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Thermoanalytical Investigation of the Guest-Release Process in Aromatic-Guest Clathrates of Three-Dimensional Metal Complex Hosts

TAKAFUMI KITAZAWA, YORIKO MIZUSHIMA, JUNKO SHIRAHA, RYOKO TAGUCHI, AKEMI KATOH, TAI HASEGAWA, SHIN-ICHI NISHIKIORI, and TOSCHITAKE IWAMOTO*

Department of Chemistry, College of Arts and Sciences, the University of Tokyo, Komaba, Meguro, Tokyo 153, Japan

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Abstract. The guest-release process was investigated in terms of the activation energy evaluated by thermogravimetry for the en-Td-type clathrates *catena*-[*catena*-μ-(ethylenediamine)cadmium(II) tetra-μ-cyanocadmate(II) or -mercurate(II)]-benzene(1/2), -benzene-d_6(1/2), and -pyrrole(1/2), the Hofmann-en-type clathrates *catena*-[*catena*-μ-(ethylenediamine)cadmium(II) tetra-μ-cyanonickelate(II)]-benzene (1/2) and -pyrrole(1/2), the Hofmann-pn-type clathrate *catena*-[*catena*-μ-(*dl*- or *l*-propylenediamine (cadmium(II) tetra-μ-cyanonickelate(II)]-pyrrole(2/3), and the pn-Td-type clathrates *catena*-[*catena*-μ-(*dl*-propylenediamine) or -(*l*-propylenediamine)cadmium(II) tetra-μ-cyanocadmate(II)]-benzene(2/3). Values of the activation energy are correlated with the structural change in the metal complex host accompanied by the release of the guest molecules. The crystal structure of *catena*-[ethylenediamine-cadmium tetra-μ-cyanonickelate(II)], the residual host of the Hofmann-en-type, has been analyzed to elucidate the correlation.

Key words. activation energy, benzene, cadmium complex, crystal structure, ethylenediamine, guest-release process, propylenediamine, pyrrole, tetracyanocadmate, tetracyanomercurate, tetracyanonickelate, thermal analysis

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1. Introduction

Among the Hofmann-type related clathrates [1] the en-Td-type clathrates *catena*-[*catena*-μ-(ethylenediamine)cadmium(II) tetra-μ-cyanocadmate(II)]-benzene(1/2) and *catena*-[ethylenediaminecadmium(II) tetra-μ-cyanocadmate(II)] are the pair for which the crystal structures of both the clathrate and the residual host left after the release of the guest molecules have been determined [2]. Although the thermally induced guest-release reaction is described simply as

$$\mathrm{Cd(en)Cd(CN)_4 \cdot 2C_6H_6 \xrightarrow{\Delta} Cd(en)Cd(CN)_4 + 2\,C_6H_6},$$

a remarkable change occurs in the metal complex host structure. The *catena*-μ-en (en = ethylenediamine) ligand of the three-dimensional host in the clathrate phase

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* Author for correspondence.

turns to a chelating ligand in the residual host phase, in which the three-dimensional structure is built up only of the ambidentate cyano ligands, which link the tetrahedral tetracyanocadmate to the en-chelated six-coordinate cadmium atom to one another. A number of dissociation-recombination and reorientation processes should be involved in giving the residual host structure from the clathrate phase, as has been discussed in the previous paper [2].

In this paper the guest-release process is investigated in terms of activation energy for the en-Td-type $Cd(en)M(CN)_4 \cdot 2G$ ($M = Cd$ or Hg; $G = C_4H_5N$, C_6H_6, or C_6D_6), the Hofmann-en-type $Cd(en)Ni(CN)_4 \cdot 2G$ ($G = C_6H_6$, C_4H_5N), the Hofmann-pn-type Cd(*dl*- or *l*-pn)$Ni(CN)_4 \cdot 1.5\, C_4H_5N$, and the pn-Td-type Cd(*dl*-pn or *l*-pn)$Cd(CN)_4 \cdot 1.5\, C_6H_6$ clathrates. The values of the activation energy, estimated by the analysis of thermogravimetric curves, are interpreted in terms of the structural change in the host metal complex accompanied by the release of the guest molecules. The crystal structure of $Cd(en)Ni(CN)_4$, being isostructural to the residual host of the Hofmann-en-type, is also described.

2. Experimental

2.1. PREPARATION

The clathrates subjected to the thermal analyses were prepared as fine crystals by the methods already reported [3–5]. The products were identified by elemental analyses, infrared spectroscopy, and powder x-ray diffractometry.

2.2. THERMOANALYTICAL MEASUREMENT

A Seiko Electronics SSC560GH thermoanalytical instrument was used to record TG (thermogravimetric), DTG (derivative thermogravimetric), and DTA (differential thermal analysis) curves at heating rates ranging from 40 to 1 K min^{-1} with appropriate intervals. In each run a *ca.* 10 mg sample specimen was loaded on an open aluminium pan of 6 mm inner diameter, 1 mm depth, and 20 mg mass [6]; an empty pan was used as the reference; the atmosphere was ambient air-flow regulated at a flow rate of 250 $cm^3\,min^{-1}$ by an oilless rotary pump. After ascertaining that the endothermic guest–release reaction occurs in a single step without release or decomposition of the diamine ligand, the TG curves recorded with the respective heating rates were analyzed by the Doyle–Ozawa method [7, 8] in order to determine the activation energy.

Doyle's p-function used was the approximation of Eq. (1),

$$p[y] = \exp(-y) \cdot y^{-2} \tag{1}$$

where $y = E/RT$ and E is the activation energy given by the Arrhenius equation (2)

$$dx/dt = A\exp(-E/RT) \cdot (1-x)^n \tag{2}$$

The values of E_x were obtained from the slopes of $\log(T_i^2/r_i)$ vs. T_i^{-1} plots determined by the least-squares procedures for the respective x values from 0.20 to 0.80 with a 0.10 interval according to Eq. (3):

$$p[E_x/RT_i]/r_i = \text{constant} \tag{3}$$

where T_i is the temperature at which the reaction proceeds to the stage of x with the given heating rate r_i. The final E value was estimated as the weighted average:

$$E = \sum E_x \sigma(E_x)^{-2} / \sum \sigma(E_x)^{-2} \tag{4}$$

where $\sigma(E_x)$ is the standard deviation for each E_x value.

The reaction order n ($n = 0$ or 1 in the present cases) was estimated from the linearity in the plots of the reduced time θ, defined as $\theta = (E/rR)/p[y]$, vs. x (for $n = 0$) or $-\ln(1-x)$ (for $n = 1$).

3. Results and Discussion

3.1. GENERAL

In Table I the values of activation energy and rate order of the reactions are listed; Figure 1 shows a typical example of a $\log(T^2/r)$ vs. T^{-1} plot. Zeroth-order reactions are observed for the en-Td type and Hofmann-en-type, whereas the reactions are first-order for the Hofmann-pn-type. The extremely large values of the activation energy for the pn-Td-type should not be compared with the values for the others, as mentioned later. The values for the en-Td-type are almost independent of the guest and the central metal atom of the tetrahedral tetracyanometalate; no significant isotope effect has been observed between the en-Td-type normal benzene clathrates and the deuterated benzene clathrates. The activation energies for the Hofmann-en-type and the Hofmann-pn-type appear to depend on the guest species, pyrrole or benzene, and the host moiety, *dl*-pn or *l*-pn, respectively. These tendencies are interpreted in terms of the change in the metal complex structure accompanied by the release of the guest molecule from the clathrate.

Before discussion of the respective values, it should be noted that the absolute values themselves do not have any definitive thermodynamical significance. The values depend on the sampling, the state of the sample, the apparatus used, and the

Table I. Activation energy, *E*, and reaction order, *n*, for the guest-release process of *catena*-[*catena*-μ-(ethylenediamine or -propylenediamine)cadmium tetra-μ-cyanometalate]-(aromatic guest)(1/2 or 2/3) clathrates.

type	clathrate	E/kJ mol^{-1}	n
en-Td	$Cd(en)Cd(CN)_4 \cdot 2\,C_6H_6$	88.5(0.3)	0
	$Cd(en)Cd(CN)_4 \cdot 2\,C_6D_6$	87.2(0.5)	0
	$Cd(en)Hg(CN)_4 \cdot 2\,C_6H_6$	87.3(0.6)	0
	$Cd(en)Hg(CN)_4 \cdot 2\,C_6D_6$	90.4(2.3)	0
	$Cd(en)Cd(CN)_4 \cdot 2\,C_4H_5N$	86.8(0.5)	0
Hofmann-en	$Cd(en)Ni(CN)_4 \cdot 2\,C_6H_6$	66.0(2.5)	0
	$Cd(en)Ni(CN)_4 \cdot 2\,C_4H_5N$	72.6(0.8)	0
Hofmann-pn	$Cd(dl\text{-pn})Ni(CN)_4 \cdot 1.5\,C_4H_5N$	95.0(0.6)	1
	$Cd(l\text{-pn})Ni(CN)_4 \cdot 1.5\,C_4H_5N$	91.6(1.2)	1
pn-Td	$Cd(dl\text{-pn})Cd(CN)_4 \cdot 1.5\,C_6H_6$	221(3)?	
	$Cd(l\text{-pn})Cd(CN)_4 \cdot 1.5\,C_6H_6$	127(5)?	

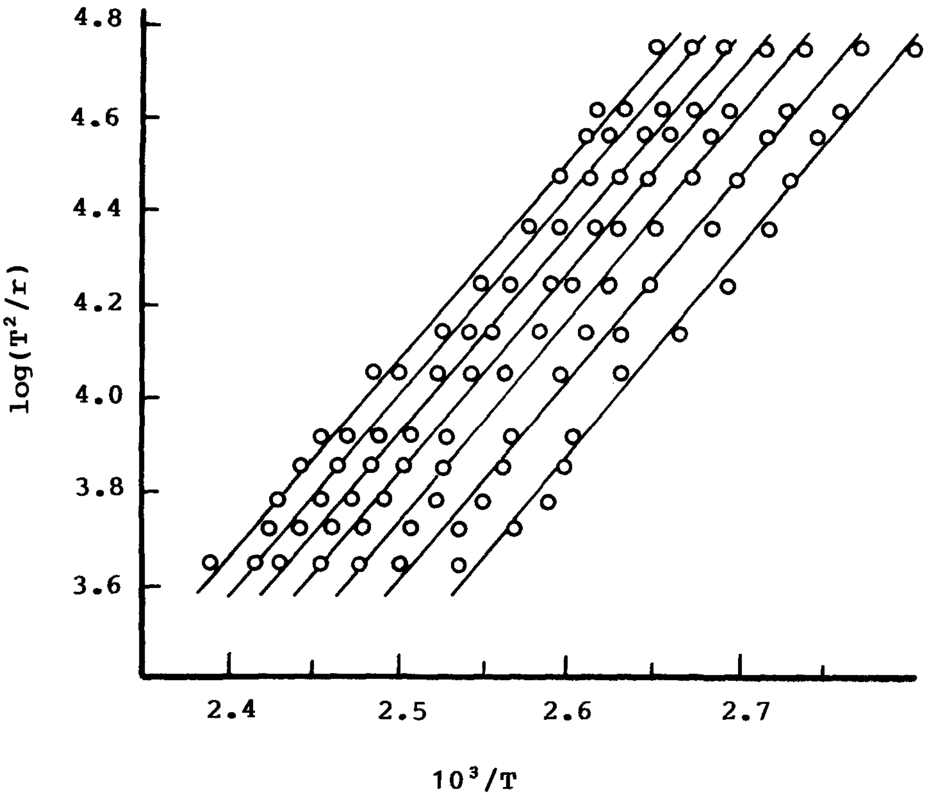

Fig. 1. Log(T^2/r) vs. T^{-1} plots for $Cd(en)Cd(CN)_4 \cdot 2\,C_6D_6$. The plots for $x = 0.2$ through 0.8 at intervals of 0.1 run from left to right.

method of data analysis, at least. Our data reported here have been obtained under experimental conditions maintained as similar as possible to one another. Hence, only relative comparison is significant under the given conditions.

3.2. RELATIVE COMPARISON

In the en-Td-type, release of the guest molecule brings about not only the change in the ligation behavior of the en from bridging to chelating but also the rearrangement of the coordination spheres about the six-coordinate (en-chelated) cadmium and the tetracyanometallate moiety after dissociation-recombination processes about the N-terminals of the $M(CN)_4$ moiety. These processes are most influential on the values of the activation energy which are similar to one another and independent of the host and the guest species, although the rate-determining step of the zeroth-order guest-release reactions should be the diffusion of the guest molecules at the surface of the microcrystalline clathrate phase.

The en-ligation also changes from bridging to chelating when the guests are released from the Hofmann-en-type clathrates. As mentioned in the Appendix, the dissociation-recombination processes occuring in the host complex are not as complicated as those in the en-Td-type. The smaller values of the activation energy in general for the Hofmann-en-type compared with the en-Td-type, and the difference in the values between the pyrrole and the benzene clathrates suggest that the activation energy can be correlated with the diffusion process at the surface in the Hofmann-en-type rather than the structural change occurring in the host metal complex. The polar pyrrole molecule may interact with the surface more strongly than the non-polar benzene molecule so that the activation energy is higher for the pyrrole clathrate than for the benzene clathrate.

In the Hofmann-pn-type, the difference in E is significantly large between the *dl*-pn-host and the *l*-pn-host pyrrole clathrates. The guest-release reaction of the Hofmann-pn-type is first-order compared with the zeroth-order for the other types. As has been demonstrated in the crystal structures [5], the bridging pn ligand, either racemic or enantiomeric, is in a random distribution with regard to the position of the methyl group, the molecular orientation, and in the case of racemic-pn, to the relative arrangement of the respective enantiomers. Assuming that the bridging pn turns to the chelating form in the residual host as well as the cases for the en-Td-type and the Hofmann-en-type, the path from the clathrate phase to the residual host should be more complicated than those in the en-Td-type and the Hofmann-en-type. The second assumption is that the residual host has an ordered arrangement of the chelating pn ligands. The random distribution of each enatiomer in the *dl*-pn host may be converted into such an ordered one in the residual metal complex that the respective enantiomers are arranged with a certain regularity like those observed for usual *dl*-pn-chelated complexes. The path for the *l*-pn host is less complicated due to the absence of the step to discriminate enantiomers as compared to the *dl*-pn host. Thus the difference in E can be interpreted in terms of the difference in the conversion processes between the *dl*-pn-host and the *l*-pn-host clathrate.

The guest-release process in the pn-Td-type is accompanied by melting of the specimens: the *dl*-pn-host benzene clathrate melts at 145–152°C and the *l*-pn-host at 143–149°C. Under visual observations, the liquefied clathrates generated bubbles of benzene vapor, and solidified again after the guest-release process finished [9]. The melting might have been overlooked, if one had subjected the solid specimen to a TG run and observed only the solid product after the run. Thus, the extremely large E values for the pn-Td-type, and the difference between the *dl*-pn-host and *l*-pn-host benzene clathrates, do not reflect the guest-release process only. The values, however, are listed in Table I in order to exemplify a pitfall which one may encounter in the thermal analysis of solid compounds. This melting of the pn-Td-type is unusual among the Hofmann-type and related clathrates, although the melting behavior has not yet been investigated thoroughly. No melting phenomena occur at the guest-release processes for the other three types of clathrates discussed here.

It should be finally noted that the Hofmann-type clathrates $Cd(NH_3)_2M'(CN)_4 \cdot 2\,C_6H_6$ ($M' = Ni$ or Pd) release the guests in two consecutive steps, whereas other Hofmann-type benzene clathrates $M(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$ ($M = Ni$ or Cu) do so in a single step with an activation energy of 66–68 kJ mol^{-1}. The value for the former group is 71–76 kJ mol^{-1} for each of the two steps, considerably higher than the value for the other systems [10]. Although the residual hosts are assumed to have layered structures not very different from those of the clathrate phase, the thermally induced guest-release process appears to be very dependent on the six-coordinate M metal in the Hofmann-type. Unfortunately, since the six-coordinate metal has been limited only to Cd in the present en- or pn-bridged host clathrates, it is impossible to discuss the effects of different metals, M, for the present series.

4. Structure Determination of Cd(en)Ni(CN)$_4$

Crystals of Cd(en)Ni(CN)$_4$ were obtained by the following procedure: into 80 mL of H_2O 1.82 g of $CdCl_2 \cdot 2.5\,H_2O$ and 2.08 g of $K_2[Ni(CN)_4] \cdot H_2O$ were added; white turbidity, once formed, disappeared by adding 8 mL of 2-hydroxyethylamine. To the clear solution 0.5 mL of ethylenediamine hydrate was added and the pH was adjusted at 9.7 by adding citric acid. The resulting solution was filtered through a plastic membrane (Millipore type HA 0.45 μm) and allowed to stand for a few days in a refrigerator. The infrared spectrum and powder X-ray diffraction pattern of the product coincided with those observed for the residual host Cd(en)Ni(CN)$_4$: the powder pattern of the residual host was consistent with the crystal data.

A single crystal of 0.3 × 0.2 × 0.15 mm dimensions was used for the refinement of the lattice constants and the collection of reflection data on a Rigaku AFC-6A diffractometer. Crystal data are: $Cd(NH_2CH_2CH_2NH_2)Ni(CN)_4$, *F.W.* = 335.27, orthorhombic, *Pbna* (No. 60), $a = 10.198(3)$, $b = 11.229(2)$, $c = 9.038(2)$ Å, $U = 1035.0(5)$ Å, $Z = 4$, $D_m = 2.11$ g cm^{-3}; $D_x = 2.15$ g cm^{-3}; ambient temperature, graphite-monochromated Mo Kα radiation ($\lambda = 0.70926$ Å), $\mu = 38.5$ cm^{-1}, $2\theta - \omega$ scan with scan width $1.30 + 0.5 \tan\theta$, scan range $2° < 2\theta < 65°$, $0 \leqslant h \leqslant 15$, $0 \leqslant k \leqslant 16$, $0 \leqslant l \leqslant 13$, Lp-corrected; 4279 observed reflections, 1221 reflections used ($I > 3\sigma(I)$), heavy-atom method to refine 74 parameters by block-diagonal least-squares procedure, $R = 0.043$, $R_w = 0.042$, $S = 1.405$; weighting scheme: $w =$

Table II. Atomic parameters for Cd(en)Ni(CN)$_4$.

atom	x/a	y/b	z/c	$B_{eq}/Å^{2a}$
Cd	0.57393(4)	0.75	0.5	1.6(0)
Ni	0.5	0.5	0.0	1.6(0)
N(1)	0.7404(5)	0.6678(5)	0.5552(6)	2.7(1)
N(2)	0.5465(5)	0.6460(5)	0.2729(6)	2.7(1)
N(en)	0.3966(5)	0.6394(4)	0.5829(6)	2.5(1)
C(1)	0.8400(6)	0.5744(4)	0.5333(5)	1.9(1)
C(2)	0.5251(5)	0.5913(5)	0.1689(6)	2.0(1)
C(en)	0.2802(6)	0.7165(6)	0.5721(8)	3.0(1)
H(1)N	0.384	0.561	0.515	4.0^b
H(2)N	0.412	0.612	0.696	4.0
H(3)C	0.192	0.663	0.581	4.0
H(4)C	0.281	0.780	0.663	4.0

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

^{b}Hydrogen atoms have been located at the sp^3-calculated positions with the isotropic thermal parameter fixed at 4.0 Å^2; these values were not refined but included in the final calculation of the structure factors.

$(50/F_0)^2$ for $|F_0| > 50$, $w = 1$ for $50 \leqslant |F_0| \leqslant 25$, and $w = 0.25$ for $|F_0| < 25$. Atomic parameters are listed in Table II and the structure is illustrated in Figure 2 [11].

The complex has a three-dimensional structure: every N-terminal of the square-planar tetracyanonickelate(II) is linked with the six-coordinate cadmium(II) atom to which the en ligand chelates bidentately. The square-planar structure of the tetracyanonickelate(II) moiety is little distorted. Three different Cd—N bond lengths, Cd—N(1) 2.309(5) Å, Cd—N(2) 2.378(5) Å, and Cd—N(en) 2.318(5) Å, are observed about the six-coordinate Cd atom with the N—Cd—N bond angles ranging from 70.4(2)° to 99.2(2)°. The bond distances and angles in the chelating en ligand are not unusual: λ- and δ-conformers are arranged alternately according to the symmetry elements of the unit cell.

The change from the clathrate host to the residual complex needs dissociation-recombination processes not only in the en ligand, which turns from bridging to chelating, but also at the N-terminals of the tetracyanonickelate(II) moieties, because the clathrate host has the two-dimensional *catena*-[cadmium tetra-μ-cyanonickelate(II)] networks and the *cataena*-μ-en linkages spanning adjacent

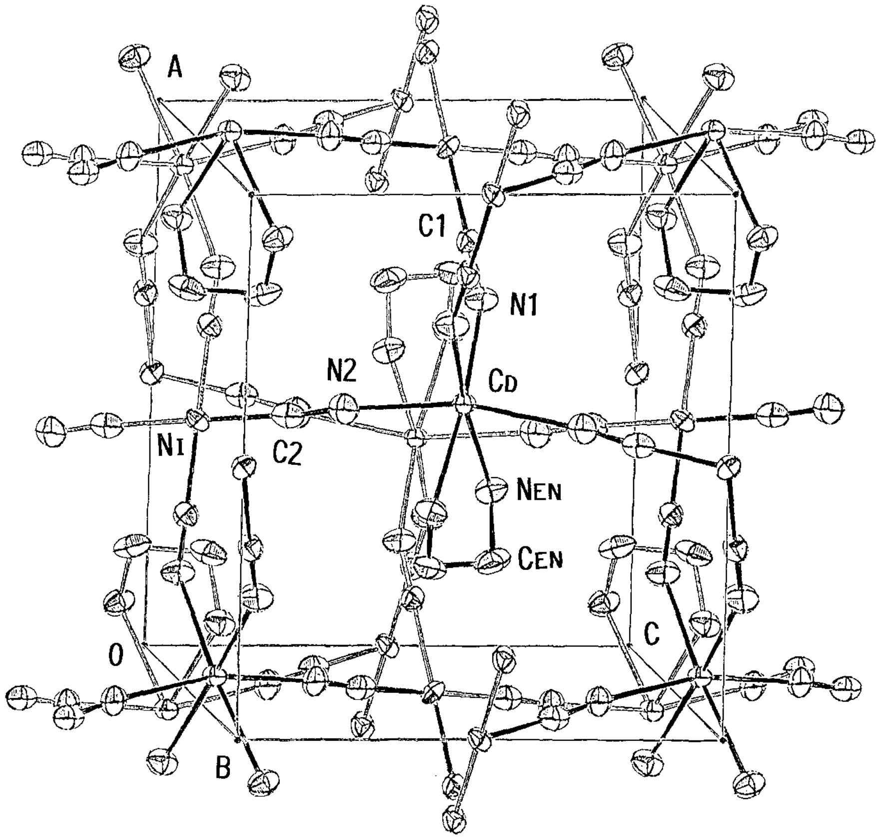

Fig. 2. An ORTEP [13] view of $Cd(en)Ni(CN)_4$: projection along the *b*-axis; 50% probability for each thermal ellipsoid; hydrogen atoms have been omitted; the bonds located in the range of $0.5 < y/b < 1$ are shown with solid lines.

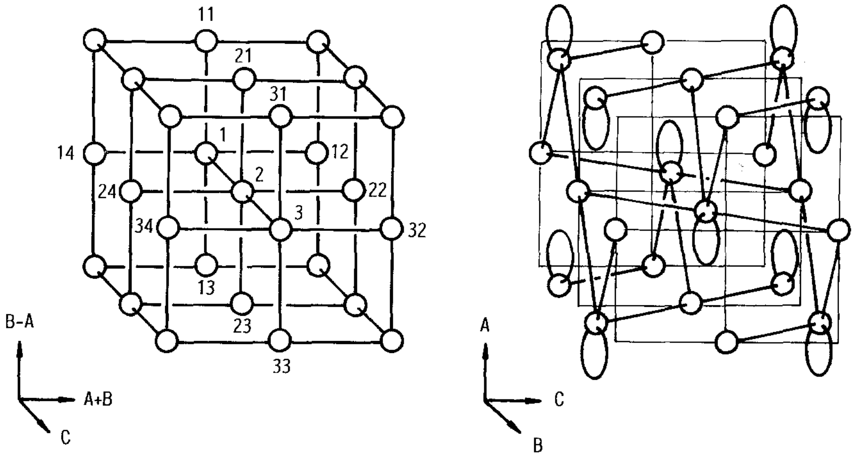

Fig. 3. The pathway from the clathrate host to the residual complex. (a) A perspective view of the tetragonal host: the 2-D networks of $[\mathrm{CdNi(CN)_4}]_\infty$ extending on the *ab*-plane are spanned by the en ligands along the *c*-axis (upward); the Cd atom numbered with one digit *n* ($n = 1, 2,$ or 3) is linked with four N-terminals of $\mathrm{Ni(CN)_4}$, the Ni atoms being numbered with two digits from *n*1 to *n*4; guest molecules have been omitted. (b) A perspective view of the orthorhombic residual host (*b*-axis upward; viewed in the same direction as that in Figure 2); the Cd atoms are located at 0.5, 0.25, 0.5 and the equivalent positions for the sake of simplicity in comparison with (a); the two-dimensional cyanometal networks in the original host structure are shown by thin lines.

networks at the Cd atoms [12]. The clathrate host structure belongs to the tetragonal space group *P*4/*mmm*: the two-dimensional network extends along the *ab*-plane, the en-bridge extending along the *c*-axis. The structures of the clathrate host and the residual complex are compared in Figure 3 as the clinographic projection along the *c*-axis of the host in (a) and that along the *b*-axis of the complex in (b); the *x*-coordinate of the Cd atoms of the latter has been approximated to 0.5 for the sake of simplicity in comparison with the former structure. The decomposition pathway may be explained about Cd(2) at the center of the host cage structure in Figure 3(a). Coinciding with the release of the guest benzene molecules, the N-terminal of en at the lower network dissociates from Cd(1) and chelates to Cd(2), which moves half-way down toward the lower network with the dissociation of the N-terminal of Ni(22)CN. The N-terminal of Ni(21)CN dissociates from Cd(2) to give the coordination site to the N-terminal of en coming up, and comes up into the upper network to be recombined to Cd(3) along with the N-terminal of Ni(22)CN. The two N-terminals of Ni(12)CN and Ni(13)CN then dissociate from Cd(1) and are recombined to Cd(2). Hence, three of the six N-terminals dissociate from, and are recombined to, a Cd atom shifting from the original network. When these dissociation-recombination and shift processes proceed alternately along the *c*-axis of the clathrate, which corresponds to the *b*-axis of the residual complex, the structure of the residual complex can be produced. The assumed processes are less complicated than those assumed for the en-Td-type [2].

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