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THE THIOPHENE AND PYRROLE CLATHRATES OF $Cd(en)Ni(CN)_4$ HOST LATTICE $Cd(en)Ni(CN)_4.2C_4H_4S$ AND $Cd(en)Ni(CN)_4.2C_4H_4NH$

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The thiophene and pyrrole clathrates $Cd(en)Ni(CN)_4.2C_4H_4S$ and $Cd(en)Ni(CN)_4.2C_4H_4NH$ were prepared. Their structures were discussed with the data of the unit cell dimensions and the infrared spectra in comparison with the known benzene clathrate $Cd(en)Ni(CN)_4.2C_6H_6$, of which the infrared spectrum was reassigned. The c-dimension of unit cell, *i. e.*, the length of Cd-en-Cd bridge in the host lattice decreases in the order of guest species, benzene, thiophene and pyrrole, identical with that of decreasing diameter of the aromatic ring.

The benzene clathrate $Cd(en)Ni(CN)_4.2C_6H_6$ (I) has the three-dimensional host lattice structure built of *catena*-μ-en and *catena*-μ-CN ligands bridging between metal ions.[1,2] The crystals of I belong to the tetragonal space group P4/m with one formula unit per unit cell.[2] The CN ligands span adjacent Ni and Cd atoms to extend CN-linked sheets in the ab-plane, and the en ligands span Cd atoms in adjacent sheets along the c-axis of crystal. The 8.06 A length of Cd-en-Cd bridge, *i. e.*, the c-dimension of unit cell, is longer by *ca*. 0.38 A than 7.68 A, the length of Pt-en-Pt bridge in $[Pt(acac)(CH_3)_3]_2en$.[3] The lengthening of the Cd-en-Cd bridge (the c-dimension) in I appears to be caused by the repulsion between the guest benzene molecule and the CN-linked metal complex sheets. If the c-dimension is affected by the size of guest molecule, its contraction will be expected in the thiophene or pyrrole clathrate of the same host lattice, because these five-membered aromatic molecules have the diameter smaller than that of benzene molecule. In fact, the c-dimension of the Hofmann-type clathrate $Cd(NH_3)_2Ni(CN)_4.2G$ decreases in the order of G guest species, aniline, benzene, thiophene and pyrrole.[4] The $Cd(NH_3)_2Ni(CN)_4$ host lattice, however, does not take three-dimensional network but takes a lamellar stacking of the metal cyanide sheets with the ammonia molecules protruding from Cd atoms.[5)]

The thiophene clathrate $\mathrm{Cd(en)Ni(CN)_4.2C_4H_4S}$ (II) was prepared as bright yellow crystals by the method similar to that for I but a thiophene-toluene mixture was used as the organic phase. Anal. Found: C, 31.14; H, 2.57; N, 18.01; Cd, 22.89; Ni, 12.65%. Calcd for $\mathrm{C_{14}H_{16}N_6S_2CdNi}$: C, 33.39; H, 3.20; N, 16.69; Cd, 22.32; Ni, 12.51%. The pyrrole clathrate $\mathrm{Cd(en)Ni(CN)_4.2C_4H_4NH}$ (III) was prepared as bright yellow crystals similarly by using liquid pyrrole as the organic phase. Anal. Found: C, 34.54; H, 3.69; N, 24.35; Cd, 24.46; Ni, 11.68 %. Calcd for $\mathrm{C_{14}H_{18}N_8CdNi}$: C, 35.82; H, 3.86; N, 23.87; Cd, 23.94; Ni, 11.66%.

The powder x-ray diffraction data and preliminary precession photographs of single crystals were indexed to the tetragonal sytems with the unit cell dimensions a = 7.67 A and c = 7.90 A for II, and a = 7.62 A and c = 7.73 A for III, respectively. In Table 1 the powder diffraction data are shown. In Table 2 the unit cell

Table 1. Powder x-ray diffraction data.

Cu-Kα, Ni-filterd, GM-counter

$\mathrm{Cd(en)Ni(CN)_4.2C_4H_4S}$ tetragonal: a = 7.67 A and c = 7.90 A					$\mathrm{Cd(en)Ni(CN)_4.2C_4H_4NH}$ tetragonal: a = 7.62 A and c = 7.73 A				
2θ	I	d_{obs}	(hkl)	d_{calc}	2θ	I	d_{obs}	(hkl)	d_{calc}
11.21	77	7.89_2	(001)	7.89_6	11.42	100	7.74_8	(001)	7.72_6
11.52	10	7.68_1	(100)	7.67_2	11.62	23	7.61_5	(100)	7.61_5
16.35	37	5.42_1	(110)	5.42_5	16.48	42	5.37_9	(110)	5.38_5
19.87	83	4.46_8	(111)	4.47_1	20.12	95	4.41_5	(111)	4.41_9
22.51	100	3.95_0	(002)	3.94_8	23.02	100	3.86_4	(002)	3.86_7
23.18	21	3.83_7	(200)	3.83_6	23.41	22	3.80_0	(200)	3.80_8
26.00	20	3.42_7	(210)	3.43_1	26.23	42	3.39_7	(201)	3.41_6
27.93	22	3.19_4	(112)	3.19_2				(210)	3.40_6
33.17	22	2.70_3	(220)	2.71_7	33.34	45	2.68_7	(220)	2.69_3
34.06	36	2.63_2	(003)	2.63_2	34.80	50	2.57_8	(003)	2.57_8
34.72	7	2.58_4	(212)	2.58_9	36.85	5	2.43_9	(103)	2.44_2
35.12	24	2.55_5	(300)	2.55_7	37.41	5	2.40_4	(310)	2.40_8
37.00	11	2.43_0	(301)	2.43_3	38.77	22	2.32_3	(113)	2.32_5
			(310)	2.42_6	39.27	11	2.29_7	(311)	2.29_8
37.97	11	2.37_0	(113)	2.36_8	40.93	16	2.20_5	(222)	2.21_1

dimensions of I, II and III, and those of the corresponding Hofmann-typ clathrates are compared. The c-dimensions of the both series of clathrates decrease in the order of guest species, benzene, thiophene and pyrrole. The c-dimension of the en-bridged host lattice is always smaller than that of the Hofmann-type host lattice for the same guest species. That of III, 7.73 A, is still longer than 7.68 A, the Pt-en-Pt length in $[Pt(acac)(CH_3)_3]_2en$. These facts give an idea that the equilibrium between the bridging force of en and the host-guest repulsive force rules the c-dimension of the en-bridged host clathrate where the length of Cd-en-Cd bridge holds a flexibility within a range 7.73 - 8.06 A depending upon the guest species. This idea is supported by another experimental fact that the en-bridged host can never enclathrate aniline molecule the diameter of which is too large for the en-bridged structure if the NH_2 group of aniline is taken into account.

Table 2. The unit cell dimensions. (A)

Host	Guest	$C_6H_5NH_2$	C_6H_6	C_4H_4S	C_4H_4NH
$Cd(en)Ni(CN)_4$	a		7.68	7.67	7.62
	c		8.06	7.90	7.73
$Cd(NH_3)_2Ni(CN)_4$	a	7.56	7.56	7.60	7.61
	c	8.66	8.32	8.22	8.13

In spite of the C_{2v} symmetry of thiophene and pyrrole molecules, the crystals of II and III contain only one formula unit per unit cell as well as those of I do with the D_{6h} symmetry of benzene molecule. The tetragonal symmetry of the crystals for II and III with these unit cell constituents can be rationalized if one assumes (i) an arrangement of the C_{2v} axis parallel to the c-axis of crystal, (ii) a statistically random orientations of the C_{2v} axes, or (iii) a rapid molecular motion about an axis perpendicular to the aromatic ring. The last case is rather improbable, because the rigid thiophene and the almost rigid pyrrole molecules have been observed for the corresponding Hofmann-type clathrates at room temperature by wide-line ^{1}H-NMR.6)

No significant effects of the host lattice contraction were observed in the infrared spectra of II and III compared with that of I. The wave numbers of bands assigned to the host lattice modes were almost indifferent among I, II and III.

Table 3. The infrared bands.[*1] (cm^{-1})

I	I-1	I-2	I-3	II	III	I'	Assignment[*2]
					3348 vs		pyrrole
3360 s 3314 m 3294 s 3258 m	2492 s 2466 wsh 2418 m	3376 m 3325 m 3282 wsh	2492 s 2462 w 2416 m	3357 m 3310 wsh 3293 m 3254 vw	3360 m 3311 s 3300 msh 3254 s	3375 s 3316 s	NH_2 asym. & sym. str.
3072 w 3055 w 3019 m	3073 m 3055 w 3019 m	2282 m	2284 m 2272 w 2260 w				benzene
					3100 vw		pyrrole
				3090 w			thiophene
2966 w 2958 w 2908 m 2864 w	----[*3] ---- ---- ----	2971 m 2911 m 2867 w	---- ---- ---- ----	2964 w 2905 m 2862 w	2968 w 2944 wsh 2932 w 2913 w 2870 w	2974 w 2906 m 2886 w	CH_2 asym. & sym. str.
2155 s 2146 s	2144 s[*4]	2152 s[*4]	2152 s[*4]	2155 s 2146 s	2154 s 2145 s	2154 s	CN str.
1592 s	1176 s	1585 s	1175 s	1590 s	1590 s	1589 s	NH_2 scic.
					1537 s		pyrrole
				1507 vw			thiophene
1479 s	1478 s	1325 m	1329 s				benzene
1462 s	----	1460 s	----	1463 w	1466 w	1451 m	CH_2 scic.
					1452 w		pyrrole
					1419 w		pyrrole
				1410 w			thiophene
1330 w	1332 w	(1325 m)[*5]	(1329 s)	1330 w	1337 w	1312 m	CH_2 wag
1320 wsh		1268 w	1260 w				benzene
1283 vw		1278 vw	1286 vw			1270 w	CH_2 twist
				1252 m			thiophene
					1244 vw		pyrrole
1148 w	1147 m	823 m	823 m				benzene
					1140 m		pyrrole
1115 vw 1089 s 1063 vw	845 s	1112 vwsh 1088 s 1062 vwsh	845 s	1113 vwsh 1083 s 1065 vwsh	1088 s	1117 w 1062 w	NH_2 wag
					1098 s 1076 s 1048 s 1028 s		pyrrole
				1026 s			thiophene
1042 s 1035 m	1040 s 1033 m	815 m 810 m	812 m 807 m				benzene
1020 s	(691 vs)	1018 s	688 m	1019 s	1019 s	1017 s	NH_2 twist
997 s	999 vs	993 vs	998 vs	995 vs	997 s	992 vs	CN str. of en
958 s	(691 vs)	956 s	699 m	957 s	958 m	957 s	NH_2 twist
					883 vw 867 w		pyrrole
856 vw	(845 s)	854 vw	(845 s)	855 vw	850 w	857 w	CH_2 rock

(Table 3. continued)

774 vw	763 vw	772 vw 758 vw	754 vw			759 vw	skeletal?
					744 vs		pyrrole
				734 s			thiophene
				713 s			thiophene
690 vs 672 s	691 vs	509 s	510 s				benzene
667 wsh		667 w					skeletal?
					641 vw		pyrrole
		615 vw	615 w			625 wbr	skeletal?
				608 vw			thiophene
585 s 550 sbr 462 s	(417 sbr)	585 s 551 sbr 467 s	(423 sbr)	552 mbr 466 m	548 sbr 466 m	585 m 560 vw 465 s	NH_2 rock
				458 m			thiophene
451 w 444 wsh 428 ssh 420 sbr	448 vwsh 435 wsh 417 sbr	449 w 440 wsh 430 vs 420 vs	449 vw 425 mbr 423 sbr	449 vw 430 msh 424 sbr	450 vwsh 442 wsh 424 sbr	448 vwsh 440 wsh 425 sbr	Ni-CN

*1. Those were measured in 4000 - 400 cm^{-1} region for the Nujol and the HCB (I, II, III and I') mulls.

*2. Those assigned to the ND_2 modes and the C_6D_6 modes are listed in the lines of the corresponding NH_2 and C_6H_6 modes respectively.

*3. Those were hidden by the Nujol's bands.

*4. Doublets may be observed by high-resolution measurements.

*5. The stronger band in parenthesis appears to overlap the corresponding band.

The bridging en molecule in its trans configuration in I was suggested from the infrared spectrum simpler than those observed for the en-chelate complexes.[1)] The en-bridged structure has been established by single crystal x-ray diffraction method.[2)] The spectral features of I, II and III, however, are not so simple as those observed for the $M(en)X_2$ complexes (M = Cd, Hg; X = Cl, Br, SCN) in which the mutual exclusions of infrared and Raman bands have been established to support the trans configuration of en molecule.[7)] The considerably complex structure of infrared bands was observed in the 1120 - 400 cm^{-1} region for I, II and III. Therefore the infrared assignments were reexamined by comparison of the spectra among those of I, $Cd(en\text{-}d_4)Ni(CN)_4.2C_6H_6$ (I-1), $Cd(en)Ni(CN)_4.2C_6D_6$ (I-2), $Cd(en\text{-}d_4)Ni(CN)_4.2C_6D_6$ (I-3), and $Cd(en)Ni(CN)_4$ (I') which is the residual host lattice obtained after removing the guest benzene molecules completely from I. In I-1 and I-3, en-d_4 refers to $ND_2CH_2CH_2ND_2$.

According to the present results, the previous assignments[1)] should be revised as shwon in Table 3. The bands sensitive to the deuteration of the NH_2 group of en displayed such complex features as follows: (i) the strong bands at 1020 cm^{-1} and 958 cm^{-1} in I disappeared in the en-d_4 specimens but the corresponding ND_2 band was a singlet at 688 cm^{-1}, (ii) the band at 1089 cm^{-1}, tentatively assigned to the NH_2 wag mode, disappeared in I' but a pair of weak satellites at 1117 cm^{-1} and 1062 cm^{-1} remained, and (iii) the strong band at 550 cm^{-1} in I disappeared in I' Besides them, a band at ca. 465 cm^{-1} was observed for all the specimens except two en-d_4 ones. These facts suggest that complex couplings occur among the NH_2 modes and that these couplings are sensitive to the host-guest interactions which may affect the effective symmetry of the en molecule in crystals.

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