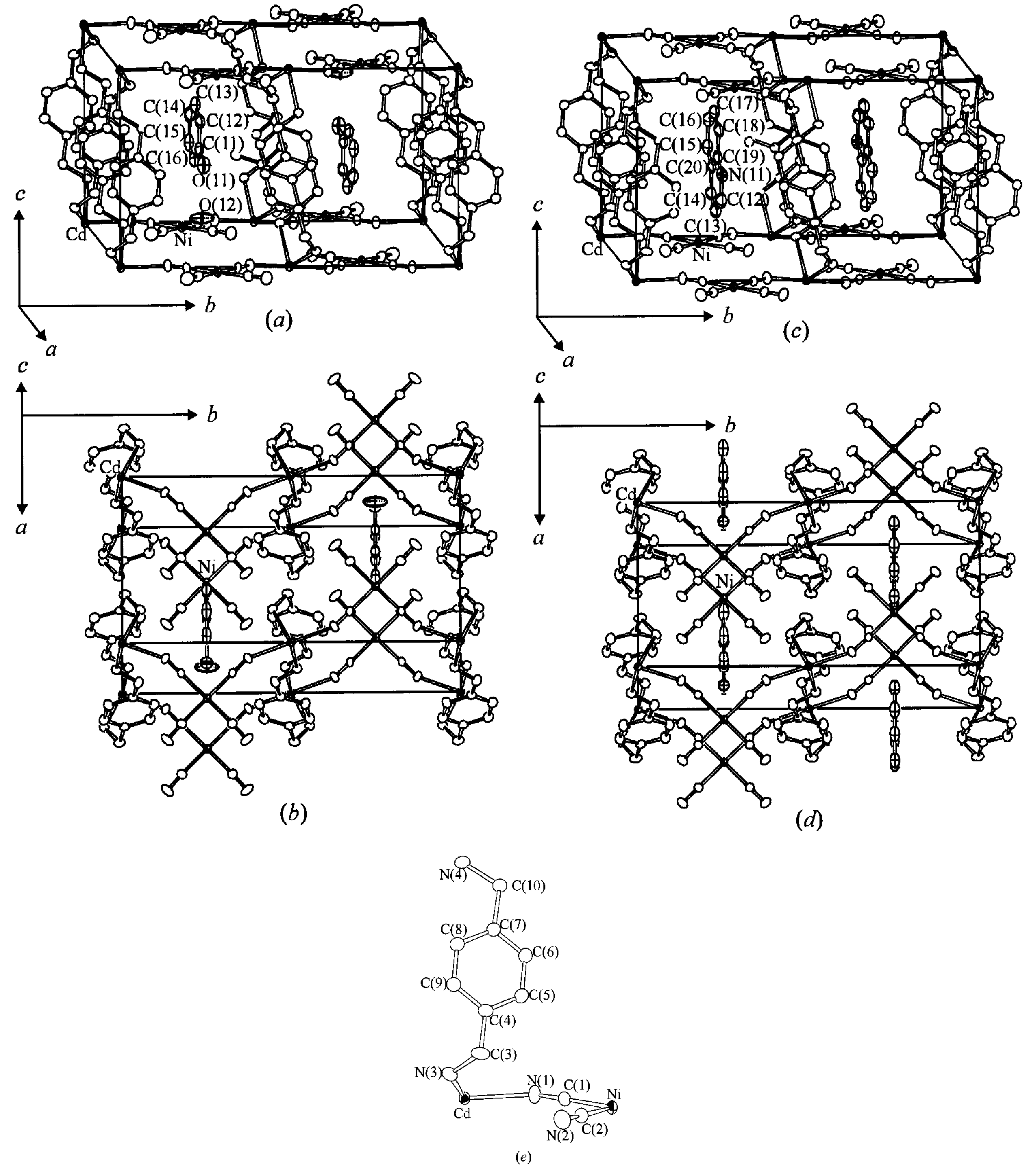

Figure 3. Structures of **3a** and **3b** showing 30% probability thermal ellipsoids: (a and c) perspective views of the unit cells for **3a** and **3b**, respectively; (b and d) projections to the (001) planes for **3a** and **3b** respectively; (e) the asymmetric unit of the host moiety.

both being shared by the couple; C(15) is in a full occupation as the methyl-C of one orientation and as the 5-C of the other. In each of the orientations, the NH_2 group is hydrogen-bonded to an unbridged CN in the host network with the distance of 3.141(12) Å for N(11)···N(2) with the N(11)−H···N(2) angle of 130.7° and H···N(2) distance of 2.40 Å supposed for the H atom at N(11) taking an sp^3 configuration with an N(11)−H distance of 1.00 Å. The aromatic plane is almost perpendicular to those of the *p*-xda ligands.

Structures of Hydrated Phenol and Quinoline Clathrates 3a and 3b. In contrast with **2**, breaking of the close-2D network is brought about at *cis* positions of $Ni(CN)_4$ in **3a** and **3b** (Figure 3). In the $-[(cis\text{-})NC-Ni(CN)_2-CN-Cd-]_\infty$ chain (*cis*-1D) running along the *b* axis, the $Ni(CN)_4$ moieties are arranged in *trans* positions with respect to the octahedral Cd; the catenation mode may be called *trans*-(*cis*-1D). The *p*-xda ligands participate in the double-1D catenation along the *c* axis as well as those in **2**. These features are in common for **3a** and **3b** and are similar in topology to those of the host structure of $[Cd(danon)_2Ni(CN)_4]\cdot 2[2,3\text{-}(CH_3)_2C_6H_3NH_2]$.[13a] The topologically two-dimensional host is reinforced by the hydrogen bonds between the unbridged CN in one network and the NH_2 groups of *p*-xda in the other: 3.079(9) and 3.027(7) Å for N(2)···N(3), 2.09 and 2.03 Å for N(2)···H(1), and 172.5 and 177.9° for N(2)···H(1)−N(3) and 3.207(8) and 3.273(6) Å

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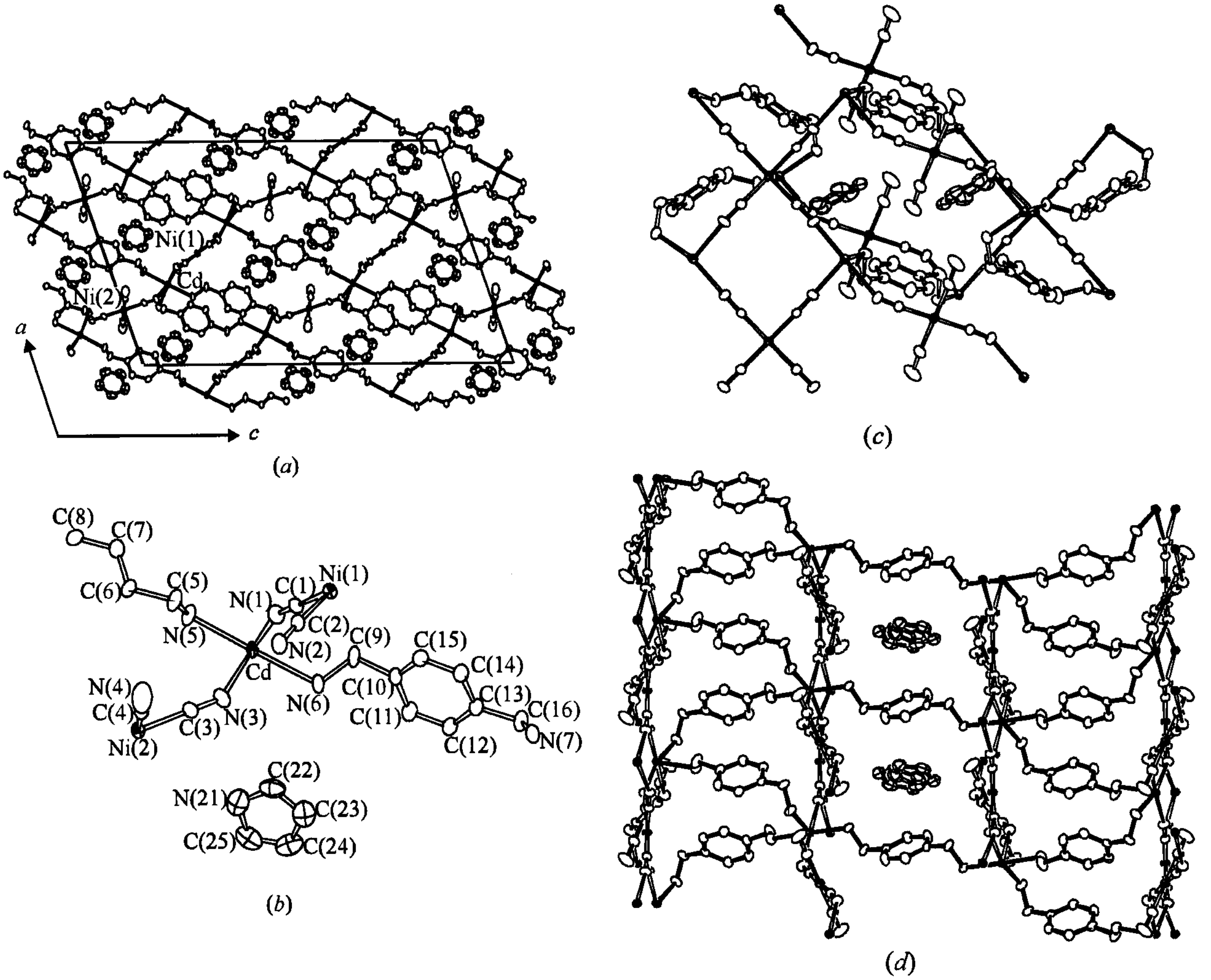

Figure 4. Structure of **4** showing 30% probability thermal ellipsoids: (a) projection along the *b* axis; (b) the asymmetric unit; (c) the cavity accommodating a couple of pyrrole molecules; and (d) the 2D network of trifurcate Cd−*p*-xda catenation (with solid bonds) along the (101) plane.

for N(2)···N(4), 2.22 and 2.39 Å for N(2)···H(14), and 170.5 and 167.6° for N(2)···H(14)−N(4) in **3a** and **3b**, respectively. The guest molecules on the mirror planes at $y = {}^1/_4$ and ${}^3/_4$ are enclathrated in the cavity similar to that in **2**. The phenol molecule in **3a**, smaller than the quinoline in **3b**, is accompanied by the hydrogen-bonded H_2O [2.725(15) Å for O(11)···O(12), 1.77 Å for O(12)···H(13), and 169.8° for O(11)−H(13)···O(12)] to preserve the effective volume comparable to that of the latter.

Structure of Pyrrole Clathrate 4. The linking behavior of the $Ni(CN)_4$ entity in **4** is similar to that of $[\{Cd(en)\}_2(en)\{Ni(CN)_4\}_2]\cdot 4C_6H_5OH$.[12a] The host structure involves two kinds of bridging $Ni(CN)_4$ moieties centered by Ni(1) on the twofold axis along the *b* direction and Ni(2) on the inversion center (${}^1/_4$, ${}^3/_4$, 0 and equivalents) (Figure 4a). Ni(1) moieties extend a double-1D meshed chain[3b,14] of $\rangle[Ni\langle(CN{-}Cd{-}NC{-})_2\rangle]_\infty$ along the *b* direction by linking the Cd atoms; the N(2) moiety, behaving as a *trans*-μ-NC−Ni(CN)$_2$−CN ligand, spans the parallel-running double-1D chains at every Cd. The connection between the double-1D meshed chains and the *trans*-μ bridges extends a 2D network along the $(40\bar{4})$ plane. Every Cd atom in the network is connected to three other Cd atoms in adjacent networks, one on one side and two on the other, through three *p*-xda bridges, to extend a 2D network of trifurcate extension $-[p\text{-xda}{-}Cd\langle(p\text{-xda}{-}Cd{-})_2]_\infty$ (Figure 4d). Eventually, a complex 3D host lattice is built up by the mutual crossing between the metal cyanide layers and the *p*-xda-bridged networks.

The guest pyrrole molecules in pair are accommodated in the cavity surrounded by the *p*-xda ligands at the sides, the Ni(1) and Ni(2) moieties at the top and bottom and vice versa (Figure 4c). The unbridged CN in Ni(2) moiety appears to form a hydrogen bond with the NH_2 of the *p*-xda in a *trans* conformation: 3.111(9) Å for N(4)···N(5), 2.29 Å for N(4)···H(1), and 139.0° for N(4)···H(1) − N(5) (Figure 4b).

Structure of Aniline Complex 5. The 3D structure of complex **5** has close relations to the above-mentioned host structures in the catenation behavior of the $Ni(CN)_4$ and *p*-xda (Figure 5). The *trans*-(*cis*-1D) chains of $-[(cis\text{-})NC{-}Ni(CN)_2{-}CN{-}Cd{-}]_2$ run along the *c* axis at $x = 0$ and ${}^1/_2$ in parallel to each other with the same orientation. The single-1D $-[Cd{-}p\text{-xda}{-}]_\infty$ chains span the *trans*-(*cis*-1D) chains by sharing the Cd atoms along the [110] direction at $z = 0$ and the $[1\bar{1}0]$ direction at $z = {}^1/_2$ to give the 3D framework. The void space among the chains is filled up by the aniline molecules ligating to the Cd atom at *trans* positions. The unbridged CN participates in the hydrogen bonds with the NH_2 groups of *p*-xda and the aniline: 3.162(6) and 2.967(8) Å for N(2)···N(3) and N(2)···N(11), 1.97 and 2.22 Å for N(2)···H(2) and N(2)···H(8), and 156.6 and 172.3° for N(2)···H(2)−N(3) and N(2)···H(8)−N(11), respectively.

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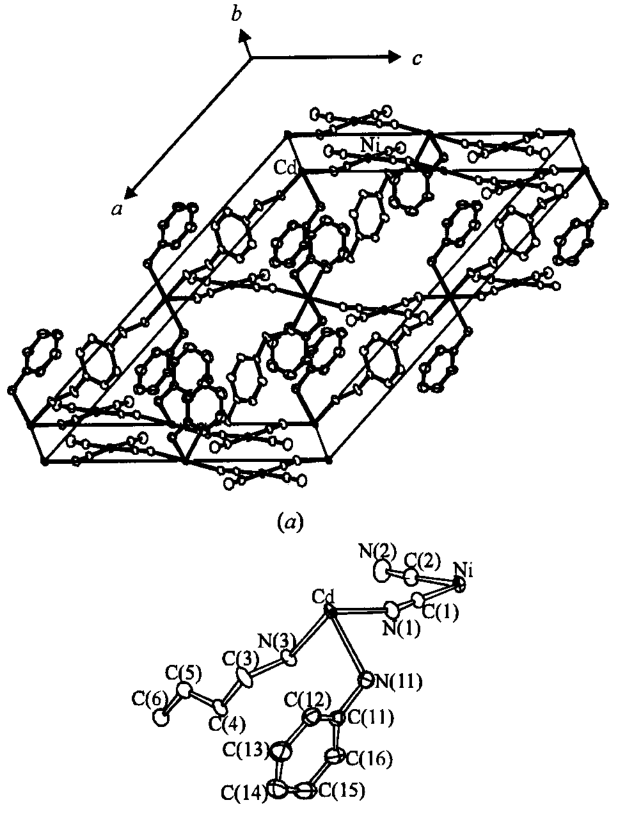

(*a*)

(*b*)

Figure 5. Structure of **5** showing 30% probability thermal ellipsoids: (a) perspective view of the unit cell and (b) the asymmetric unit. In part the a, single-1D Cd−*p*-xda catenation is shown with solid bonds.

Table 2. Selected Interatomic Distances (Å) and Angles (deg)[a]

(i) [Cd(*p*-xda)Ni(CN)$_4$]·*o*-CH$_3$C$_6$H$_4$NH$_2$ (**1**)			
Ni−C(1)	1.863(3)	Cd−N(3)	2.357(3)
Ni−C(2)	1.849(3)	C(1)−N(1)	1.137(4)
Cd−N(1)	2.350(3)	C(2)−N(2)	1.142(4)
Cd−N(2^{I})	2.319(3)		
C(1)−Ni−C(2)	88.6(1)	Ni−C(1)−N(1)	176.8(3)
N(1)−Cd−N(2^{I})	86.6(1)	Ni−C(2)−N(2)	178.4(3)
N(1)−Cd−N(3)	90.2(1)	Cd−N(1)−C(1)	153.4(3)
N(2^{I})−Cd−N(3)	93.0(1)	Cd−N(2^{I})−C(2^{I})	157.0(3)
(ii) [Cd(*p*-xda)$_2$Ni(CN)$_4$]·*m*-CH$_3$C$_6$H$_4$NH$_2$ (**2**)			
Ni−C(1)	1.868(5)	C(1)−N(1)	1.132(7)
Ni−C(2)	1.876(7)	C(2)−N(2)	1.137(8)
Cd−N(1)	2.373(5)	N(2)···N(3^{III})	3.362(9)
Cd−N(3)	2.399(5)	N(2)···N(4^{IV})	3.093(10)
Cd−N(4^{II})	2.352(5)	N(2)···N(11^{V})	3.141(12)
C(1)−Ni−C(2)	90.1(2)	Ni−C(1)−N(1)	178.8(6)
N(1)−Cd−N(3)	94.0(2)	Ni−C(2)−N(2)	179.2(6)
N(1)−Cd−N(4^{II})	93.8(2)	Cd−N(1)−C(1)	171.6(5)
N(3)−Cd−N(4^{II})	86.3(2)		
(iii) [Cd(*p*-xda)$_2$Ni(CN)$_4$]·C$_6$H$_5$OH·H$_2$O (**3a**)			
Ni−C(1)	1.862(6)	C(1)−N(1)	1.124(7)
Ni−C(2)	1.864(7)	C(2)−N(2)	1.138(8)
Cd−N(1)	2.403(5)	N(2)···N(3^{VI})	3.079(9)
Cd−N(3)	2.337(5)	N(2)···N(4^{VII})	3.207(8)
Cd−N(4^{II})	2.374(5)		
C(1)−Ni−C(2)	89.6(3)	Ni−C(1)−N(1)	179.3(5)
N(1)−Cd−N(3)	93.6(2)	Ni−C(2)−N(2)	177.4(7)
N(1)−Cd−N(4^{II})	92.0(2)	Cd−N(1)−C(1)	156.3(5)
N(3)−Cd−N(4^{II})	87.4(2)		
(iv) [Cd(*p*-xda)$_2$Ni(CN)$_4$]·C$_9$H$_7$N (**3b**)			
Ni−C(1)	1.859(4)	C(1)−N(1)	1.141(5)
Ni−C(2)	1.869(5)	C(2)−N(2)	1.146(6)
Cd−N(1)	2.368(4)	N(2)···N(3^{VI})	3.027(7)
Cd−N(3)	2.331(3)	N(2)···N(4^{VII})	3.273(6)
Cd−N(4^{II})	2.383(3)		
C(1)−Ni−C(2)	88.3(2)	Ni−C(1)−N(1)	177.1(4)
N(1)−Cd−N(3)	94.8(1)	Ni−C(2)−N(2)	178.5(5)
N(1)−Cd−N(4^{II})	94.4(1)	Cd−N(1)−C(1)	156.4(4)
N(3)−Cd−N(4^{II})	88.6(1)		
(v) [Cd$_2$(*p*-xda)$_3${Ni(CN)$_4$}$_2$]·2C$_4$H$_5$N (**4**)			
Ni(1)−C(1)	1.856(6)	cd−N(7^{VIII})	2.367(5)
Ni(1)−C(2)	1.855(6)	C(1)−N(1)	1.140(7)
Ni(2)−C(3)	1.854(6)	C(2)−N(2)	1.143(7)
Ni(2)−C(4)	1.860(7)	C(3)−N(3)	1.137(7)
Cd−N(1)	2.347(5)	C(4)−N(4)	1.136(9)
Cd−N(2^{III})	2.311(5)	N(4^{III})···N(5)	3.111(9)
Cd−N(3)	2.410(6)	N(4^{VIII})···N(7)	3.313(12)
Cd−N(5)	2.329(5)	N(4^{IX})···N(21)	3.592(15)
Cd−N(6)	2.385(5)	N(7^{VIII})···N(21)	3.588(12)
C(1)−Ni(1)−C(2)	91.1(2)	N(3)−Cd−N(6)	91.3(2)
C(3)−Ni(2)−C(4)	92.1(3)	N(3)−Cd−N(7^{VIII})	80.6(2)
N(1)−Cd−N(2^{III})	95.0(2)	N(5)−Cd−N(6)	177.6(2)
N(1)−Cd−N(3)	84.9(2)	N(5)−Cd−N(7^{VIII})	92.6(2)
N(1)−Cd−N(5)	94.5(2)	N(6)−Cd−N(7^{VIII})	89.6(2)
N(1)−Cd−N(6)	83.2(2)	Ni(1)−C(1)−N(1)	177.9(5)
N(1)−Cd−N(7^{VIII})	163.7(2)	Ni(1)−C(2)−N(2)	176.8(6)
N(2^{III})−Cd−N(3)	177.8(2)	Ni(2)−C(3)−N(3)	175.5(6)
N(2^{III})−Cd−N(5)	89.5(2)	Ni(2)−C(4)−N(4)	176.0(8)
N(2^{III})−Cd−N(6)	90.8(2)	Cd−N(1)−C(1)	160.8(5)
N(2^{III})−Cd−N(7^{VIII})	99.7(2)	Cd−N(2^{III})−C(2^{III})	170.5(5)
N(3)−Cd−N(5)	88.3(2)	Cd−N(3)−C(3)	141.2(6)
(vi) [Cd(C$_6$H$_5$NH$_2$)$_2$(*p*-xda)Ni(CN)$_4$] (**5**)			
Ni−C(1)	1.855(4)	C(1)−N(1)	1.144(5)
Ni−C(2)	1.860(5)	C(2)−N(2)	1.141(6)
Cd−N(1)	2.315(4)	N(2)···N(3^{X})	3.162(6)
Cd−N(3)	2.354(3)	N(2)···N(11^{XI})	2.967(8)
Cd−N(11)	2.455(4)		
C(1)−Ni−C(2)	90.3(2)	Ni−C(1)−N(1)	178.1(4)
N(1)−Cd−N(3)	89.8(1)	NI−C(2)−N(2)	177.4(5)
N(1)−Cd−N(11)	86.2(1)	Cd−N(1)−C(1)	164.3(4)
N(3)−Cd−N(11)	90.3(1)	Cd−N(3)−C(3)	115.2(3)

[a] Symmetry operations. (I) $x-1, y, z$; (II) $x, y, z-1$; (III) $x, y-1, z$; (IV) $x, y-1, z-1$; (V) $x+1, y, z$; (VI) $1-x, -y, -z$; (VII) $1-x, -y, 1-z$; (VIII) $^1/_2-x, y-{}^1/_2, {}^1/_2-z$; (IX) $^1/_2-x, {}^3/_2-y, -z$; (X) $-x, 1-y -z$; (XI) $x, y+1, z$; (XII) $-x, 1-y, 1-z$; (XIII) $x, y, z+1$.

Comparison of the Structures. In all of the present structures the Ni(CN)$_4$ entity is little distorted from regular square-planar configuration: the greatest deviation in the C−Ni−C angle from 90° is 2.1° in Ni(2) of **4**, with the greatest difference in the Ni−C distances being 0.014 Å in **1**. The Ni(CN)$_4$ keeps its structural rigidity as a cross member, although the catenation modes are different as close-2D in **1** and double-1D in **4** using the four linking sites in full, and *trans*-1D in **2**, *cis*-1D in **3a**, **3b**, and **5**, and *trans*-μ ligand in **4** using two of the four sites. Such rigidity has been observed in common for the Ni(CN)$_4$ entity involved in the Hofmann type and related multidimensional structures.[2,3]

As for probable $\pi-\pi$ interactions no direct stacking between the aromatic rings of *p*-xda and guest has been observed for these structures.

The variations in the composition and the structure among the four types of the clathrates and the aniline-ligated complex can be interpreted in terms of the rigidity of the square-planar Ni(CN)$_4$ and the *p*-xda skeleton, and the structural features of the respective guest molecules. As for the toluidine isomers in **1** and **2**, the *o*-isomer in **1** with an orientationally-averaged disklike shape is accommodated in the cavity comparable with that of the Hofmann dahxn-type. Since the guest is disordered to a high extent, there should be no strong host−guest interactions between the NH$_2$ groups of the *o*-CH$_3$C$_6$H$_4$NH$_2$ and the *p*-xda: hydrogen bond formation of the NH$_2$ in the guest may be hindered sterically by the CH$_3$ group at the *ortho* position. However, the guest *m*-CH$_3$C$_6$H$_4$NH$_2$ in **2** is favorable for hydrogen bond formation with the host moieties, the NH$_2$ of *p*-xda, and unbridged CN, so that the close-2D network breaks into the *trans*-1D chains, leaving two N ends of Ni(CN)$_4$ free from coordination. The less slant double-1D catenation of *p*-xda makes the *c* dimension elongate slightly to adjust the interlayer distance to the longer molecular axis of *m*-CH$_3$C$_6$H$_4$NH$_2$ than *o*-$CH_3C_6H_4NH_2$. Since the guest locates on one of the statistically distributed positions shifted from the cavity center to unbridged CN at either top or bottom side, the packing in the expanded cavity is rather loose. However, either position is equally favorable for hydrogen-bond formation between the NH_2 group and the unbridged CN, which may stabilize the crystal structure.

Further elongation of the interlayer distance than that in **2** is necessary for the hydrated phenol and quinoline guests in **3a** and **3b**: the *trans*-(*cis*-1D) array of $-[\{(cis\text{-})NC-Ni(CN)_2-CN-\}-Cd-]_\infty$ increases the allowance for the guests along the *c* direction in comparison with the *trans*-1D array in **2**.

On the other hand, the smaller pyrrole guest induces the complicated but more compact host structure of **4**. The hydrogen bonds among the host moieties may contribute to the compact packing; the calculated density is the highest among the present five clathrates.

The aniline molecule in the *p*-xda-bridged host appears to be intermediate in size and function. It would be too small for a clathrate structure like **2**, **3a**, and **3b** but too large for that like **4** as a guest; the NH_2 group is not so weak a Lewis base in ligating to Cd unlike *o*- and *m*-toluidine. The structure of complex **5**, not a clathrate, is compared with that of $[Cd(p\text{-}CH_3C_6H_4NH_2)_2(dahxn)Ni(CN)_4]$,[2d,f,h] in which the $Ni(CN)_4$ participates in *trans*-1D catenation and dahxn in single-1D to give a 2D network structure in contrast with the *trans*-(*cis*-1D) array and crossing of the single-1D catenation in **5** to give the 3D lattice.

Concluding Remarks

In the not too short history of chemical architecture using cyanometalates as the main building blocks, a number of attempts to use complementary bridging or chelating ligand have been applied to modify the multidimensional structures in combination with octahedral Cd and square-planar $Ni(CN)_4$ as well as tetrahedral $Cd(CN)_4$, linear $Ag(CN)_2$, and $Ag_2(CN)_3$.[2,15] In comparison with rigid bridging ligands such as pyrazine and 4,4′-bipyridine, though both were applied for $Cd-[Ag(CN)_2]_2$ systems to materialize interpenetrating 3D frameworks,[15a] *p*-xda has shown a characteristic feature due to its partial flexibility at the $-CH_2-NH_2-Cd$ joint in the present structures; configuration about the C−N bond in the $-CH_2-NH_2-Cd$ moieties on both sides is *trans*−*trans* in **1**, *trans*−*gauche* in **2**−**4**, and *trans*−*trans* in **5**. On the other hand, the $Ni(CN)_4$ moiety is rigid in structure approximated to a cross member with a donating N at every end, but flexible in utilizing which ends for linking. The rigidity and the flexibility are counterbalanced for both *p*-xda and $Ni(CN)_4$ in the present structures. With this respect the hydrogen bond formation between the NH_2 and unbridged N of $Ni(CN)_4$ appears to play the role of a prop in building up the 2D and 3D structures with the $Ni(CN)_4$ moiety unsaturated in bridging through a coordination bond.

Supporting Information Available: X-ray structural information for **1**−**5**, and for $(p\text{-}xdaH_2)[Ni(CN)_4]$ (**6**), including tables of atomic coordinates, crystallographic data, thermal parameters, interatomic distances, and bond angles (25 pages). Ordering information is given on any current masthead page.

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