

$\text{Cd}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($\text{M}' = \text{Ni}, \text{Pd}$):
A New-type of the Clathrates with an Etylenediamine-
bridged Host Lattice of Three Dimensions*

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A new-type of the clathrates, $\text{Cd}(\text{en})\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($\text{M}' = \text{Ni}, \text{Pd}$; $\text{en} = \text{ethylenediamine}$), with a host lattice of three dimensions was prepared. The host lattice was developed from that of the Hofmann-type clathrate $\text{M}(\text{NH}_3)_2\text{M}'(\text{CN})_4 \cdot 2\text{G}$ by bridging the two-dimensional metal-complex networks with ethylenediamine. The new clathrates belong to the tetragonal system, as does the Hofmann-type clathrate. The lattice constant a is almost identical with that of the corresponding Hofmann-type clathrate, $\text{Cd}(\text{NH}_3)_2\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$, but the lattice constant c is shortened by the en -bridge between the cadmium atoms in the adjacent cyano-metal complex networks. The formation of the en -bridge was ascertained from the infrared spectroscopic and X-ray diffractometric data.

Introduction

The Hofmann-type clathrate $\text{M}(\text{NH}_3)_2\text{M}'(\text{CN})_4 \cdot 2\text{G}$ is composed of layers of a polymeric metal-complex network $[\text{M}(\text{NH}_3)_2\text{M}'(\text{CN})_4]_\infty$, as the host lattice, with molecules of an aromatic compound, G, clathrated among the layers as the guest molecules.¹⁻⁵ The crystal structure has been illustrated in Figure 1 of a previous paper.⁵ There is no direct chemical bond between the networks; the guest molecules are trapped as if they were adhesive combining adjacent networks of the metal-complex. Thus, the host lattice is substantially of two dimensions.

A host lattice of three dimensions may be built when the metal, M, in a network is combined with that of the adjacent network with a bridging ligand. As the bridging ligand, ethylenediamine (en) can most simply replace two ammonia molecules protruding oppositely from the two M's in the Hofmann-type clathrate. Although en is known to be a typical bidentate chelating ligand in coordination chemistry,

its bridging behavior has also been reported in several cases. The infrared spectra of $\text{M}(\text{en})\text{Cl}_2$ ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$)^{6,7} and $[(\text{C}_2\text{H}_4)\text{PtCl}_2]_2(\text{en})$ ⁸ have supported bridge structures of the en molecules in these complexes, because the absorption bands can be assigned to the *trans*-form of an en molecule. From a minute analysis of the powder X-ray diffraction pattern of $\text{Hg}(\text{en})\text{Cl}_2$, an infinite bridge structure of $(-\text{Hg}-\text{NH}_2\text{CH}_2-\text{CH}_2-\text{NH}_2-)_\infty$ was also proposed by Brodersen.⁷

In this paper, by using en instead of ammonia, two en-host clathrates, $\text{Cd}(\text{en})\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ and $\text{Cd}(\text{en})\text{Pd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$, were prepared by a method similar to that used in the case of Hofmann-type clathrates. The bridge structure of the en in these compounds was ascertained by infrared spectroscopy and X-ray diffractometry. The state of clathrated benzene will be discussed in comparison with that in the corresponding Hofmann-type clathrate, $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$.

Experimental Section

Preparation of $\text{Cd}(\text{en})\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$. To a mixed aqueous solution of CdCl_2 , $\text{K}_2\text{Ni}(\text{CN})_4$ and en (1:1:3), an excess of benzene was added and the two phases were thoroughly mixed with vigorous stirring. The precipitate thus formed was filtered out on a glass filter and washed with water, ethanol, and ether successively. The pale yellow crystalline powder thus obtained was dried in calcium chloride desiccator in the presence of benzene vapor.

Anal. Found: C, 42.1; H, 3.83; N, 16.8; Cd, 22.8; Ni, 11.9%. Calcd. for $\text{C}_{18}\text{H}_{20}\text{N}_6\text{CdNi}$: C, 43.99; H, 4.10; N, 17.10; Cd, 22.87; Ni, 11.95%.

By using $\text{K}_2\text{Pd}(\text{CN})_4$ instead of $\text{K}_2\text{Ni}(\text{CN})_4$ in the above-mentioned method, $\text{Cd}(\text{en})\text{Pd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ was obtained. The product was checked by infrared spectroscopy and X-ray diffractometry.

Infrared Spectroscopy and X-ray Diffractometry.

The measurements were carried out by methods previously reported.^{1,4} In order to compare the infrared spectra, $\text{Cd}(\text{en})\text{Cl}_2$ and a deuterobenzene clathrate $\text{Cd}(\text{en})\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{D}_6$ were also prepared.

(6) G. Newman and D. B. Powell, *J. Chem. Soc.*, 477 (1961).

(7) K. Brodersen, *Z. anorg. u. allgem. Chem.*, 298, 142 (1959).

(8) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 3089 (1959).

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(1) T. Iwamoto, T. Miyoshi, T. Miyamoto, Y. Sasaki, and S. Fujiwara, *Bull. Chem. Soc. Japan*, 40, 1174 (1967).

(2) T. Nakano, T. Miyoshi, T. Iwamoto, and Y. Sasaki, *ibid.*, 40, 1297 (1967).

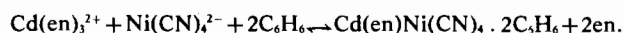
(3) M. Morita, T. Miyoshi, T. Miyamoto, T. Iwamoto, and Y. Sasaki, *ibid.*, 40, 1556 (1967).

(4) T. Miyoshi, T. Iwamoto, and Y. Sasaki, *Inorg. Chim. Acta*, 1, 120 (1967).

(5) T. Iwamoto, T. Nakano, M. Morita, T. Miyoshi, T. Miyamoto, and Y. Sasaki, *Inorg. Chim. Acta*, 2, 313 (1968).

Results and Discussion

Formation Reaction. Upon the gradual addition of en to an aqueous solution of cadmium chloride, a white precipitate of Cd(en)Cl_2 appears at first. This precipitate is not completely dissolved unless three times as much as the total amount of cadmium is added. By mixing aqueous solutions of cadmium chloride and potassium tetracyanonickelate, a yellow precipitate of cadmium tetracyanonickelate is obtained. To dissolve this precipitate completely also, three times as much of en is necessary. Thus, under these conditions, the cadmium can be present as a chelate cation, Cd(en)_3^{2+} , in the aqueous phase. The clathrate must be produced by a reaction among the chelate cation, tetracyanonickelate anion, and benzene as follows:



In the aqueous Cd^{2+} -en- Cl^- system, bis-ethylenediaminecadmium ion can not exist as a stable species. The complex salt previously reported to be $\text{Cd(en)}_2\text{CdCl}_4$ ⁹ is thus not possible; it must be Cd(en)Cl_2 . The infrared spectrum of the complex prepared by the method in the literature was just the same as that of Cd(en)Cl_2 .

Bridge Structure of the en Molecule. Geometry of

the en Molecule. As the starting species of the preparation reaction was the «chelate» Cd(en)_3^{2+} , careful consideration was needed to determine the en molecule in the present compound whether bridging or chelating. It is possible for the molecule of en to have one of four molecular forms, *trans*, *cis*, *gauche-1*, or *gauche-2*. The chelate complexes of en with structures already known have *gauche*-forms without exception. The *cis*-form may be possible in a chelate complex, although it has not been reported in the literature. On the other hand, in a bridge structure, not only the *trans*-form but also the *cis*- and *gauche*-forms can hold. The distance between two bridged metal atoms with an en molecule may depend on the molecular form of the en. We can, however, conclude unambiguously that the *trans*-form must have a bridge structure.

Infrared Spectra. When a model of the bridge structure of an en in the *trans*-form (C_{2h}) is described as follows:

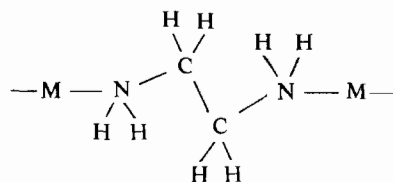


Table 1. IR Bands of *trans*-Ethylenediamine Bridging Complex

	Number of vibration mode				IR-active	Absorption Bands (cm^{-1})		
	A_g	B_g	B_g	A_u		$\text{Cd(en)Ni(CN)}_4 \cdot 2\text{C}_6\text{H}_6$	$\text{Cd(en)Ni(CN)}_4 \cdot 2\text{C}_6\text{D}_6$	Cd(en)Cl_2
CC str.	1				0	---	---	---
CN str.	1	1			1	1017 s 995 s 957 s	1018 s 993 s 956 s	1017 s ---
NM str.	1	1			1	265 w	265 w	248 w
CH_2 asym. str.			1	1	1	2921 m	2911 s	2980 m
CH_2 sym. str.	1	1			1	2877 m	2867 s	2914 m
CH_2 sic.	1	1			1	1462 s	1460 s	1480 m
CH_2 wag.	1	1			1	1367 w	1368 w	1374 w
CH_2 twist.			1	1	1	1278 w	1278 w	1278 w
CH_2 rock.			1	1	1	855 w	854 w	(847)
NH_2 asym. str.			1	1	1	3318 s br	3317 s	3277 s
NH_2 sym. str.	1	1			1	---	3146 m sh	3180 s
NH_2 sic.	1	1			1	1589 s	1585 s	1611 s
NH_2 wag.	1	1			1	1327 s	1327 m	1329 s
NH_2 twist.			1	1	1	1089 s	1088 s	1102 s br
NH_2 rock.			1	1	1	551 s br	552 s br	538 s br
MNC bend.	1	1			1	---	---	---
NCC bend.	1	1			1	---	---	---
CC tort.				1	1	---	---	---
CN tor.			1	1	1	---	---	---
Total	11	10	7	8	18			

The Bands due to the Cyanide-metal System

	$\text{Cd(en)Ni(CN)}_4 \cdot 2\text{C}_6\text{H}_6$	$\text{Cd(en)Ni(CN)}_4 \cdot 2\text{C}_6\text{D}_6$	$\text{Cd(NH}_2)_2\text{Ni(CN)}_4 \cdot 2\text{C}_6\text{H}_6$
CN str. of CN^-	2149 s	2144 s	2155 s
NiC str.	432 s	431 s	427 s
	430 s	430 s	
Ni-CN-Cd bend.-1	585 s	585 s	555 m br
Ni-CN-Cd bend.-2	466 s	466 s	448 w

(9) G. Spacu and P. Spacu, *Bull. Soc. Stiinte. Cluj.*, 6, 384 (1931/32); Gmelins Handbuch d. anorg. Chem., Sys.-Nr. 33 «Cadmium», Verlag Chemie GmbH, Weinheim, p. 783 (1959).

as listed in Table I, there must be eighteen infrared-active bands due to the fundamental vibration modes of the system, while for the *cis*-form (C_{2v}) or the *gauche*-form (C_2) the number of infrared-active vibrations is twenty-five or thirty-six respectively. The en-bridging complexes already reported^{6,8} gave maximal thirteen bands due to the en in the region from 500 cm^{-1} to 3400 cm^{-1} . This fact supports the *trans*-form of en in those complexes. In the present compound, as is shown in Table I, fourteen bands due to the system have been observed. Among them, the CN stretching band (B_u) was split into three components. The cause of splitting will be interpreted in the following section with respect to the crystal structure. The spectrum is shown in Figure 1, along with those of $\text{Cd(en)Ni(CN)}_4 \cdot 2\text{C}_6\text{H}_6$ and Cd(en)Cl_2 . The assignment of each band was established by means of comparison with the others. The band due to the CH_2 rocking mode (A_u) appeared around 855 cm^{-1} on the spectra of both the en-host clathrates.

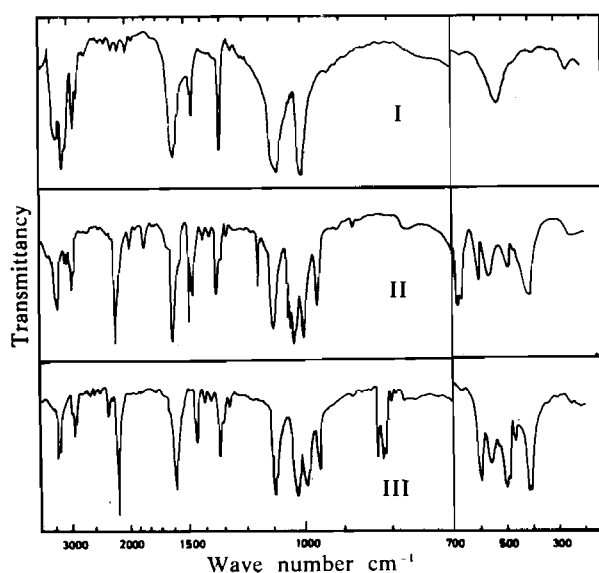


Figure 1. The infrared spectra of (i) Cd(en)Cl_2 , (ii) $\text{Cd(en)Ni(CN)}_4 \cdot 2\text{C}_6\text{H}_6$, and (iii) $\text{Cd(en)Ni(CN)}_4 \cdot 2\text{C}_6\text{D}_6$. Synthesized from those in the Nujol mull and the HCB mull.

As Nakagawa and Mizushima pointed out,¹⁰ the CH_2 rock. mode of *trans*- $\text{XCH}_2\text{CH}_2\text{X}$ gives an absorption band in the region from 600 cm^{-1} to 900 cm^{-1} . The wave number observed (855 cm^{-1}) supports the estimate that the en molecules in these en-host clathrates have *trans*-form as well. Although Newmann and Powell⁶ reported the wave number of the CH_2 rock. band to be 847 cm^{-1} in Cd(en)Cl_2 , the present author could not detect it even by using the thickest samples in the Nujol mulls. An accurate calculation of the fundamental vibrations seems to be very difficult because of the coupling between the CH_2 and NH_2 modes. However, from the above-mentioned observations, it can be concluded that the en molecule has the *trans*-form with a bridge structure in the present en-host clathrate.

X-Ray Diffractometry. The powder X-ray diffraction patterns of $\text{Cd(en)Ni(CN)}_4 \cdot 2\text{C}_6\text{H}_6$ can be assigned to the tetragonal system, much as can those of the corresponding Hofmann-type clathrates. The lattice constants determined are listed in Table II, along with the diffraction data. For the sake of comparison, the lattice constants of the corresponding Hofmann-type clathrates are also listed. Each of the a values is almost identical with that of the corresponding Hofmann-type clathrate. The values of c in the en-host clathrates are almost the same and are independent of the change of M' from nickel to palladium, as in the case of the Hofmann-type clathrates. Therefore, the structure of the present compounds seems to be very similar to that of the Hofmann-type clathrate. The metal-complex network bridged with the cyanide anions is almost the same size as that of the corresponding Hofmann-type clathrate, as is illustrated in Figure 2. The distance between the networks is shorter in the present compounds than in the Hofmann-type, however. The shortening must be caused by the bridging of the en molecule between the adjacent networks. Since the space group of the $\text{Cd(en)Ni(CN)}_4 \cdot 2\text{C}_6\text{H}_6$ is $P4_1/n_1$, as has been determined from the Weissenberg and precession photographs of the single crystal,¹¹ the arrangement of cadmium atoms, $-\text{Cd}-(\text{en})-\text{Cd}-(\text{en})-$, must be linear and parallel to the c -axis of the crystal.

Table II. The Lattice Constants and Diffraction Data

		$M' = \text{Ni}$		$M' = \text{Pd}$	
		a	c	a	c
$\text{Cd}(\text{NH}_3)_2 M'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$		7.64	8.37	7.77	8.38
$\text{Cd}(\text{en})M'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$		7.64	7.97	7.77	8.00

		Cu-K α Ni-filter GM-counter					
		$\text{Cd}(\text{en})\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$		$\text{Cd}(\text{en})\text{Pd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$			
2θ	$d_{\text{obs.}}$	(hkl)	$d_{\text{calcd.}}$	2θ	$d_{\text{obs.}}$	(hkl)	$d_{\text{calcd.}}$
11.10	7.97 s	(001)	7.97	11.00	8.04 s	(001)	8.00
11.60	7.63 m	(100)	7.64				
16.12	5.50 w	(101)	5.51				
16.44	5.39 s	(110)	5.40	16.10	5.51 w	(110)	5.50
19.80	4.48 vs	(111)	4.47	19.60	4.53 m	(111)	4.53
22.30	3.99 s	(002)	3.98	22.22	4.00 vs	(002)	4.00
23.30	3.82 s	(200)	3.82				
25.08	3.56 w	(102)	3.53				
26.08	3.42 m	(210)	3.41				
27.80	3.21 s	(112)	3.21	27.56	3.24 m	(112)	3.24
				32.10	2.79 vw	(202)	2.79
33.14	2.70 m	(220)	2.70	32.50	2.76 vw	(220)	2.76
33.72	2.66 m	(003)	2.66	33.66	2.66 s	(003)	2.67
34.76	2.59 w	(212)	2.59				
35.04	2.56 m	(221)	2.56	34.36	2.61 w	(221)	2.60
37.12	2.42 w	(310)	2.42				
37.66	2.39 w	(113)	2.38	37.48	2.40 w	(113)	2.40
38.90	2.32 w	(311)	2.31				
40.32	2.24 w	(222)	2.24	39.70	2.27 vw	(222)	2.27
41.33	2.18 w	(203)	2.18	41.00	2.20 vw	(203)	2.20
				43.08	2.10 vw	(312)	2.09
				45.34	2.00 w	(004)	2.00
47.60	1.91 w	(400)	1.91				
47.90	1.90 w	(223)	1.89				
48.54	1.87 w	(114)	1.87	48.40	1.88 w	(114)	1.88
49.00	1.86 w	(401)	1.86				

(10) I. Nakagawa and S. Mizushima, *J. Chem. Phys.*, **21**, 2195 (1953).

(11) Y. Sasaki, T. Miyoshi, and T. Iwamoto, unpublished.

This arrangement may give a slight distortion to the en molecule. Thus, the distances between the networks, *i. e.*, the values of c , 7.97 and 8.00 Å, are slightly longer than the distance between the bridged mercury atoms in Hg(en)Cl_2 (7.79 Å).⁷

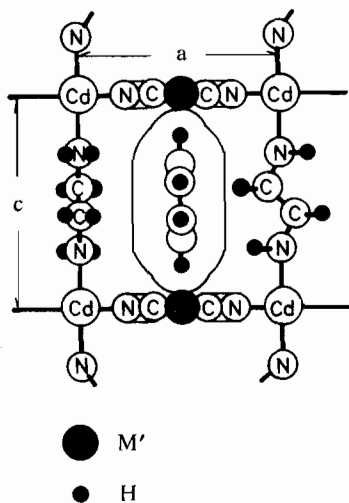


Figure 2. The proposed structure of $\text{Cd(en)M'(CN)}_4 \cdot 2\text{C}_6\text{H}_6$. The right hand side column of the en molecule is at the nearest approach to the benzene molecule, and the left hand side is at the farthest.

As for the orientation of the en molecule, as it has a rotation axis connecting the two cadmium atoms parallel to the c -axis, there are two possibilities; one is an averaged distribution of the random orientations, and the other is the reorientation about the axis. The splitting of the CN str. band (B_u) of en in the infrared spectrum (see Table I) must be caused by the structural distortion or inequality of the en molecule. However, on the basis of only the results of infrared spectroscopy and X-ray diffractometry which have so far been obtained, it is impossible to discuss the molecular motion of en. It can, though, be concluded that the orientation of the en molecule in this compound is macroscopically averaged.

The State of the Benzene Molecule. In Table III are listed the wave numbers of the infrared absorption bands due to the benzene in the en-host clathrate and the corresponding Hofmann-type clathrate. The good agreement between the two values supports the idea that the benzene is clathrated in the present compound. However, there are some differences in behavior between them. One is the splitting of the bands around 1038 cm^{-1} (E_{1u}) and around $670\text{--}705$

Table III. The IR Absorption Bands due to Benzene, cm^{-1}

	I	I'	II'	II''
CH str. i.p. (E_{1u})	3076	2282	3076	2278
CH str. i.p. (B_{1u})	3034	---	3026	---
Combination	1968	---	1987	---
Combination	1823	---	1852	---
Combination	---	---	1567	---
Ring str. + def. i.p. (E_{1u})	1479	---	1476	1325
Ring str. i.p. (B_{2u})	1315	---	1311	1280
CH bend. i.p. (B_{2u})	1147	823	1147	823
CH bend. i.p. (E_{1u})	1041	815	1034	811
	1033	810	---	---
CH bend. o.p. (E_{2u})	---	805	985	891
CH bend. o.p. (A_{2u})	686	509	704	515
	672	498	---	---
Ring. def. o.p. (E_{2u})	407	358	407	356

I: $\text{Cd(en)Ni(CN)}_4 \cdot 2\text{C}_6\text{H}_6$; I': $\text{Cd(en)Ni(CN)}_4 \cdot 2\text{C}_6\text{D}_6$; II: $\text{Cd}(\text{NH}_3)_2\text{Ni(CN)}_4 \cdot 2\text{C}_6\text{H}_6$; II': $\text{Cd}(\text{NH}_3)_2\text{Ni(CN)}_4 \cdot 2\text{C}_6\text{D}_6$.

cm^{-1} (A_{2u}) in the en-host clathrate. The splitting of the degenerate E_{1u} band is rather reasonable because the benzene molecule in the clathrate can hardly hold exactly the D_{6h} symmetry. In the Hofmann-type clathrate, in which the site symmetry of benzene is C_{2h} ,⁴ the splitting may be too small to be resolved. The splitting of the A_{2u} band was accompanied by another feature, *i. e.*, by a shift by *ca.* 20 cm^{-1} to the lower frequency side in comparison with that of the Hofmann-type clathrate. The splitting and the shift on the spectrum recorded at the temperature of liquid nitrogen were substantially the same to those at room temperature. As is illustrated in Figure 2, the benzene molecule in the en-host clathrate is in close contact with the en molecule by van der Waals radii when the en molecule approaches nearest to the benzene molecule, but it is considerably apart from the en molecule when the en molecule is farthest distant. Therefore, the magnitude of the host-guest interaction ranges between the nearest and the farthest approaches, although no precise description of the potential function has yet been made. The splitting and the shift of the A_{2u} band may be ascribed to the varying host-guest interaction, which has a different nature from that in the Hofmann-type due to the three-dimensional structure of the en-host lattice.

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