Cyclohexadienyl Radicals in γ-Irradiated *catena*-μ-Ethylenediaminecadmium(II) *catena*-Tetra-μ-cyanomercurate(II)-Benzene (1/2) and the Analogous Clathrates

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Cyclohexadienyl radicals produced by γ-ray irradiation are thermally stable up to 423 K in the mother benzene clathrates $Cd(en)Hg(CN)_4 \cdot 2C_6H_6$, $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$, $Cd(tn)Hg(CN)_4 \cdot 2C_6H_6$, and $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_6$. However, no thermally stable $C_6H_7\cdot$ radicals have been observed in $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ and $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$ even immediately after irradiation. The ESR spectra of $C_6H_7\cdot$ show the hyperfine splitting constants of the methylene, para, ortho, and meta protons 48, 13, 9, and 3 G, respectively.

The cavity for a guest molecule is expected to be a good reservoir of chemically unstable species in the host structure of a clathrate compound when the interaction between the guest and the host is negligibly weak. As has been demonstrated in the crystal structures determined by X-ray diffraction,[1] the guest benzene molecules in Hofmann type and the analogous benzene clathrates are individually imprisoned in the cavities surrounded by three-dimensional bridged metal complex host structures. Each benzene molecule apprears to be an isolated molecule trapped in a container of the volume slightly larger than that of the molecule itself. If a chemically unstable radical is once trapped in the container surrounded by an inactive wall, the radical may survive for a long time even at high temperature. From this point of view the present authors undertook to produce paramagnetic radicals from the guest species by γ-ray irradiation of diamagnetic Hofmann type and the analogous clathrates, and to investigate the stability of the radicals in the mother clathrates. A preliminary communication[2] gave a brief account of the thermal stability of the cyclohexadienyl $C_6H_7\cdot$ radicals up to 423 K which were produced by γ-irradiation of $Cd(en)M(CN)_4 \cdot 2C_6H_6$ (M=Cd or Hg) clathrates. This paper reports on detailed experimental results obtained from γ-irradiated $Cd(diam)M(CN)_4 \cdot 2C_6H_6$ (diam=en, tn, or $(NH_3)_2$; M=Cd, Hg, or Ni) clathrates, and on the correlation of clathrate structure with stability of the radicals.

Experimental

The benzene clathrates examined are as follows: $Cd(en)Hg(CN)_4 \cdot 2C_6H_6$,[3] $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$,[3] $Cd(tn)Hg(CN)_4 \cdot 2C_6H_6$,[15] $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_6$,[4] $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$,[5] and $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$.[6] $Cd(en)Hg(CN)_4 \cdot 2C_6D_6$, $Cd(en)Hg(CN)_4 \cdot 2C_4H_5N$, and $Cd(en)Hg(CN)_4$ were also irradiated for the sake of comparison.

The polycrystalline specimens were evacuated at 195K and sealed in silica ampoules at 1.3×10^{-3} Pa. The sealed specimens were irradiated with 6.5×10^3 J/kg ^{60}Co γ-rays at liquid nitrogen temperature. The irradiated specimens were kept at liquid nitrogen temperature till their ESR measurements. The ESR spectra were recorded on a JEOL-JES-PE-3X spectrometer with an X-band frequency and a field modulation of 100 kHz in the temperature range 77—423 K.

Results and Discussion

General Features of the ESR Spectra. At liquid nitrogen temperature all the irradiated specimens gave ESR signals due to radicals produced from the host constituents. Also observed were strong signals due to organic radicals centered at $g=2.003$ for the pyrrole and the benzene clathrates except for $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$ and $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$. The signals due to the host constituents are thought to be those of the hot ions Cd(I) and Hg(I),[7] H·, and other unidentified radicals. These signals were observed over a wide (0.2 T) range of magnetic field with intensities far lower than those of the organic radicals as shown in Fig. 1. Their features differ with specimen, depending on host constituent. As the temperature is increased to 200 K, the signals due to the host constituents decay showing their thermal instability. Furthermore, the hyperfine structure in signals centered at $g=2.003$ becomes more clearly resolved with increasing temperature. For the benzene clathrates, the strong absorptions are assigned to cyclohexadienyl $C_6H_7\cdot$ radicals produced from the

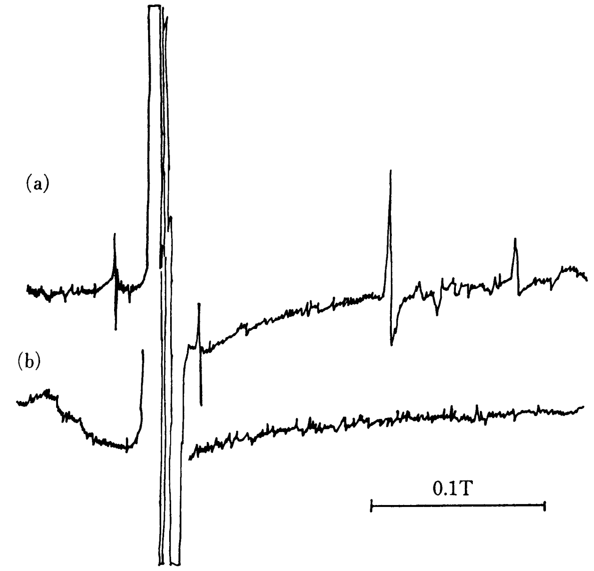


Fig. 1. ESR Spectra of the irradiated $Cd(en)Hg(CN)_4 \cdot 2C_6H_6$ measured (a) at 100 K and (b) at 200 K. The strongest absorption centered at $g=2.003$ in due to organic radicals, and it is omitted is (b).

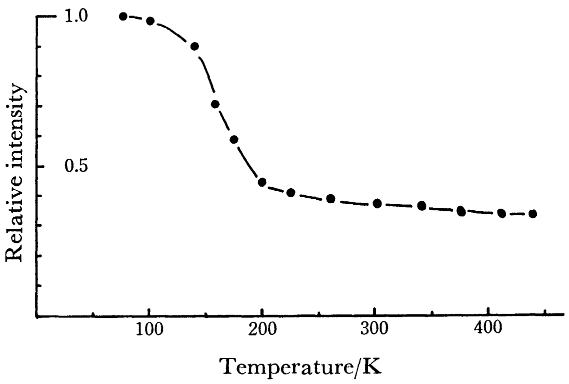


Fig. 2. Temperature dependence of the relative ientensity of the $C_6H_7\cdot$ absorption in the ESR spectrum of the irradiated $Cd(en)Hg(CN)_4\cdot 2C_6H_6$. The intensity was measured at each temperature with 1 h interval successively from 77 to 423 K.

enclathrated benzene molecules. The apparent intensity of the $C_6H_7\cdot$ absorption decreases strongly with increasing temperature up to 200 K where it is approximately 40% of that at liquid nitrogen temperature, the decrease becoming more gradual from 200 to 423 K (Fig. 2). The spectral linewidths become narrower with increasing temperature. Except for the two cases mentioned above, the thermal behavior of the $C_6H_7\cdot$ ESR signal is the same for all the irradiated benzene clathrates. Above 423 K the host metal complex begins to decompose thermally in the sealed ampoules.

The irradiated pyrrole clathrate also gave ESR signals due to organic radicals produced from the guest pyrrole. The spectral analysis, however, has not yet been completed.

Spectral Assignment of $C_6H_7\cdot$. The ESR spectrum assigned to $C_6H_7\cdot$ has a main triplet of the intensity ratio 1: 2: 1 with about 48 G splitting, where $G=10^{-4}$ T. The 48 G splitting of the triplet has been observed by a number of workers.[8–12] The 1: 2: 1 intensity ratio excludes significant formation of $C_6H_5\cdot$ observed for irradiated neat benzene.[8] The triplet is due to the hyperfine coupling of the electron spin with two methylene protons. The irradiated benzene-d_6 clathrate $Cd(en)Hg(CN)_4\cdot 2C_6D_6$ gave a broad doublet (*ca.* 40 G) structure in its ESR spectrum at low temperature. With increasing temperature the spectra became so complicated that the hyperfine structures except for a doublet (41.5 G) with a triplet (7.2 G) substructure could hardly be interpreted. The doublet may be due to the proton in the methylene position of $C_6D_6H\cdot$ and the triplet to the deuteron in the same position.[10] According to these observations, the formation scheme of $C_6H_7\cdot$ in the irradiated benzene clathrate is suggested as follows:

$$\text{HostH} \xrightarrow{\gamma\text{-rays}} \text{Host}\cdot + \text{H}\cdot$$

$$\text{H}\cdot + C_6H_6 \longrightarrow C_6H_7\cdot$$

The H· may be produced from the diamine or diammine ligand of the host metal complex.

Each component of the 48 G triplet shows a pseudoquartet structure with a 13 G splitting between the inner pair and a 9 G splitting between the outer and the inner components. A third hyperfine splitting (hfs) of a triplet (3 G) becomes clearer in each component of the pseudoquartet with increasing temperature above 200 K owing to the motional narrowing of linewidths. As has been demonstrated by wide-line ^{1}H-NMR of the benzene clathrates,[13] the enclathrated benzene molecules begin to reorientate about the molecular sixfold axis at 125 K and rotate with little hindrance above 160 K. The motional behavior of the $C_6H_7\cdot$ resembles that of the benzene molecule judging from the narrowing of ESR linewidths.

No radicals other than $C_6H_7\cdot$ have been identified, although in some cases broad and very weak signals are observed which overlap with the $C_6H_7\cdot$ absorption up to 323 K.

The Hfs Constants of $C_6H_7\cdot$. According to the calculations by Shida and Hanazaki,[12] the hfs constants for the *p*-proton and the *o*-protons of $C_6H_7\cdot$ are 11.2 G and 10.6 G, respectively. Morokuma *et al.*[14] reported another set of −11.4 and −11.1 G. However, the

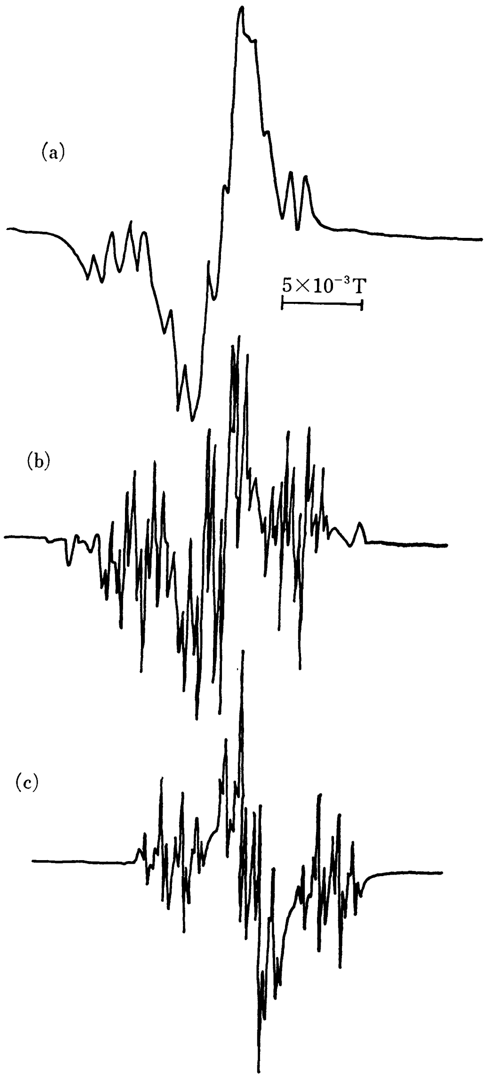


Fig. 3. ESR Spectra of the irradiated $Cd(en)Cd(CN)_4\cdot 2C_6H_6$ measured (a) at 77 K and (b) at 293 K, and that of the irradiated $Cd(en)Hg(CN)_4\cdot 2C_6H_6$ measured (c) at 373 K.

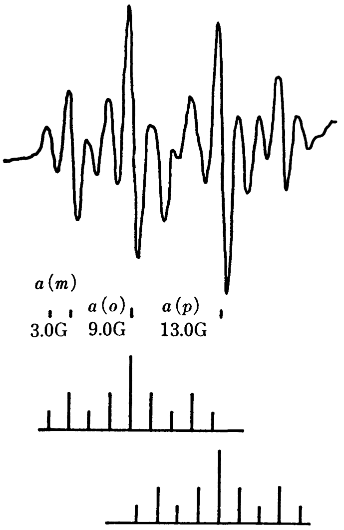
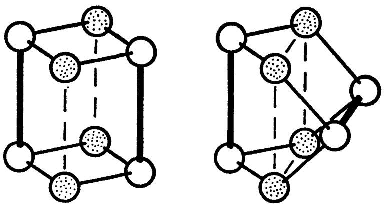


Fig. 4. The ESR hyperfine structure of $C_6H_7\cdot$ in the irradiated $Cd(en)Hg(CN)_4\cdot 2C_6H_6$ observed at 423 K. The lower field side of the 48.3 G main triplet is shown along with Fessenden-Schuler's scheme.[11]

difference between these hfs constants has never been observed for $C_6H_7\cdot$ produced by the irradiation of neat benzene or benzene solutions because of the thermal instability of the $C_6H_7\cdot$ radicals in the matrices used. The previous workers assigned the observed pseudo-quartet to the hfs due to the three protons at the para and ortho positions with nearly the same hfs constants. As shown in Fig. 3 for the present clathrates, it is possible to observe the ESR spectrum of $C_6H_7\cdot$ with a fairly good resolution up to such a high temperature that all of the unstable species collapse and the intermolecular dipole interactions become negligible. Although the resolution is still not high enough to make all the hfs components split clearly, we can discriminate between the hfs constants of the *p*-proton and the *o*-protons (Fig. 4). It is clearly seen that the spectrum of $C_6H_7\cdot$ in the irradiated $Cd(en)Hg(CN)_4\cdot 2C_6H_6$ is composed of a main triplet due to methylene protons (*a*(methylene)=48.3 G), a doublet due to the *p*-proton (*a*(*p*)=13.0 G), a triplet due to *o*-protons (*a*(*o*)=9.0 G), and a triplet due to *m*-protons (*a*(*m*)=3.0 G). The magnitude of the respective splitting constants is nearly the same for the $C_6H_7\cdot$ radicals in all the irradiated benzene clathrates. These observations do not agree with the previous observations with low resolution spectra for which approximately the same hfs constants were assigned for the *p*-proton and *o*-protons. However, the present results are in good agreement with those of Fessenden and Schuler.[11] They observed the ESR spectrum of liquid 1,4-cyclohexadiene during the course of irradiation with 0.4 μA of 2.8 mV electrons. Although their spectrum was not displayed, 72 resolved lines were assigned to $C_6H_7\cdot$ with *a*(methylene)=47.71 G, *a*(*p*)=13.04 G, *a*(*o*)=8.99 G, and *a*(*m*)=2.65 G. They observed that the central region of the main triplet splits into two sets of 18 lines owing to the release of degeneracy of the two m=0 states because of the second order effect for the large splitting constant. In the present spectrum of the solid specimen, the 1.5 G linewidth hides the second order splitting (0.69 G), only 13 lines being observed even in the central region. However, the spectrum can be interpreted substantially in terms of the scheme by Fessenden and Schuler.

Clathrates as Chemical Reservoir of Radicals. The $C_6H_7\cdot$ radicals produced in these benzene clathrates are thermally stable up to 423 K and survive for at least a few hours at 423 K. When the irradiated clathrates were kept at liquid nitrogen temperature even after the temperature of the specimen had been raised up to 423 K, the radicals still survived for at least a few weeks. Thus, the host metal complex $Cd(diam)M(CN)_4$ (diam=en, tn, or $(NH_3)_2$; M=Cd or Hg) is an excellent reservoir for the $C_6H_7\cdot$ radicals. However, it should be noted that no ESR spectrum for $C_6H_7\cdot$ was observed for the γ-irradiated $Cd(en)Ni(CN)_4\cdot 2C_6H_6$ and $Cd(NH_3)_2Ni(CN)_4\cdot 2C_6H_6$ even at liquid nitrogen temperature, although signals due to the thermally unstable radicals originating from the host constituents were observed.



(a) (b)

Fig. 5. Two kinds of guest cavities in $Cd(diam)M(CN)_4\cdot 2C_6H_6$ clathrates. (a) Tetragonal or rhombic frame is built up with square-planar $Ni(CN)_4$, or tetrahedral $Cd(CN)_4$ or $Hg(CN)_4$ moieties. (b) Biprismatic frame is possible only with the tetrahedral moieties. Open circle: Cd, dotted circle: M, thick line: diam (en, tn, or $(NH_3)_2$), thin line: CN.

The Hofman type $Cd(NH_3)_2Ni(CN)_4\cdot 2C_6H_6$ and the Hofmann-en type $Cd(en)Ni(CN)_4\cdot 2C_6H_6$ have a host of two-dimensionally extended $CdNi(CN)_4$ sheets containing the square-planar $Ni(CN)_4$ moieties. In the Hofmann type host two ammonia molecules protrude from adjacent sheets at the Cd atoms; in the Hofmann-en type host the protrusions between adjacent sheets are replaced by an ambident en ligand. These hosts have only one kind of guest cavity with a tetragonal or rhombic shape, as is shown in Fig. 5, while the hosts of the other clathrates, which stabilize $C_6H_7\cdot$, have both tetragonally and biprismatically shaped cavities due to the linkages of tetrahedral $Cd(CN)_4$ or $Hg(CN)_4$ moieties.[15] It appears that only the biprismatic cavity is effective in stabilizing $C_6H_7\cdot$. The partial volume of unit cell per benzene molecule was found to be *ca.* 270 Å^3 (Å$=10^{-10}$ m) for the clathrate having biprismatic cavity. It is larger by *ca.* 30 Å^3 for the Hofmann type and Hofmann-en type, which gave no stable $C_6H_7\cdot$. The effective volume of the cavity might also be a critical factor in radical stability.

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