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Magnetic Properties of Aromatic Hydrocarbon-Alkali Metal Salts. II. Anthracene-Alkali Metal Salts

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In a previous paper[1] we have reported that the magnetic susceptibility of the solvent-free biphenyl-potassium salt was paramagnetic and that it exhibited a broad maximum at 130±4°K. This susceptibility can be interpreted approximately by this expression:

$$\chi_M = \frac{2Ng^2\beta^2}{kT}\cdot\frac{1}{3+e^{\delta/kT}} \tag{1}$$

which implies the existence of singlet-triplet dimers. The biphenyl-rubidium and biphenyl-cesium systems also obey the above equation rather than Curie-Weiss law in the higher temperature range. The singlet-triplet separations of these salts are very small in comparison with that of the TCNQ radical salts. In order to investigate whether or not the susceptibilities of the aromatic hydrocarbon radical salts follow the singlet-triplet dimer model, we have measured the static magnetic susceptibilities and the EPR absorption of solid complexes composed of anthracene with sodium, potassium, rubidium, and cesium. In this paper we will discuss qualitatively the structures of the anthracene anion radical solids in comparison with those of the corresponding TCNQ radical salts.

Experimental

These powder salts were prepared in the same way in the previous paper.[1] Anthracene of the scintillation-counter grade was used without further purification. The anthracene was reduced with potassium or sodium in tetrahydrofuran, and with rubidium or cesium in dimethoxyethane, which could dissolve these ion pairs better than tetrahydrofuran. These solutions were then evacuated *in vacuo*, and powder crystals were precipitated. The anion radical salts were titrated with a standard oxalic acid solution, using phenolphtalein as the indicator. The ratios of alkali metal to anthracene were 0.9±0.1 for potassium, rubidium, and cesium. Three samples were obtained for sodium anthracene complexes: $\text{An–Na}_{0.7}$, $\text{An–Na}_{1.0}$, and $\text{An–Na}_{1.5}$. (These formulas represent the complexes in which the ratios of sodium to anthracene are 0.7, 1.0, and 1.5 respectively). Although Holmes-Walker and Ubbelohde[2] have reported their findings as to the magnetic susceptibility and conductivity of $\text{An–Na}_{2.02}$ synthesized in diethyl ether, we could obtain it in tetrahydrofuran. The solids were brown for An–Na and blue-black for the other alkali metal complexes.

Results and Discussion

Temperature Dependence of Magnetic Susceptibility. The measured paramagnetic susceptibilities of the radical salts on 1 mol of anthracene (χ_M) are shown in Fig. 1 as a function of the temperature. The diamagnetic contribution was calculated by Pascal's method ($\chi_M^{\text{An-Na}}=-1.37$, $\chi_M^{\text{An-K}}=-1.45$, $\chi_M^{\text{An-Rb}}=-1.53$, and $\chi_M^{\text{An-Cs}}=-1.65\times10^{-4}$ emu/mol). The magnetic susceptibility of An–K varies with the temperature and exhibits a broad maximum (T_c), as is shown in Fig. 1, which gradually shifts to a higher temperature as the solvent residual in the solid sample decreases. The T_c of An–K (IV), which was evacuated for about one day, is estimated to be 135±5°K. However, in the case of An–K(III) evacuated for about 2 days the susceptibility passes through its maximum at 165±5°K and the maximum susceptibility decreases in comparison with (IV). The shifts of the maximum point may be due partly to the mixing of the susceptibility of the monomer with that of the dimer and partly to the presence of a

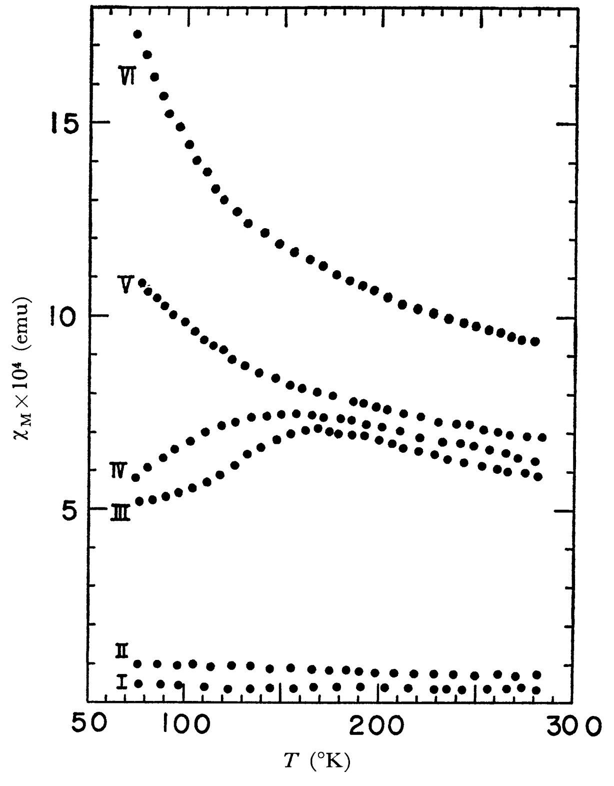

Fig. 1. Temperature dependence of the magnetic susceptibilities of anthracene-alkali metal salts.
I, $\text{An–Na}_{0.7}$; II, $\text{An–Na}_{1.5}$; III, An–K (solvent); IV, An–K; V, An–Rb; VI, An–Cs

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1) H. Nishiguchi, This Bulletin, **40**, 1587 (1967).

2) W. A. Holmes-Walker and A. R. Ubbelohde, *J. Chem. Soc.*, **1954**, 780.

residual solvent between anion radicals. Using the value for $T_c=165$°K determined from the experiment, we can estimate the singlet-triplet separation to be 0.0231 eV. The comparison of this result with the cases of biphenyl-K (0.0182 eV) and *meta*-terphenyl-K (0.0252 eV)[3] indicates that the singlet-triplet separations in the aromatic hydrocarbon anion(Ar)–K complexes do not vary in the order of magnitude. The singlet-triplet separation of the dimer may depend on the distance between the two constituent radicals; therefore, the small difference implies that the distance between the two anion radicals of these Ar–K complexes is of the same order of magnitude. It is instructive to compare the singlet-triplet separations of Ar–K and that of K(TCNQ) (0.2 eV),[4] since both salts are 1 : 1 complexes of the organic compounds and potassium. The large difference implies that the two anion radicals in Ar–K complexes are more separated from each other than in the case of K(TCNQ). As was suggested in the previous paper,[1] the difference in the singlet-triplet separations may indicate the existence of a potassium cation between the two radicals constituting the An–K complexes; the two spins interact indirectly, while the TCNQ anions in the K(TCNQ) complexes couple directly. The magnetic susceptibilities of the three samples of anthracene sodium complexes are very small and change little with the temperature or with various alkali metal concentrations. If one assumes the singlet-triplet dimer model, An–Na$_{1.0}$ and An–Na$_{0.7}$ could be attributed to the low-temperature range ($\boldsymbol{k}T/\delta<1$). The small χ_M of An–Na$_{1.5}$ is probably due to its compositions containing dinegative ions and dimer clusters. The magnetic susceptibilities of An–Rb and An–Cs salts increase as the temperature decreases down to 77°K and do not show any maximum. They would be more suitable for the higher-temperature range ($\boldsymbol{k}T/\delta>1$) of Eq. (1) than the same temperature range of the Curie-Weiss law on condition that $\delta_{\text{An-Na}}>\delta_{\text{An-K}}>\delta_{\text{An-Rb}}>\delta_{\text{An-Cs}}$.

Electron Paramagnetic Resonance Absorption. We have also observed the electron paramagnetic resonance of alkali metal complexes of anthracene. The EPR spectra of these salts changed with different alkali metals and with the temperature, as is shown in Fig. 2. The EPR spectrum of An–K salt which was evacuated for 2 days *in vacuo* exhibits an exchange-narrowed single line (1.8 G) broader than that (1.0 G) of the An–K which was evacuated for 2 hr, and the line width changed little with the temperature. The EPR spectra of An–Na exhibit an exchange-narrowed sharp single line comparatively broader than that of An–K, and the line width changed little with temperature. The EPR spectra of An–Cs salt exhibits a broad single line, and the line width increases with the temperature up to 28 gauss. These phenomena can also be seen in the cases of Bp–Cs and cupric acetate monohydrate.[5] The absorption of An–Rb varies from one sample to another. The EPR spectrum of An–Rb, which was evacuated for 1 hr, shows two lines at room temperature; one of them is sharp, and the other, comparatively broad. When the solvent was introduced to this sample, these two lines coalesced into a single sharp line. The EPR spectrum of An–Rb evacuated for 2 days shows a single lines at 77°K, one of them sharp, and the other, very broad. This broad line may correspond to the absorption of dimer clusters, and the other, to the single spin, as was seen in the cases of Bp–K and Bp–Rb.

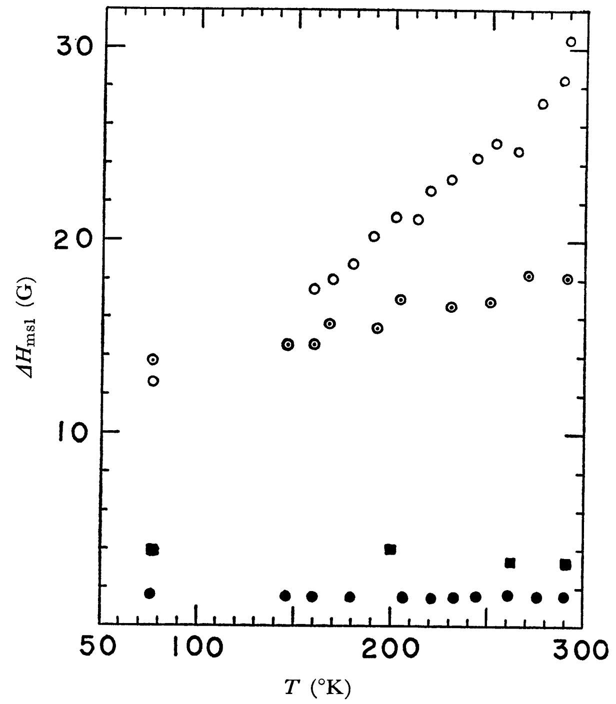

Fig. 2. Temperature dependence of the line width of the paramagnetic resonance absorption of the salts.
○, An–Cs; ⊙, An–Rb; ■, An–Na; ●, An–K.

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[3] Unpublished work.

[4] R. G. Kepler, *J. Chem. Phys.*, **39**, 3528 (1963).

[5] B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, **1956** 3837.