The amount of snow white carbon monofluoride produced averaged 0.2–0.3 g per run. The material remaining on the lower nickel screen (F) was found to be carbon monofluoride of lower stoichiometry $\sim CF_{0.68}$ as determined by its infrared spectra and X-ray powder pattern. If finely powdered graphite is substituted for the flake graphite, more surface contact with the plasma occurs and as expected, the reaction proceeds more rapidly. However, it is difficult to keep the finer particles fluidized with the 30 cm^3/min fluorine flow because they stick to the upper screen (F) out of the plasma region. If this new synthesis is run on a larger industrial scale, finer particles will be used and the apparatus will be appropriately adapted. One other change would be necessary to perfect this system. The Vycor particle return (D) and the Vycor inlet to the reactor tube (A) is attacked by the fluorine plasma to such an extent that they may only be used for two or three runs. This attack removes a very significant amount of fluorine atoms from the plasma and this efficiency loss results in longer reaction times. Fabrication of these parts of alumina, although expensive, would completely eliminate this problem.

Carbon Monofluoride.—The total yield of carbon monofluoride was 80% based on a mass balance study of the system. The major by-product, carbon tetrafluoride, was recovered in the U-trap. A 10% yield of the snow white carbon monofluoride of composition $CF_{1.19}$ was obtained. This white material was recovered in the particle trap as previously indicated. Carbon tetrafluoride is the principal by-product and accounts for essentially all of the remaining 20%. *Anal.* Found: C, 34.2; F, 64.75. Calculated empirical formula: $CF_{1.19\pm0.04}$.

The infrared spectra of the samples consisted of a strong carbon–fluorine stretch at 1217 cm^{-1} and two medium bands at 1342 and 1072 cm^{-1} which are due to asymmetric and symmetric stretching vibrations of the peripheral CF_2 groups. A 332 cm^{-1} far-infrared band was observed and is due to bending in CF_2 groups.

The X-ray powder pattern contained nine lines. The observed "*d*" spacings (Å) were 5.80 vs, br; 3.4 w; 2.85 diffuse, m; 2.55 w; 2.2–2.25 vs, br; 1.83 w; 1.71 w; 1.66 w; and 1.289 s.

Results and Discussion

The plasma technique provides a new synthesis for poly(carbon monofluoride) $(CF_x)_n$. The infrared spectrum is in substantial agreement with that reported by Rudorff and Brodersen[10] and by workers at Rice University.[1] The X-ray powder pattern "*d*" spacings are in agreement with those of workers at Rice University[1] and in rough agreement with the spacings of 6.0, 2.23, and 1.30 Å reported by Palin and Wadsworth.[11] We have noted that the lines change slightly with fluorine content. The elemental analysis is consistent with the carbon monofluoride structure and corresponds to a stoichiometry of $CF_{1.19}$. This new synthesis for poly(carbon monofluoride) has several advantages over previous high-temperature syntheses. A much lower temperature was used. Measurement revealed that the gas temperature of the plasma is less than 150°. The amount of energy required to generate the plasma (480 W) is much less than is required to maintain a furnace of corresponding size in the 600° temperature range. Also it may prove easier to generate a larger plasma than to keep a large reactor uniformly in the rather narrow temperature range required for the thermal synthesis of the snow white $CF_{1.1}$. The fluidized bed method also avoids the necessity for batch processing since graphite may be continually added or withdrawn from the system.

This synthesis provides an example of the use of a fluidized bed plasma reactor design to prepare an industrially important material. This synthesis also demonstrates some of the advantages of a fluorine plasma in preparative fluorine chemistry.

Acknowledgments.—This work was supported by the National Science Foundation.

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[10] W. Rudorff and R. Brodersen, *Z. Naturforsch.*, **126**, 595 (1957).

[11] D. E. Palin and K. D. Wadsworth, *Nature (London)*, **162**, 925 (1948).

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Benzene Clathrates with a Novel Kind of Metal Complex Host Lattice. $Cd(en)Cd(CN)_4\cdot 2C_6H_6$ and $Cd(en)Hg(CN)_4\cdot 2C_6H_6$

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Two new benzene clathrate compounds, $Cd(en)Cd(CN)_4\cdot 2C_6H_6$ (I) and $Cd(en)Hg(CN)_4\cdot 2C_6H_6$ (II), have been prepared, which appear to have a new kind of host structure. These clathrates were prepared as colorless crystals by contacting benzene with an aqueous solution of $Cd(en)_3Cl_2$ mixed with a solution of $K_2Cd(CN)_4$ or $K_2Hg(CN)_4$. *Anal.* Calcd for $C_{18}H_{20}N_6Cd_2$: C, 39.66; H, 3.70; N, 15.41; Cd, 41.23. Found: C, 39.68; H, 3.65; N, 15.30; Cd, 40.40. Calcd for $C_{18}H_{20}N_6CdHg$: C, 34.13; H, 3.18; N, 13.27; Cd, 17.75; Hg, 31.67. Found: C, 34.09; H, 3.15; N, 13.55; Cd, 17.89; Hg, 32.1. The chemical composition is analogous to that of the known clathrate Cd(en)Ni-

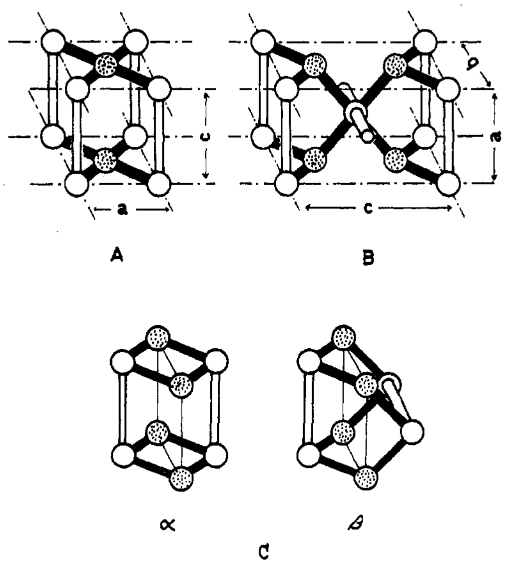

Figure 1.—(A) The tetragonal unit cell of $Cd(en)Ni(CN)_4\cdot 2C_6H_6$, (B) the proposed pseudotetragonal (orthorhombic) unit cell of $Cd(en)M(CN)_4\cdot 2C_6H_6$ (M = Cd or Hg), and (C) cavities for guest molecules: open circles, octahedral Cd; shaded circles, square-planar Ni and tetrahedral Cd or Hg; open columns, en; solid columns, CN. For $Cd(en)Ni(CN)_4\cdot 2C_6H_6$ a = 7.675 and c = 8.056 Å.[2]

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TABLE I

THE VIBRATIONAL BANDS OF $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$ (I), $Cd(en)Hg(CN)_4 \cdot 2C_6H_6$ (II), AND $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$ (III)

I	II	III[a]	Tentative assignment
		Host Species	
3358 w	3353 mw	3360 w	NH_2 asym and sym str
3320 m	3314 ms	3314 m	
3296 w, sh	3295 m	3294 s	
3264 w	3260 m	3258 m	
2966 w, sh		2966 w	CH_2 asym str
2940 w	2956 w, sh	2958 w	
2874 w	2875 w	2908 m	CH_2 sym str
2864 w		2864 w	
2171 s	2171 s	2155 s	
		2146 vs	CN str[b]
$\underline{2174}$	$\underline{2176}$	$\underline{2162}$	
$\underline{2170}$	$\underline{2172}$	$\underline{2152}$	
1589 s	1588 s	1592 s	NH_2 scis
1462 m	1463 m	1462 m	CH_2 scis
1372 vvw	1372 vvw	1371 vvw	?
1325 m	1327 m	1330 w	CH_2 wag
		1283 vvw	CH_2 twist?
1074 s	1077 ms	1089 s	NH_2 wag
1001 s	1003 vs	1020 s	NH_2 twist
980 s	980 m	997 vs	CN(en) str
957 w, sh	956 w, sh	958 s	NH_2 twist
944 vw	944 vw		?
		856 vw	CH_2 rock
774 vw, sh		774 vw	?
769 vw	769 vw		
576 m	576 m	585 s	NH_2 rock
522 s	523 s, br	550 s, br	NH_2 rock
		Guest Benzene	
3076 w	3076 w	3072 w	CH str in plane (E_{1u})
3056 w	3056 vw	3055 w	
3020 w	3023 w	3019 w	CH str in plane (B_{1u})
1961 vw	1969 vw	1972 vw	Combination
1824 vw	1822 vw	1827 vw	Combination
1478 s	1481 s	1479 s	Ring str and def in plane (E_{1u})
1315 vw		1315 vw	Ring str in plane (B_{2u})
1147 vvw	1147 vvw	1147 w	CH bend in plane (B_{2u})
1036 s	1035 s	1042 m	CH bend in plane (E_{1u})
		1035 m	
688 vs	688 s, sh	690 vs	
682 vs	684 v, s	672 s	CH bend out of plane (A_{2u})
677 s, sh	677 s, sh		

[a] The previous data[1] should be revised. For details of the revised assignments see T. Iwamoto and Y. Ohtsu, *Chem. Lett.*, 463 (1972). [b] The wave numbers of Raman bands are underlined.

TABLE II

THE POWDER X-RAY DIFFRACTION DATA[a]

$Cd(en)Cd(CN)_4 \cdot 2C_6H_6$[b]					$Cd(en)Hg(CN)_4 \cdot 2C_6H_6$[c]				
2θ	I	d_{obsd}	(hkl)	d_{calcd}	2θ	I	d_{obsd}	(hkl)	d_{calcd}
10.69	20	8.27_6	(100)	8.27_1	10.76	37	8.23_7	(100)	8.23_0
12.13	68	7.29_6	(101)	7.29_4	12.17	50	7.27_2	(101)	7.26_2
					15.25	8	5.81_0	(110)	5.82_1
15.65	44	5.66_2	(102)	5.65_6	15.73	48	5.63_4	(102)	5.62_7
18.99	100	4.67_3	(112)	4.66_9	19.09	100	4.64_9	(112)	4.64_7
20.25	10	4.38_5	(103)	4.38_2	20.36	8	4.36_2	(103)	4.36_1
21.49	100	4.13_5	(200)	4.13_6	21.56	69	4.12_2	(200)	4.11_5
22.92	52	3.88_0	(004)	3.87_6	23.04	14	3.86_0	(004)	3.85_8
24.11	6	3.70_6	(210)	3.69_9	24.11	14	3.70_6	(210)	3.68_1
					24.46	5	3.63_9	(202)	3.63_1
24.76	8	3.59_6	(211)	3.59_7	24.91	5	3.57_4	(211)	3.58_0
26.72	46	3.33_6	(212)	3.33_8	26.82	61	3.32_4	(212)	3.32_0
27.63	24	3.22_8	(114)	3.23_2	27.74	16	3.21_6	(114)	3.21_5
29.70	26	3.00_8	(213)	3.00_8	29.84[d]	17	2.99_3	(213)	2.99_3
33.6–30.75 broad band					30.72	7	2.90_7	(220)	2.91_0
31.63	42	2.82_9	(204)	2.82_8	31.81	56	2.80_9	(204)	2.81_5
32.48	24	2.75_7	(300)	2.75_7	32.64	31	2.74_2	(300)	2.74_3
33.03	14	2.71_2	(301)	2.71_4	33.14	12	2.70_2	(301)	2.70_1
33.48	26	2.67_6	(214)	2.67_6	33.68	35	2.66_0	(214)	2.64_9
34.55	8	2.59_6	(302)	2.59_7	34.72	11	2.58_1	(302)	2.58_5
			(312)	2.47_8				(205)	2.46_9
36.27	42	2.47_7			36.42	35	2.46_5		
			(205)	2.47_3				(312)	2.46_6
37.86	12	2.37_6	(215)	2.37_6	38.03	17	2.36_4	(215)	2.36_5
38.06	12	2.36_4	(116)	2.36_4	38.41	15	2.34_1	(116)	2.35_5
38.58	25	2.33_4	(224)	2.33_4	38.73	37	2.32_3	(224)	2.32_3
39.34	8	2.29_0	(320)	2.29_4	39.47	17	2.28_2	(320)	2.28_3

[a] Cu Kα, Ni filtered, and GM counter. [b] Pseudotetrahedral (orthorhombic) $a = b = 8.27_1$ and $c = 15.50_3$ Å. [c] Pseudotetrahedral (orthorhombic) $a = b = 8.23_0$ and $c = 15.43_0$ Å. [d] In the case of $Cd(en)Hg(CN)_4 \cdot 2C_6H_6$, angles larger than 29° were obtained from Cu Kα_1 peaks.

$(CN)_4 \cdot 2C_6H_6$ (III) the structure of which has been elucidated in detail by spectroscopy and X-ray diffraction.[2,3] This structure consists of sheets of square-planar $Cd(NC)_4$ and $Ni(CN)_4$ arrays in which the CN ligand bridges adjacent Cd and Ni atoms. The sheets are held together by en bridges, which span the Cd atoms in adjacent sheets and lead to an octahedral coordination of Cd. Each guest benzene molecule is enclathrated in a cavity surrounded by $8 \times {}^1/_4$CN, $2 \times {}^1/_4$en, $4 \times {}^1/_8$Cd, and $4 \times {}^1/_8$Ni (Figure 1A). The crystals of III belong to the tetragonal space group *P4/m* with one formula weight per unit cell.[3] It is apparent that if I and II were to adopt the structure of III, $Cd(CN)_4^{2-}$ and $Hg(CN)_4^{2-}$ would have to adopt a square-planar structure which represents a large change from the tetrahedral structure of these ions in solution.

The catena μ nature of the en and the CN is revealed by their ir spectra (Table I). The bands assigned to the en molecule vibrations showed the features similar to that of III in which the en-bridging structure has been established. The CN stretch bands at 2171 cm^{-1} for both I and II are higher by *ca.* 35 cm^{-1} than those observed for $Cd(CN)_4^{2-}$ and $Hg(CN)_4^{2-}$ in the aqueous solution.[4] Such an increase in wave number of the CN stretch band due to the biterminal bridging of the CN group has been observed for many compounds.[5]

Raman spectra in the CN stretch region were observed for polycrystalline samples of I and II sealed in glass capillaries which were illuminated with 5145-Å Ar ion laser excitation. A broad doublet with two barely resolved maxima was observed. One of these at lower frequency coincides with the ir band. These results are consistent with the selection rules for tetrahedral $Cd(CN)_4$ and $Hg(CN)_4$ in I and II, respectively.

Preliminary X-ray precession photographs taken for the single crystals of I and II support their tetragonal or pseudotetragonal symmetry with the unit cell dimensions $a = b = 8.27$ and $c = 15.50$ Å for I, and $a = b = 8.23$ and $c = 15.43$ Å for II, respectively. The densities 1.68 and 1.98 g/cm³ for I and II measured in benzene–methyl iodide mixtures are in good agreement with the calculated values 1.72 and 2.02 from the unit cell volumes containing two formula weights. The powder diffraction lines were assigned as listed in Table II.

From these observations a structure can be visualized for the host lattice in which tetrahedral $Cd(CN)_4$ or $Hg(CN)_4$ moieties replace the square-planar $Ni(CN)_4$ in III. As with the structure of III one metal Cd or Hg is tetracoordinate to four CN carbons and another metal Cd is hexacoordinate to four μ-CN ni-

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(2) T. Iwamoto, *Inorg. Chim. Acta*, **2**, 269 (1968).

(3) T. Miyoshi, T. Iwamoto, and Y. Sasaki, *Inorg. Nucl. Chem. Lett.*, **6**, 21 (1970); *Inorg. Chim. Acta*, **6**, 59 (1972).

(4) R. A. Penneman and L. H. Jones, *J. Inorg. Nucl. Chem.*, **20**, 19 (1961).

(5) D. F. Shriver, S. A. Shriver, and S. E. Anderson, *Inorg. Chem.*, **4**, 725 (1965); *cf.* K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970, p 186.

trogens and two μ-en nitrogens. As illustrated in Figure 1B, this could occur by a rectangular twist of the CN-linked planes at alternate tetrahedral sites, with each octahedral Cd linked by μ-en along the axes perpendicular to the CN-linked planes. This structure has an orthorhombic symmetry with three perpendicular twofold axes, although the $a = b$ relationship of unit cell dimensions has been observed. There are two kinds of cavities, α and β, for the guest molecules in this structure. As shown in Figure 1C, the α cavity is a rectangular box, while the β cavity is biprismatic. Both cavities have nearly equal volumes and the same framework components. From the stoichiometry, each cavity may enclathrate a benzene molecule. These cavities have more tunnel-like character than that found for III, since the span of the en bridge is longer by *ca.* 0.2 Å in I and II than in III. The analyses of single-crystal diffraction data are in progress to determine the positions of benzene molecules.

The ir bands assigned to the benzene molecule vibrations in I and II display the following features which are different from those of III: (i) the intensity of the B_{2u} (CH bend in plane) bands of I and II has decreased remarkably from that of III, (ii) the E_{1u} (CH bend in plane) doublet of III has coalesced into a singlet for I and II, and (iii) the doublet B_{2u} (CH bend out of plane) mode of III split into a triplet for I and II. Thus the vibrational data for both CN stretching and the various benzene C–H modes agree with the proposal that the new clathrates have structures significantly different from that of $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$.

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