The Crystal Structure of a Hofmann-en Type Pyrrole Clathrate, *catena-μ*-Ethylenediaminecadmium(II) *catena*-Tetra-*μ*-cyanonickelate(II)-Pyrrole (1/2)

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(Received April 24, 1975)

The crystal structure of the titled pyrrole clathrate $Cd(NH_2CH_2CH_2NH_2)Ni(CN)_4 \cdot 2C_4H_5N$ has been determined from three-dimensional X-ray data collected by counter techniques. The clathrate crystallizes in the orthorhombic space group Pmmm with $a=7.618(3)$, $b=7.641(10)$, $c=7.861(4)$Å, $Z=1$, $D_m=1.69$ g cm^{-3}, and $D_x=1.70$ g cm^{-3}. The structure has been refined by the full-matrix least-squares procedure to a conventional R index (on F) of 0.057 for 462 observed reflections. The metal complex host-framework has a three-dimensional infinite cage structure where the ambident ethylenediamine molecules span Cd atoms at the corners of unit cell along the [001] direction and the ambident cyanide ions make infinite two-dimensional networks parallel to (001) by spanning the Cd atoms with the Ni atom at (1/2, 1/2, 0). The two crystallographically independent pyrrole molecules are enclathrated in the molecular spaces of the cages in the host-framework. The statistical dispositions observed for en and pyrrol molecules can be interpreted in terms of motional behavior of these molecules in the crystal.

The crystal structures of the Hofmann type and analogous clathrates have been determined only for those of the benzene guest[1-7] except a Hofmann type biphenyl clathrate $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_{12}H_{10}$,[8] in spite that various polar molecules such as pyrrole, thiophene or aniline can be the guest.[9] With respect to the guest benzene molecule, the reorientational motion about its sixfold axis has been observed for Hofmann type clathrates above 140 K by wide-line PMR.[10] The atomic coordinates of the carbons in the crystal have been determined as the potential minima during the reorientational motion by single crystal X-ray analysis. It is a matter of interest how the polar molecules are arranged in the molecular spaces. The molecular electric dipole moments will play an important role in determining the arrangements of the polar molecules in the crystal. For the first attempt at the crystal structure analysis of the polar-guest clathrate of these types, a Hofmann-en type pyrrole clathrate Cd(en)-$Ni(CN)_4 \cdot 2C_4H_5N$ (en$=NH_2CH_2CH_2NH_2$) was taken up, since pyrrole has a large dipole moment (1.80 D) and since the structure of the Hofmann-en type benzene clathrate $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$ had already been determined.[3] The structural features of the pyrrole clathrate will be discussed in comparison with those of the benzene clathrate.

Experimental

The crystals of $Cd(en)Ni(CN)_4 \cdot 2C_4H_5N$ were prepared by the method previously reported.[11] An approximately equidimensional crystal of 0.1×0.1×0.1 mm in size was sealed in a thin-walled glass capillary (0.1 mmϕ) with a small amount of liquid pyrrole. Preliminary Weissenberg photographs suggested a tetragonal symmetry of the crystal and the cell-dimensions $a=7.62$ and $c=7.86$ Å, supporting the previous results obtained from the powder diffraction pattern.[11] Before intensity collection, however, the unit cell dimensions and the intensity distribution were reexamined on a Rigaku four-circle automated diffractometer,[12] and it was revealed that the crystal is orthorhombic with $a=7.618(3)$, $b=7.641(10)$ and $c=7.861(4)$ Å, the values being determined by the least-squares calculations with eight 2θ values in the range 20—40°, for Cu$K\bar{\alpha}$ radiation. The intensity data were collected with Cu$K\bar{\alpha}$ radiation monochromated by a graphite crystal ($\lambda=1.5418$ Å) using $2\theta-\theta$ scanning technique for 462 independent reflections with 2θ less than 120°. All the reflections had the non-zero intensities; 31 reflections had the values comparable with or less than three times the standard deviations. Three standard reflections were remeasured every 50 reflections; no significant variation in the intensities was observed. The LP correction was applied, but no corrections for absorption and extinction were made. The density was measured by flotaion method in bromoform-xylene mixture.

Crystal data are:

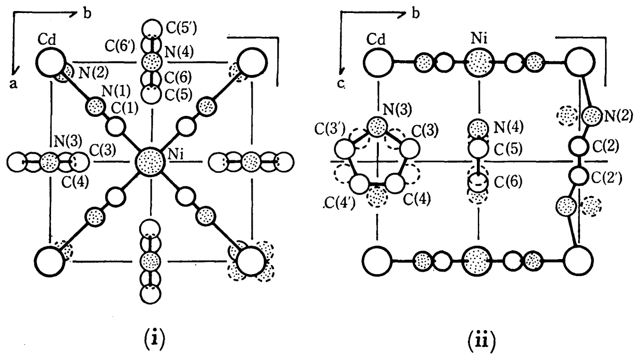
$Cd(NH_2CH_2CH_2NH_2)Ni(CN)_4 \cdot 2C_4H_5N$, M.W.$=469.38$

Orthorhombic, D_{2h}^1-Pmmm, $a=7.618(3)$, $b=7.641(10)$, $c=7.861(4)$ Å, $Z=1$. $D_m=1.69$, $D_x=1.70$ g·cm^{-3}. No systematic absence. μ(Cu$K\bar{\alpha}$)$=109.6$ cm^{-1}.

Structure Refinement

All the calculations were carried out on a HITAC 8800/8700 computer at the Computation Center of this University. The programs used were those in UNICS[13] and BLAN-2.[14] The atomic scattering factors used were those listed in the usual tabulation[15] for C and N, and those from Cromer and Waber[16] for Cd and Ni. In the least-squares calculations the quantity minimized was $\sum w(||F_O|-|F_C||)^2$ with $w=1/[\sigma(F_O)]^2$. The reliability indices of conventional $R_1=\sum w(||F_O|-|F_C||)/\sum|F_O|$ and $R_2=\sum w(||F_O|-|F_C||)^2/\sum|F_O|^2$ were defined in order to check the results of refinement. All the 462 observed reflections were used in the calculations.

Because of no systematic absence of the reflections, the possible space groups are P222, Pmm2 and Pmmm. Since the unit cell contains only a formula unit of $Cd(en)Ni(CN)_4 \cdot 2C_4H_5N$, most of the atoms should lie on the special positions. From the three-dimensional Patterson synthesis, the Cd and the Ni atoms were placed at the positions 0,0,0 and 1/2,1/2,0, respectively. The centrosymmetric space group Pmmm was assumed prior to the other two non-centrosymmetric ones. The Fourier map phased with the heavy atoms gave clear peaks due to cyanide C and N atoms on the (001) plane, and the more diffused peaks due to en-C and -N atoms along the twofold axis parallel to [001] spanning two Cd atoms. The difference Fourier map then calculated revealed the positions of two crystallographically independent pyrrole molecules. Ten cycles of block-diagonal least-squares calculations with isotropic temperature factors gave an R_1 index of 0.114. The similar calculations were carried out by assuming P222 and Pmm2, but the R_1 indices not less than 0.169 were obtained. Therefore, Pmmm was definitively adopted. The Fourier map synthesized at this stage suggested that the en-N and en-C atoms were to be located slightly apart from the [001] axis with statistical distributions. Full-matrix least-squares calculations were carried out on two models by assigning anisotropic temperature factors for all the atoms, and by applying the real and imaginary dispersion corrections for Cd and Ni atoms. Both en-C and en-N were placed at general positions in one of the models, while the en-C was fixed on the twofold axis in the other. After two cycles of the calculations, it was found that the latter model gives better results. On the former assumption, negative temperature factors were obtained for the en-C and en-N atoms. Thus, the final atomic parameters were determined for all the atoms except hydrogen atoms. The final R_1 and R_2 indices were 0.057 and 0.080, respectively.[17]



(i) (ii)

Fig. 1. The projections of the structure (i) along the c axis and (ii) along the a axis.
Thick lines indicate chemical bonds and thin lines are the mirror planes of the crystal. Each set of the atomic positions belonging to a definite molecule is shown with solid lines for the pyrrole and en molecules, and the positions of the mirror images are shown with bloken lines. The weights of occupancy are 0.5 for the C and N aomts of pyrroles, and 0.25 for the N of en. In (ii), the overlapping of the pyrrole and en molecules are avoided by omitting one of molecules.

Description and Discussion of the Structure

The structure is illustrated in Fig. 1. The atomic parameters are given in Table 1. The bond lengths and bond angles are listed in Table 2.

As has been estimated from the powder diffraction and IR data,[11] the host lattice structure is similar to that of the Hofmann-en type benzene clathrate.[3] However, the both structures are slightly different each other in the orientation of en molecule and in the symmetry of the two-dimensional network of the metal cyanide. In the benzene clathrate the en-N atoms are supposed to rotate freely about the [001] axis of the tetragonal unit cell. The rotation of en molecule was also supported by wide-line PMR.[3] In the pyrrole clathrate the final results are interpreted in terms either of a statistical distribution of en-N atoms over the given position and its equivalents with an equal probability 0.25, or of a reorientation about the [001] axis with the potential minima at the given coordinates with the equal probability. The C–C and C–N bond lengths of en (C(2)–C(2′) 1.38(3) Å and C(2)–N(2) 1.19(4) Å) are unusually short like in the benzene clathrate where the C–C and C–N bond lengths are 1.38(6) and 1.33(5) Å, respectively. Although no great confidence can be placed on both of these parameters, there may occur the similar reorientation or rotation of en in the both clathrates.

The metal cyanide network is slightly distorted to the rectangular symmetry pmm in the pyrrole clathrate from the square symmetry p4 in the benzene clathrate. The degree of distortion is so small that the angle between the diagonal of the plane and the b axis is 44.96(5)°. The molecular symmetry of $Ni(CN)_4$ moiety can be approximated to D_{4h} in the pyrrole clathrate. With regard to the IR spectra, almost the same features have been observed for the host lattice constituents of Hofmann-en type clathrates.[11] An unresolved problem was the splitting of CN stretch E_u mode of the D_{4h}

TABLE 1. THE FINAL ATOMIC PARAMETERS ($\times 10^3$) AND THEIR ESTIMATED STANDARD DEVIATIONS (IN PARENTHESES)
Anisotropic temperature factors ($\times 10^4$) are of the form: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)]$

atom	Point symmetry	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cd	mmm	000	000	000	60(4)	67(4)	96(3)	000	000	000
Ni	mmm	500	500	000	36(11)	44(11)	24(11)	000	000	000
N(1)	m	223(2)	222(2)	000	115(34)	122(34)	241(11)	−66(33)	000	000
C(1)	m	327(2)	327(2)	000	79(33)	99(33)	276(29)	−32(32)	000	000
N(2)	1	50(6)	51(5)	278(4)	144(121)	185(134)	191(64)	−96(68)	48(62)	−2(58)
C(2)	mm	000	000	412(4)	310(49)	314(49)	147(45)	000	000	000
N(3)	mm	500	000	325(19)	260(134)	343(333)	391(265)	000	000	000
C(3)	m	500	148(8)	435(10)	210(71)	294(136)	236(111)	000	000	−49(72)
C(4)	m	500	83(11)	614(11)	146(129)	500(341)	327(324)	000	000	−106(142)
N(4)	mm	000	500	333(13)	284(253)	194(115)	365(198)	000	000	000
C(5)	m	148(10)	500	432(14)	325(171)	233(85)	268(133)	000	−44(101)	000
C(6)	m	90(11)	500	605(14)	458(330)	192(133)	326(273)	000	−95(178)	000

TABLE 2. THE BOND LENGTHS, INTERATOMIC DISTANCES LESS THAN 3.0 Å, AND BOND ANGLES

Cd–N(1)	2.40(1) Å	Cd–N(2)	2.25(3) Å
Ni–C(1)	1.87(1)	C(1)–N(1)	1.12(2)
N(2)–C(2)	1.19(4)	C(2)–C(2′)	1.38(3)
N(3)–C(3)	1.43(8)	N(4)–C(5)	1.37(8)
C(3)–C(4)	1.49(11)	C(5)–C(6)	1.42(13)
C(4)–C(4′)	1.27(11)	C(6)–C(6′)	1.37(11)
N(3)–C(4)	2.36(10)	N(4)–C(6)	2.24(11)
C(3)–C(3′)	2.27(8)	C(5)–C(5′)	2.26(10)
C(3)–C(4′)	2.26(10)	C(5)–C(6′)	2.27(12)
Cd–N(1)–C(1)	180(1)°	N(1)–C(1)–Ni	180(1)°
Cd–N(2)–C(2)	139(3)	N(2)–C(2)–C(2′)	153(2)
N(3)–C(3)–C(4)	108(5)	N(4)–C(5)–C(6)	107(6)
C(3)–C(4)–C(4′)	109(7)	C(5)–C(6)–C(6′)	108(8)
C(3)–N(3)–C(3′)	105(6)	C(5)–N(4)–C(5′)	111(5)
N(2)–Cd–C(2)	14(1)		

Key to symmetry operations: C(2) at $((0,0,z)$, C(2′) at $(0,0,\bar{z})$; C(3) at $(\frac{1}{2},y,z)$, C(3′) at $(\frac{1}{2},y,\mathrm{z})$; C(4) at $(\frac{1}{2},y,z)$, C(4′) at $(\frac{1}{2},\bar{y},z)$; C(5) at $(x,\frac{1}{2},z)$, C(5′) at $(\bar{x},\frac{1}{2},z)$; C(6) at $(x,\frac{1}{2},z)$, C(6′) at $(\bar{x}.\frac{1}{2},z)$.

square-planar $Ni(CN)_4$ into a doublet, 2155 and 2146 cm^{-1} in the benzene, and 2154 and 2145 cm^{-1} in the pyrrole clathrates. In the orthorhombic D_{2h}^{1}-Pmmm unit cell of the latter, the Ni atom locates at the D_{2h} site, 1/2,1/2,0. The correlation among the molecular (effective) D_{4h}, the site D_{2h} and the crystal D_{2h} groups makes the degenerate E_u mode split into a B_{2u} and a B_{3u} modes. Although this interpretation cannot be directly applied to the benzene clathrate with the tetragonal C_{4h}^{1}-P4/m space group, the similar doublet structure suggests that the effective site symmetry of the Ni atom is lowered from tetragonal to orthorhombic probably owing to the reorientation of en molecules.

There are two crystallographically independent pyrrole molecules in the unit cell. The aromatic plane of one molecule is vertical to the (010) plane, and that of the other is vertcial to the (100) plane; the twofold axes of the molecules are parallel to [001]. Each pyrrole molecule is statistcially distributed with an equal probability in two orientations which are related one another by the mirror plane perpendicular to [001]. There are fairly large differences between the bond lengths and angles in the two independent molecules, but the differences are not significant in view of the large estimated standard deviations. The shapes of molecules appear to be elongated along the twofold axis and compressed along the direction vertical to the axis in comparison with the structure estimated by microwave spectroscopy.$^{18)}$ In the molecular spaces, the reorientational motions of pyrrole molecules may occur, which are similar to that observed in a Hofmann type pyrrole clathrate $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_4H_5N$ by wide-line PMR.$^{10)}$ The large estimated standard deviations of atomic coordinates and the considerably large temperature factors support the motional behavior of the pyrrole molecules. Therefore, the atomic coordinates should be interpreted to be the postions of potential minima during their reorietnational motions, by which the directions of molecular dipoles are statistically in parallel and anti-parallel along the [001] direction.

The authors' thanks are due to Professor Niro Matsuura at this College for his kind support to this work.

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