Orientation of Guest Benzene Molecules in Hofmann-Type and Related Clathrates by Molecular Mechanics Calculation

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Abstract. Molecular mechanics calculations were carried out to interpret the observed orientational angle of the benzene molecule enclathrated in the Hofmann-type $M(NH_3)_2Ni(CN)_4 \cdot 2\,C_6H_6$ (M = Mn, Ni, Cu, and Cd), Hofmann-en-type $Cd(en)Ni(CN)_4 \cdot 2\,C_6H_6$ (en = $NH_2CH_2CH_2NH_2$), and Hofmann-mea-type(2) $Cd(mea)Ni(CN)_4 \cdot 2\,C_6H_6$ (mea = $NH_2CH_2CH_2OH$) clathrates using the van der Waals potential functions in Molecular Mechanics Version 2. The angle is most influenced by the guest-to-guest contact in the interlayer space between the two-dimensional *catena*-[metal(II) tetra-μ-cyanonickelate(II)] networks for the Hofmann-type series. The discrepancy between the calculated and the observed angles in each crystal structure was at largest 3.5°; the structures of $Cd(NH_3)_2Ni(CN)_4 \cdot 2\,C_6H_6$ and $Cd(en)Ni(CN)_4 \cdot 2\,C_6H_6$ have been revised using new data collected by counter-methods.

Key words. Molecular mechanics, Hofmann-type clathrate, benzene, guest orientation.

1. Introduction

The layered structure of Hofmann-type clathrates $M(NH_3)_2M'(CN)_4 \cdot 2\,G$ is comprised of the alternate stacking of two-dimensionally extended *catena*-[metal(M) tetra-μ-cyanometallate(M')] network and the layer of guest G molecules (see Figure 1). The network is planar in all the tetragonal crystal structures so far determined for the benzene clathrates (G = C_6H_6) with the M = Mn [1], Ni [2], Cu [3], and Cd [4]. A similar planar network has also been observed in the Hofmann-en-type [5] and Hofmann-mea-type(2) [6] benzene clathrates, Cd(en or mea)$Ni(CN)_4 \cdot 2\,C_6H_6$ (en = $NH_2CH_2CH_2NH_2$; mea = $NH_2CH_2CH_2OH$), which are derived by replacement of the ammine ligands in the Hofmann-type by the bridging en and mea ligand, respectively. When the ammine or amine ligand protruding from the network up and down at the M(II) metal is distributed statistically about the fourfold axis of the tetragonal system, the stacking of the network itself gives the space group $P4/mmm$ assuming that the M(II)—N—C—M'(II) linkage is linear in the network. In the earliest structure analysis of Hofmann's benzene clathrate $Ni(NH_3)_2Ni(CN)_4 \cdot 2\,C_6H_6$ by Rayner and Powell [2], however, the $P4/m$ space

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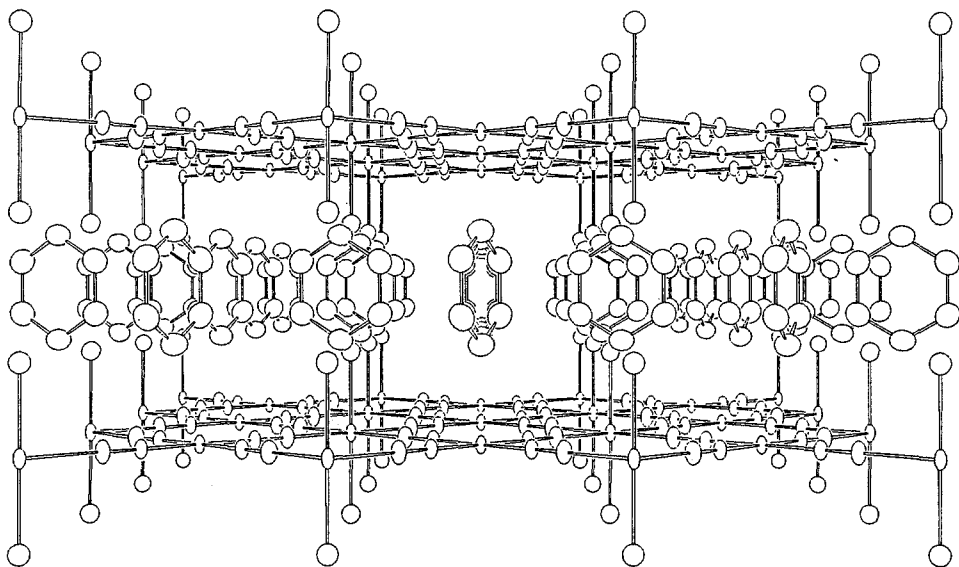
Fig. 1. A perspective view of the Hofmann-type benzene clathrate $M(NH_3)_2M'(CN)_4 \cdot 2\ C_6H_6$; hydrogen atoms are omitted. In the Hofmann-en-type or Hofmann-mea-type benzene clathrate, an en or mea ligand spans adjacent layers in place of a pair of the ammine ligands confronting each other in the interlayer space.

group was adopted due to the aromatic plane of the benzene molecule being inclined to (100) with an angle of 65.9°; hydrogen atoms of the NH_3 coordinating to the Ni atom along the crystal c-axis were neglected. If the angle were 90°, the space group should have been $P4/mmm$. The inclined orientation of the benzene molecule was also reported for the other three Hofmann-type benzene clathrates, and for the Hofmann-en-type one [5], whereas the $P4/mmm$ space group was adopted for the Hofmann-mea-type(2) assuming the statistical distribution of the mea ligand about the fourfold axis and the mirror plane vertical to the c axis [6].

Generally the greater angle of inclination has been observed for the longer crystal a-dimension in the known crystal structures of the Hofmann-type clathrates. However, no definite relationship has been observed between the values of the angle and the a-dimension. At any rate, the angle should be the consequence of the crystal packing dominated by the host–guest and guest–guest interactions. In order to evaluate the interaction energies, i.e., to reason about the variation of inclination angle, we carried out molecular mechanics calculations for those Hofmann-type and related benzene clathrates whose crystal structures are known. For the Hofmann-type $Cd(NH_3)_2Ni(CN)_4 \cdot 2\ C_6H_6$ and the Hofmann-en-type $Cd(en)Ni(CN)_4 \cdot 2\ C_6H_6$ the structures have been revised based on new intensity data collected by counter methods; the previous structure determinations were based on the photographic data. The calculated values of the inclination angles showed good agreement with those observed in the crystal structures.

2. Experimental

2.1. CRYSTAL DATA

The data in the literature were used for $Mn(NH_3)_2Ni(CN)_4 \cdot 2\,C_6H_6$, **I** [1], $Ni(NH_3)_2Ni(CN)_4 \cdot 2\,C_6H_6$, **II** [2], $Cu(NH_3)_2Ni(CN)_4 \cdot 2\,C_6H_6$, **III** [3], $Cd(en)Ni(CN)_4 \cdot 2\,C_6H_6$, **V**, and $Cd(mea)Ni(CN)_4 \cdot 2\,C_6H_6$, **VI** [6]. The revised data were used for $Cd(NH_3)_2Ni(CN)_4 \cdot 2\,C_6H_6$, **IV** (see Appendix). These data are listed in Table I along with the previous ones for **IV** and **V**; the results of the calculations are also included in this table. All the hydrogen atoms were placed at calculated positions. In Figure 2 the structure is illustrated along with the definition of the inclination angle θ.

2.2. CALCULATIONS

For a guest benzene molecule arbitrarily chosen in the crystal structure, each of the atoms constituting the guest molecule (guest-atom) is seen to interact with the atoms constituting the host moieties and those constituting other guest molecules located within an 8 Å distance from the center of gravity of the chosen guest molecule. The sum of the van der Waals energies, $E(\theta) = \Sigma\,E_{ik}$, is calculated at each inclination angle $\theta + 1°$ intervals in the range from $0°$ to $180°$ under the conditions to satisfy the symmetry of the $P4/m$ space group. The value giving the minimum of $E(\theta)$ is read as the calculated inclination angle θ_c.

All the calculations were carried out on the HITAC M680H system at the Computation Center of the University of Tokyo; the parameters necessary for the calculations were cited in the library program Y4/TC/MM2 edited by Ōsawa [7]

(a)   (b)
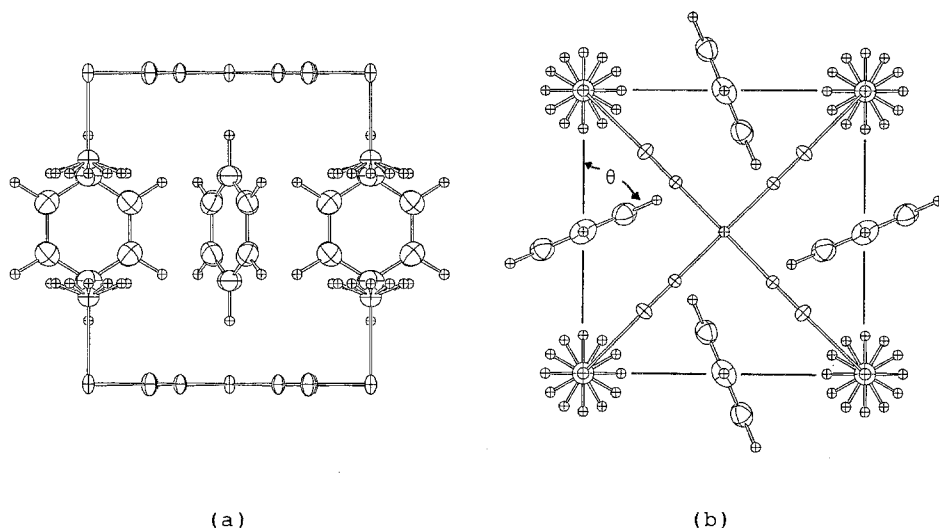
Fig. 2.   Structure of $Cd(NH_3)_2Ni(CN)_4 \cdot 2\,C_6H_6$, **IV**. (a) Projection along a axis; (b) projection along c axis. Hydrogen atoms of the benzene molecule are located at the calculated positions with the C—H distance of 1.08 Å; those of the ammine ligand, being located based on the structure of the ammonia molecule (N—H: 1.011 Å; H—N—H: 106.7°), are distributed about the fourfold c axis.

Table I. Crystal data and θ_c angles for $M(L)Ni(CN)_4 \cdot 2 C_6H_6$

M	Mn I	Ni II	Cu III	Cd IV	Cd V	Cd VI
L	$(NH_3)_{3/2}$	$(NH_3)_2$	$(NH_3)_2$	$(NH_3)_2$	en	mea
space group	P4/m	P4/m	P4/mcc	$P4/m[P4/m]^a$	P4/mmm[4/m]	P4/mmm
a/Å	7.432(6)	7.242(7)	7.345(3)	7.542(2)[7.575(6)]	7.657(1)[7.675(3)]	7.592(1)
c/Å	8.335(5)	8.277(8)	16.519(4)	8.308(4)[8.317(5)]	8.013(2)[8.056(10)]	8.094(1)
θ_x/°	65.5	65.9	64.3	66.5[66.7]	90[85]	90
	66.9					
θ_c/°	68	66	66	70[70]	90^b	90
M—N(am)/Å^c	2.27(1)	2.08(6)	2.05(2)	2.325(8)	2.253(9)	2.31(1)
M—N(CN)/Å	2.243(6)	2.15(14)	2.20(1)	2.334(4)	2.399(2)	2.346(4)
C—N(CN)/Å	1.141(8)	1.20(22)	1.12(2)	1.140(6)	1.147(3)	1.158(5)
Ni—C/Å	1.871(5)	1.78(7)	1.88(1)	1.859(4)	1.868(2)	1.865(4)

a Those reported previously are shown in brackets.
b Calculated value based on the P4/m space group.
c The distance between M and N of ammine or amine ligand.

based on the original Molecular Mechanics Version 2 (MM2) by Allinger [8]. A working program was written in FORTRAN for the calculation of the potential function. The potential function E_{ik} due to the interaction between atoms i and k was selected from MM2 as follows:

$$E_{ik} = EPS^*[2.9 \times 10^5 \exp(-12.5/P) - 2.25P^6] \quad \text{when} \quad P < 3.311, \quad \text{or}$$

$$E_{ik} = 336.176EPS^* \times P^2 \quad \text{when} \quad P > 3.311,$$

where $EPS^* = [EPS(i) \times EPS(k)]^{1/2}$ ($EPS(i)$ and $EPS(k)$ are the hardness of atoms i and k, respectively), and $P = [R(i) + R(k)]/R$ ($R(i)$ and $R(k)$ are van der Waals radii of atoms i and k, and R is the distance between atoms i and k, respectively). The values of $R(i)$ and $EPS(i)$ used were as follows: for C(sp^3) 1.900 Å and 0.184 kJ mol^{-1}; for C(sp^2) 1.940 Å and 0.184 kJ mol^{-1}; for H(C—H) 1.500 Å and 0.197 kJ mol^{-1}; for H(N—H) 1.325 Å and 0.142 kJ mol^{-1}; for N 1.820 Å and 0.197 kJ mol^{-1}.

The conditions applied are as follows: (i) the interactions between the guest-atom and the metal atoms in the host were neglected, because no data on potentials were available for those between the metal atoms concerned and the C or H atoms; (ii) the effective range was limited within the 8 Å distance, because no significant improvement had been observed in the tentative results of calculations within the 10, 12, 14 and 16 Å ranges; and (iii) each atom of the ammine (H of NH$_3$), en (N and H of NH$_2$, and H of CH$_2$), and mea (N and H of NH$_2$, H of CH$_2$, and O and H of OH) ligands at the general positions was distributed statistically with 0.25 each probability about the fourfold axis in order to satisfy the requirements from the $P4/m$ or $P4/mmm$ space group. In the case of III, the requirements from the $P4/mcc$ space group were taken into account; in the case of V the $P4/m$ space group was applied for the calculation.

3. Results and Discussion

The results are shown as $E(\theta) - \theta$ curves for the four Hofmann-type benzene clathrates I–IV in Figure 3(a), and for the Hofmann-en-type, V, and Hofmann-mea-type(2), VI, in Figure 3(b). As listed in Table I, the calculated θ_c values agreed with the observed θ_x values in the respective crystal structures: the largest discrepancy, 3.5°, was seen for IV. In the case of V, the calculation based on the $P4/m$ space group, which had been adopted in the previous structure refinement, gave the minimum at $\theta = 90°$, a value which means the space group should be $P4/mmm$. The structure refinement revised in this work gave better convergence for the $P4/mmm$ space group than for the $P4/m$, as described in the Appendix. It is a matter of course that the $P4/mmm$ space group predicts the benzene molecule to take the orientation of $\theta = 90°$ in V and VI.

Among the terms comprising $E(\theta)$ the angle-sensitive ones are those related to the neighboring benzene molecules in the same interlayer space. The sensitivity to angle θ is negligible for the terms related to the host atoms (see Figure 4). As shown in Figures 1 and 2, the guest benzene molecule is surrounded by six neighboring benzene molecules, and four ammine ligands in I–IV, or two en or mea ligands in V and VI, in the interlayer space extending along the crystal ab-plane. Since the van
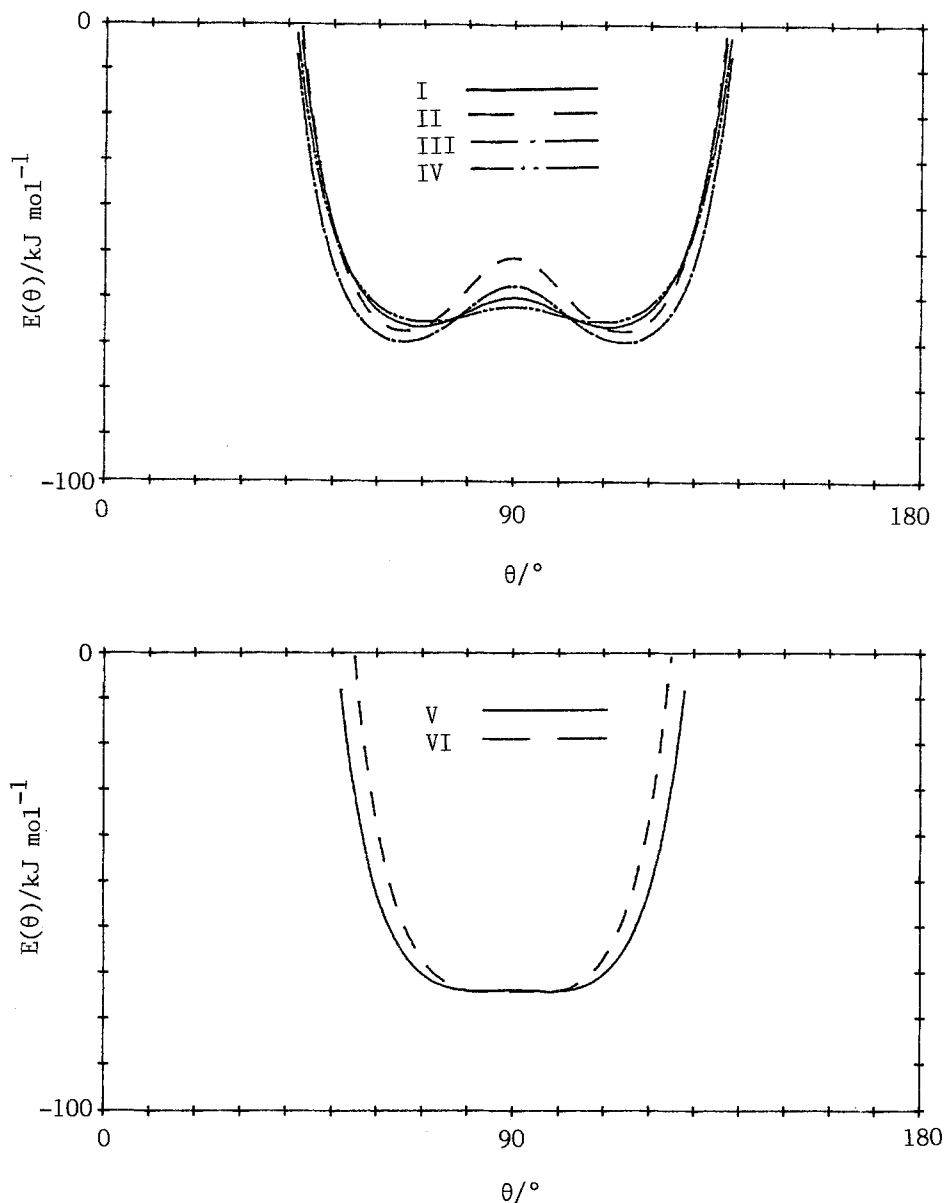
Fig. 3. Calculated $E(\theta) - \theta$ curves for Hofmann-type benzene clathrates I–IV (top) and for Hofmann-en-type V and Hofmann-mea(2)-type VI (bottom).

der Waals radius of the methylene group is greater than that of the ammine or amino group, the packing in the crystal structure makes the a-dimension greater for V (7.657(1) Å) and VI (7.592(1) Å) than for I–IV (from 7.242(7) Å for II to 7.542(2) Å for IV). Apparently the greater calculated angle, i.e. the less inclined angle, was given to I–IV with the greater a-dimension; the angle was 90° for V and VI. As for I–IV the coordination structure of the M(II) is influential on the a-dimension: the smaller ionic radius of M^{2+} gives the smaller a-dimension.
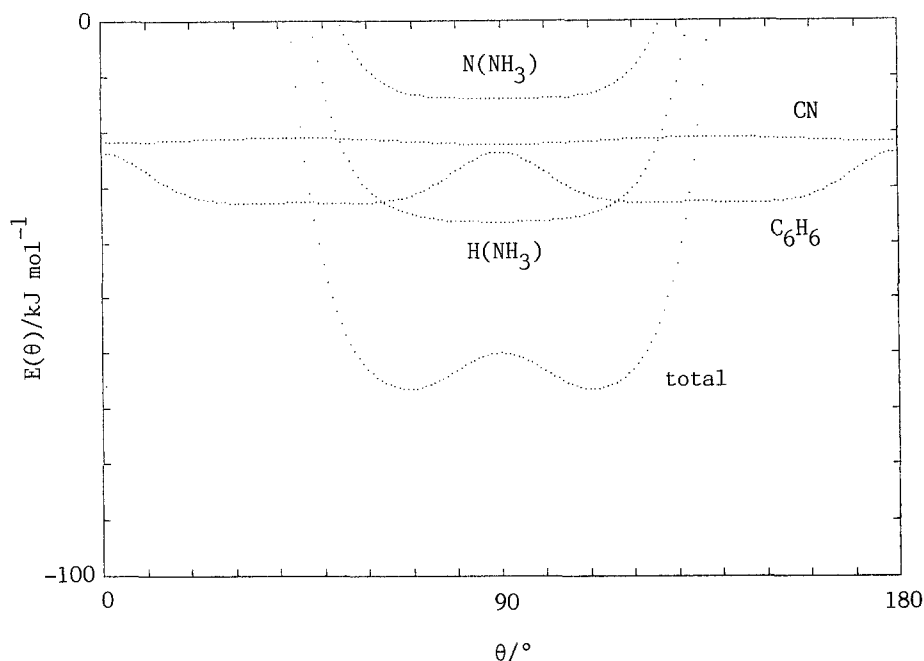
Fig. 4.   Respective contributions from C_6H_6, H of NH_3, N of NH_3, and CN exemplified for **I**.

Another factor is the $M(II)-N(NH_3)$ distance: the longer distance may cause the greater repulsion between the guest benzene molecule and the ammine ligand. Owing to the Jahn–Teller effect on the copper(II) ion in **III**, the compressed CuN_6 octahedron has a $Cu-N(NH_3)$ distance of 2.05(2) Å which is shorter by 0.15 Å than the equatorial $Cu-N(CN)$ 2.20(1) Å distance; such a compressed structure is also seen for the NiN_6 octahedron in **II**. In comparison with these two structures, the octahedron in **IV** is little distorted and that in **I** is elongated. In summary, the shorter the $M-N(NH_3)$ bond distance, the smaller the calculated angle is given; the observed angles obey this tendency, too.

With respect to the layers of guest benzene molecules, **III** differs from the others in the manner of stacking: the layers are stacked alternately with the inclination angle of 64.3° and of $115.7(=180-64.3)°$ to give the $P4/mcc$ space group and the doubled c-dimension [3]. The potential function calculated for **III** by applying the $P4/mcc$ space group showed the minimum deeper than those for the other Hofmann-type clathrates with the $P4/m$ space group. The distance between the adjacent layers, which is equivalent to half of the c-dimension for **III** and to the c-dimension for the others, is the shortest for **III** among **I** through **IV**. Although the interlayer interaction should become larger due to the shorter interlayer distance, it is not the case for **I** with the longest c-dimension. In the structure refinement of **I** [1], the reflection intensities sensitive to the inclination angle were closely examined to lead to the conclusion that there is a local alternate array of the layers of benzene molecules with the inclination angles 65.5° and $113.1(=180-66.9)°$, but that the stacking of the arrays is at random. Thus, the interlayer distance appears not to be closely related to the interactions between adjacent layers of guest molecules.

A molecular orbital calculation has been done for the Hofmann-type clathrate to interpret the inclination angle of the guest molecule in terms of hydrogen-bonding between π-electrons of the benzene molecule and hydrogen atoms of the ammine ligands, and between π-electrons of cyanide groups and hydrogen atoms of the benzene molecule [9]; the hydrogen-bonding has been discussed in the infrared and NMR spectroscopic investigations [10–12]. With regard to the hydrogen bond between the π-electrons and the protons of the ammine or amine ligands, the bond distance is longer in the clathrate of the greater a-dimension: the contribution of the hydrogen bond should be less in **V** and **VI** than in **I–IV**. In the present work, only the van der Waals interactions were applied using the rather simple model and potential function. It would be precarious to extract any quantitative conclusion about the absolute value of the inclination angle and to refer to the way of the stacking. Our conclusion is that the inclination angles can be interpreted in terms of the van der Waals interactions to the first approximation. The interactions appear to be most influenced by the coordination structure of the six-coordinate metal M involved with the ammine or amine ligands and the N-terminal of the square-planar $Ni(CN)_4$ moieties, although the difference of M in the crystal structure was not directly taken into account in the energy calculations for the Hofmann-type clathrates.

4. Appendix

The structures of **IV** and **V** were refined by the heavy-atom method using the intensity data collected on a Rigaku AFC-6A four-circle automated diffractometer. The structure of **IV** has been revised to the conventional $R = 0.047$ using 817

Table II. Revised atomic parameters for **IV** and **V**

atom	x/a	y/b	z/c	$B_{eq}/Å^{2a}$
IV: $Cd(NH_3)_2Ni(CN)_4 \cdot 2\,C_6H_6$				
Cd	0	0	0	2.01(1)
Ni	0.5	0.5	0	1.83(2)
C1(CN)	0.3268(5)	0.3246(5)	0	2.3(1)
N1(CN)	0.2202(5)	0.2175(5)	0	3.2(2)
N2(NH_3)	0	0	0.2798(9)	4.0(2)
C2(C_6H_6)	0	0.5	0.3334(9)	5.5(4)
C3(C_6H_6)	0.1440(9)	0.4374(7)	0.4164(7)	5.6(3)
V: $Cd(en)Ni(CN)_4 \cdot 2\,C_6H_6$				
Cd	0	0	0	1.93(1)
Ni	0.5	0.5	0	2.22(2)
C1(CN)	0.3275(4)	0.3275(4)	0	2.72(9)
N1(CN)	0.2216(4)	0.2216(4)	0	3.5(1)
N2(en)	0.069(1)	0	0.273(1)	3.7(4)
C2(en)	0	0	0.413(1)	7.7(3)
C3(C_6H_6)	0.5	0	0.3283(7)	4.8(4)
C4(C_6H_6)	0.5	0.1513(8)	0.4131(6)	6.0(3)

^{a} $B_{eq} = 4(\Sigma_i \Sigma_j B_{ij} a_i a_j)/3$.

reflections; in the previous work [4] 356 reflections were used to $R = 0.118$. The revised results showed no significant difference from those obtained previously except a slight contraction of the a-dimension.

The structure of **V** with the space group $P4/mmm$ has been revised to $R = 0.041$ using 577 reflections, the number which corresponds to 898 for the $P4/m$ space group; in the previous work [5] 619 reflections were used to $R = 0.089$. The Laue group $4/mmm$ of **V** was ascertained to support the $P4/mmm$ space group from the distribution of intensities for 552 reflections in all directions within the range of 2θ from 20° to 30°. The refinement assuming the $P4/m$ space group gave results ($R = 0.046$) essentially similar to those adopting the $P4/mmm$ space group.

The refined atomic coordinates and the equivalent isotropic thermal parameters are listed in Table II. Tables of the experimental conditions, anisotropic thermal parameters, and structure factors have been deposited. Of course, the precision of each parameter has been remarkably improved.

Acknowledgement

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