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Magnetic Properties of Aromatic Hydrocarbon-Alkali Metal Ion-Pair Salts. I

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Measurements of magnetic susceptibility and electron paramagnetic resonance absorptions have been carried out on biphenyl (Bp)-potassium (K), -rubidium (Rb), and -cesium (Cs) ion-pair salts. These powder salts were prepared by the evaporation of the solvent from the corresponding anion radical solutions *in vacuo*. The magnetic susceptibility of the Bp-K system is paramagnetic and exhibits a maximum at 130±4°K. This susceptibility can be fitted approximately to the expression:

$$\chi_{\mathrm{M}} = \frac{2Ng^2\beta^2}{\boldsymbol{k}T}\cdot\frac{1}{3+e^{\delta/\boldsymbol{k}T}},$$

which leads to a singlet-triplet dimer model consisting of a singlet ground state and a triplet state lying slightly above the ground state. The line width of the electron paramagnetic resonance (EPR) spectrum is also temperature-dependent and becomes broader as the temperature decreases. The Bp-Rb and Bp-Cs systems also exhibit susceptibilities which monotonously increase as the temperature decreases. These can be fitted to the higher temperature range ($\boldsymbol{k}T/\delta > 1$) of the above equation rather than to the Curie-Weiss law. For these compounds single absorption lines have also been observed at $g=2.002$ in the EPR spectra at room temperature. The results suggest that these salts may be interpreted generally by means of the singlet-triplet dimer model proposed for the organic salts based on the anion radical of tetracyanoquinodimethane (TCNQ). However, one marked difference is that the singlet-triplet separations of these compounds are very small in comparison with those of the TCNQ radical salts.

The alkali metals react with a large number of aromatic hydrocarbons in various ethereal solvents by transferring one, two, or, in special cases, three electrons to one molecule of hydrocarbon. Thus intensely colored anions are produced.[1,2] The properties of these anions in solution have been studied by a number of investigators with the aid of the electron spin resonance (ESR) and/or electronic absorption spectra.

Solvent-free solids composed of the anions produced with such reactions were studied by Holmes-Walker and Ubbelohde[3]; they exhibited a paramagnetic contribution in some cases. However, it has not been clear whether the observed paramagnetism was an intrinsic property of the solids or whether it arose from magnetic impurities. A further question is whether the susceptibility generally follows the Curie-Weiss law or not. In order to obtain information about the general nature of these radical solids, we have measured the magnetic susceptibilities and EPR absorptions of the solid complexes formed between biphenyl and either potassium, rubidium, or cesium. As a preliminary study it may be appropriate to investigate the solids based on the biphenyl anion radical with which alkali metals make 1 : 1 complexes called "ion-pairs."[4,5] Some organic salts based on the anion radical of tetracyanoquinodimethane (TCNQ) have been found by Siemons, Bierstedt and Kepler to exhibit a very high conductivity.[6] Measurements of the temperature dependence of the magnetic susceptibilities of these compounds have also been undertaken by Kepler, Bierstedt and Merrifield,[7] and by Kepler.[8] They have shown that such high-conductivity materials as quinolinium$(\mathrm{TCNQ})_2$ exhibit a temperature-independent paramagnetism which may be explained by a degenerate electron gas model (Pauli spin paramagnetism). On the other hand, the susceptibility of intermediate or low conductivity materials such as triethylammonium$(\mathrm{TCNQ})_2$ has been found to fit approximately the expression:

$$\chi_{\mathrm{M}} = \frac{2Ng^2\beta^2}{\boldsymbol{k}T}\cdot\frac{1}{3+e^{\delta/\boldsymbol{k}T}}. \qquad (1)$$

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[1] W. D. Scott, J. F. Walker and V. L. Hansley, *J. Am. Chem. Soc.*, **58**, 2442 (1936).

[2] P. Brassem, R. E. Jesse and G. J. Hoijtink, *Mol. Phys.*, **7**, 587 (1964).

[3] W. A. Holmes-Walker and A. R. Ubbelohde, *J Chem. Soc.*, **1954**, 780.

[4] T. L. Chu and S. C. Yu, *J. Am. Chem. Soc.*, **76**, 3367 (1954).

[5] H. Nishiguchi, Y. Nakai, K. Nakamura, K. Ishizu, Y. Deguchi and H. Takaki, *J. Chem. Phys.*, **40**, 241 (1964); *Mol. Phys.*, **9**, 153 (1965).

[6] W. J. Siemons, P. E. Bierstedt and R. G. Kepler, *J. Chem. Phys.*, **39**, 3523 (1963).

[7] R. G. Kepler, P. E. Bierstedt and R. E. Merrifield, *Phys. Rev. Letters*, **5**, 503 (1960).

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

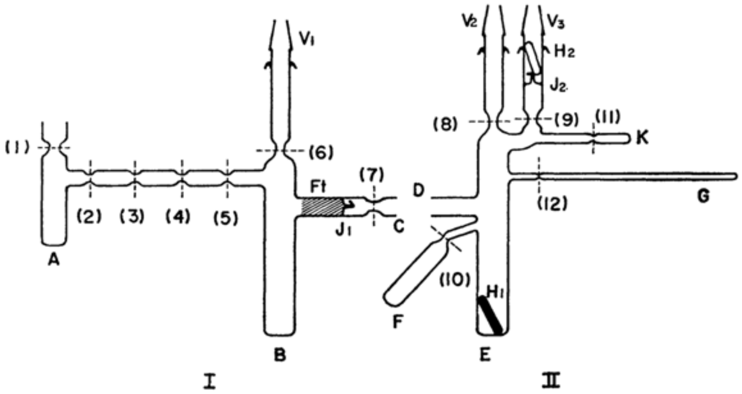

Fig. 1. Apparatus for preparing biphenyl-alkali metal ion-pair salts.

This leads to the conclusion that the odd electrons associated with the TCNQ anion radicals are paired in quasimolecular states consisting of a singlet ground state and a triplet state lying above the ground state. Here the quantity $\mathcal{N}$ is the number of the cluster consisting of two anion radicals and δ, the singlet-triplet separation in eV. Therefore, biphenyl anion radical solids prepared by the reaction mentioned above may exhibit properties similar to those of TCNQ anion radical salts. However, it should be noted that there is a clear difference between them in their properties in solution. The ESR spectra of the biphenyl anion radicals in solution exhibit the hyperfine splittings due to the counter ions,[5] but those of the TCNQ anion radicals have not yet exhibited them even through vaious solvents and various metals have been used.[9] Thus another problem to discuss in the present paper is whether this difference contributes to the intrinsic features of the " ion-pair " salts.

Experimental

In preparing the solutions containing the products of the hydrocarbon-alkali metal reactions, high-vacuum techniques similar to those described previously were used,[10,11] using an apparatus made of " Terex " glass (See Fig. 1). Some alkali metal (about 1 g) and a weighed amount of pure biphenyl were placed in the vessels A and B respectively. After sealing up the apparatus at (1), we connected it to the high-vacuum line. A trace of water in the hydrocarbon was removed by introducing completely dried tetrahydrofuran (THF)[*1] into the vessel B containing biphenyl, by dissolving the hydrocarbon, and afterward by evaporating the solvent. This procedure was very effective in removing the trace of water in the hydrocarbon. The apparatus was then sealed off at (2), (3), (4), and (5) successively, and the sublimation of the metal was repeated. Finally, the alkali metal mirror was prepared in the reaction vessel B by sublimation. After the distillation of the solvent, THF or DME (about 10 m*l*), into the vessel B, we separated the apparatus from the vacuum line by sealing it off at (6). After the completion of the reaction in B, we connected Apparatus I to Apparatus II at C and D, and V_2 to the vacuum line. For several hours the apparatus was held on the high vacuum line, sometimes being irradiated with a tesla coil in order to remove any traces of adsorbed gases and vapours. The anion solution in B was transferred to a vessel E through a filter packed with glass wool after sealing off at (8) and breaking the breakable joint, J_1, with a hammer, H_1, in E. The apparatus II was sealed off at (7) and removed from the apparatus I. The next procedure was to evaporate the solvent very slowly. After carefully putting a hammer, H_2, on J_2 and connecting V_3 to the vacuum line, we broke J_2 with H_2 and evaporated the solvent; a black powder was thus crystallized in E. For one day or two the apparatus was held on the high-vacuum line. In the cases of Rb and Cs, the residues were purple-black. In order to remove the small amount of nonreacted biphenyl left in the powder by the sublimation, a bulb, F, was cooled with liquid nitrogen after having been sealed off at (9); afterward this bulb, F, was separated from the apparatus. By tilting the apparatus, black powder was introduced to K and G, which were sealed off at (11) and (12) respectively and used for the magnetic susceptibility and EPR measurements.

The magnetic measurements were carried out by a magnetic torsion balance described previously.[12] All the EPR measurements were taken with a JEOL 3BX spectrometer, with a 100 kc field modulation and equipped with a field dial and a variable temperature control unit. The anion radical salts were analyzed after the measurements. The sealed ampoule containing the sample was weighed and broken into 50 m*l* or 100 m*l* of distilled water. After the liberated hydrocarbon had been filtered off, a known volume of the solution was titrated against a standard oxalic acid solution, using phenolphthalein as an indicator. Within the limits of

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9) Unpublished work.

10) D. E. Paul, D. Lipkin and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

11) G. J. Hoijtink, E. de Boer, P. H. Van Der Meij and W. P. Weijland, *Rec. trav. chim.*, **74**, 277 (1955).

[*1] Dry THF or dimethoxyethane (DME) had been stored in a storage bottle containing Na-K alloy and connected to the vacuum line.

12) M. Mekata, *J. Phys. Soc. Japan*, **17**, 796 (1962).

experimental error (4%), the analyzed values of the alkali metal in the compound coincided with those obtained by assuming that the compound consisted of a 1: 1 complex.

Results and Discussion

Temperature Dependence of Magnetic Susceptibility. The paramagnetic susceptibilities of the radical anion salts, based on 1 mol of biphenyl (χ_M), are shown in Fig. 2 as a function of the temperature. These have been corrected for the diamagnetic contribution of $\chi_M^{\text{Bp-K}}=-1.17$, $\chi_M^{\text{Bp-Rb}}=-1.24$, and $\chi_M^{\text{Bp-Cs}}=-1.35\times10^{-4}$ emu/mol respectively, as calculated by Pascal's method.[13] If the solids consist of aggregates of the anion radicals without any exchange interaction among them, the χ_M's will follow the Curie law and their magnitude could easily be calculated. Moreover, if the spins associated with the anion radicals interact with the neighbours, one can describe the susceptibility by means of the Curie-Weiss law. However, if the salts consist of small clusters in which the magnetic entities have an interaction, J, among themselves, the χ_M's will exhibit a temperature dependence different from the Curie or Curie-Weiss law.[14] For example, in the case of a dimer cluster in which two magnetic entities with a spin of $\frac{1}{2}$ interact with each other, the temperature dependence of the magnetic susceptibility becomes equal to Eq. (1). If the temperature at which the susceptibility shows a maximum is defined as T_c, one can determine the singlet-triplet separation (δ) using $\delta=1.61\,\boldsymbol{k}T_c$. The magnetic susceptibility of Bp-K varies with the temperature and exhibits a maximum, shown in Fig. 2, which gradually shifts to the higher-temperature side as the hours of the evaporation of the solvent are varied. The T_c of Bp-K (709), which was evacuated for about 12 hours, is estimated to

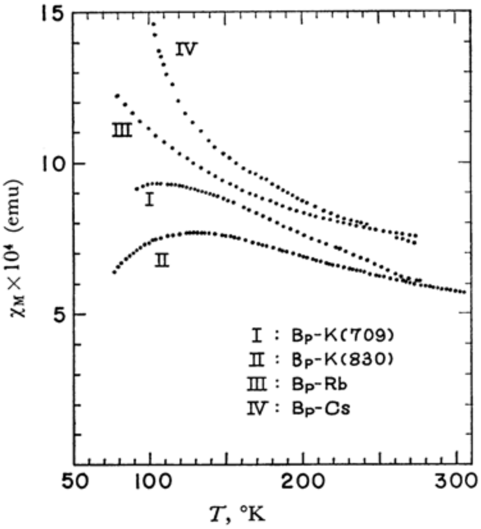

Fig. 2. Temperature dependence of the magnetic susceptibility of biphenyl-alkali metal ion-pair salts.

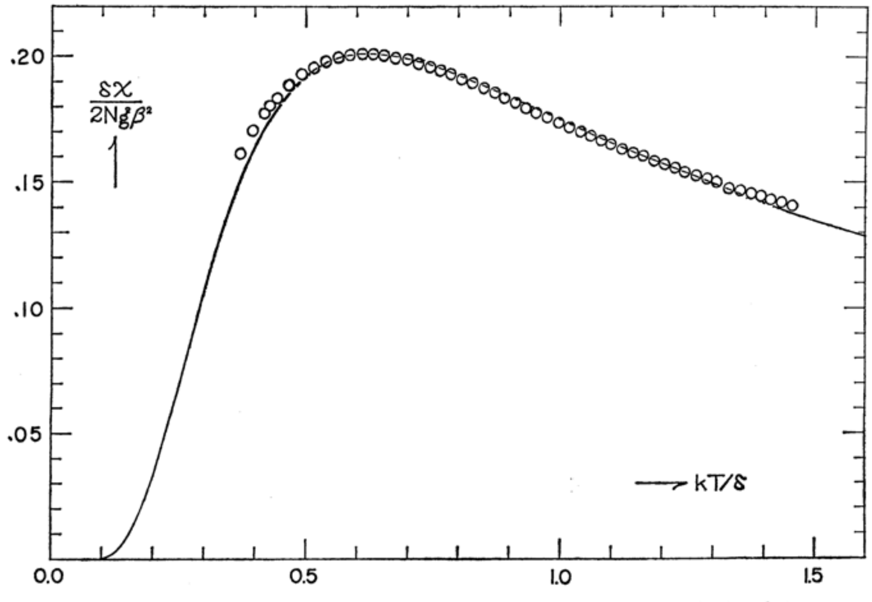

Fig. 3. Temperature dependence of the magnetic susceptibility calculated theoretically using Eq. (1) in the text. Open circles are the experimental results of Bp-K (830) fitted at the maximum to the theoretical line.

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[13] P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publisher, New York (1956).

[14] J. S. Smart: "Magnetism", ed. by G. T. Rado and H. Suhl, Vol. 3, Academic Press, New York, London (1963), pp. 63.

be 104 ± 2°K. However, in the case of Bp-K(830), which was evacuated for about 2 days, the susceptibility passes through its maximum at 130 ± 4°K and its magnitude decreases in comparison with curve I. In Fig. 3 we show the reduced theoretical curve of Eq. (1) and the experimental results (II) of Fig. 2 fitted at the maximum point to the theoretical curve. The agreement between theory and experiment in the case of Bp-K(830) is enough to conclude that the Bp-K(830) salt consists of ion-pair dimers. Since the electron paramagnetic resonance spectrum of Bp-K(709) at 133°K consists of two absorption lines, as will be discussed in the next section, it may be appropriate to conceive that the salt is a mixture of the monomer and the dimer of the ion-pairs. Therefore, the shift of the maximum point may be due to the mixing of the susceptibility of the monomer with that of the dimer. Using the value for $T_c(130\pm4$°K) determined from the experiment, we can estimate the singlet-triplet separation to be $\delta=0.0182$ eV. It should be noted that the separation is just as large as that of 4-cyano-*N*-methyl quinolinium$(\mathrm{TCNQ})_2$,8) which may suggest that the salt is also a comparatively high conductive material, since the electrical conductivity of 4-cyano-*N*-methyl quinolinium$(\mathrm{TCNQ})_2$ is $2\times10^{-2}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ at 23°C.8)

It is also instructive to compare the δ of Bp-K and that of K(TCNQ) (0.2 eV), since both salts are 1 : 1 complexes of the organic compounds and potassium. The singlet-triplet separation of the dimer depends on the distance between the two constituting radicals; therefore, the large difference implies that the two anion radicals in the Bp-K cluster are more separated from each other than in the case of K(TCNQ). The EPR measurements of Bp-K in ethereal solutions suggested that the counter ion resides above the biphenyl molecular plane.5) On the other hand, the crystal structure of $\mathrm{Cs_2(TCNQ)_3}$ shows that the Cs cation resides on the molecular plane of TCNQ.15) Therefore, a possible interpretation of the difference in the singlet-triplet separations may be that, as a result of the existence of the potassium cation between the two radicals constituting the Bp-K cluster, the two spins interact indirectly, while the TCNQ anions in the K(TCNQ) cluster couple directly. The magnetic susceptibilities of Bp-Rb and Bp-Cs increase as the temperature decreases to 77°K and do not show any maximum; they can thus be more suitably fitted to the higher temperature range ($\boldsymbol{k}T/\delta>1$) of Eq. (1) than to the Curie-Weiss law on condition that $\delta_{\mathrm{Bp-K}}>\delta_{\mathrm{Bp-Rb}}>\delta_{\mathrm{Bp-Cs}}$. In the light of these results, it is possible that the small singlet-triplet separations are mainly due to the presence of the alkali metal cation between two radicals in the cluster.

Electron Paramagnetic Resonance Absorption. Electron paramagnetic resonance absorption measurements of potassium complexes of aromatic compounds have been carried out by Pastor and Turkevich.16) However, the absorption of biphenyl, *p*-terphenyl, and *p*-quarterphenyl was not large enough to permit measurements of their absorption line widths. We have observed the EPR absorptions of the alkali metal complexes of biphenyl. The absorption curves of Bp-K vary from one sample to another, as is shown in Fig. 4, and the temperature dependence of the magnetic susceptibility also varies, as was discussed in the last section. First of all, Bp-K(007), the susceptibility of which increases monotonously as the temperature decreases, was prepared by two hours' evaporation of the solvent *in vacuo*. The paramagnetic absorption spectrum of the sample exhibits one sharp line, with a line width of 0.7 gauss (Fig. 4A), which is temperature-independent from 77°K to room temperature. The line shape is slightly asymmetric; this may be due to the anisotropy of the gyromagnetic ratio, *g*. The EPR spectrum of Bp-K(709) at 133°K shows two lines, one of which is sharp and the other, broad. The former, which may correspond to the absorption of Bp-K(007), showed the increase in intensity to be expected from the Curie law for paramagnetism. Bp-K(830) at 133°K shows only a broad absorption line corresponding to the latter in the case of Bp-K(709). No forbidden $\Delta m=\pm2$ transitions for these samples have been observed over the accessible temperature range.

Since the magnetic susceptibility of Bp-K(830) follows Eq. (1), as is shown in Fig. 3, it may be appropriate to consider that the broad line in Fig. 4 is due to the dimer clusters consisting of two ion-pairs,

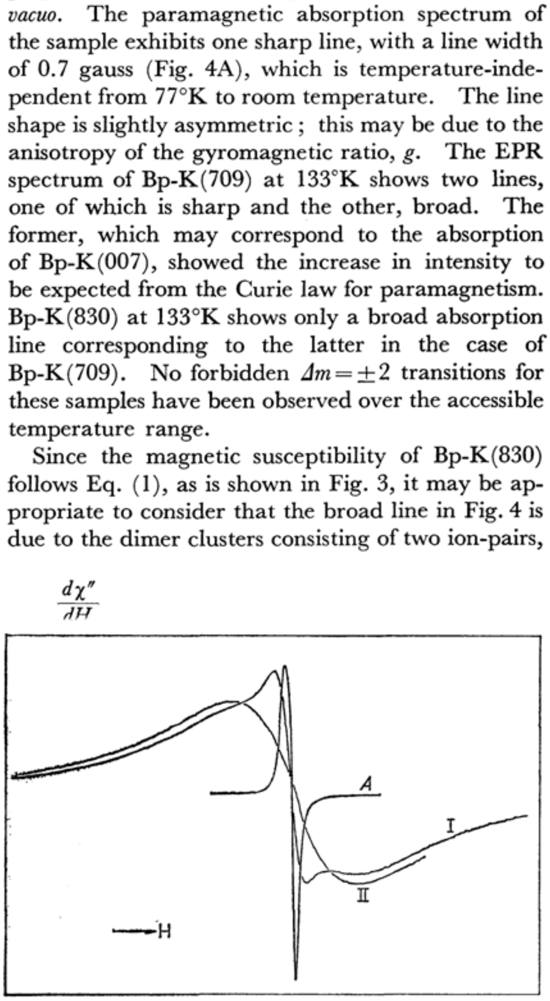

Fig. 4. Electron paramagnetic resonance absorption of the biphenyl-potassium complexes: A, Bp-K(007); I, Bp-K(709); II, Bp-K(830). The spectra were obtained with different spectrum gain at 133 ± 3°K.

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15) C. J. Fritche and P. Arthur, *Acta Cryst.*, **21** 139, (1966).

16) R. C. Pastor and J. Turkevich, *J. Chem. Phys.*, **23**, 1731 (1955).

and that the sharp line is due to monomer radicals with a spin of $\frac{1}{2}$. The existence of triplet-state entities is best shown by the presence of an anisotropic splitting of the resonance line into a doublet (zero-field splitting) as well as by the observation of the usually forbidden $\Delta m = \pm 2$ transition. Chesnut and Phillips showed that, with respect to the (methyl-triphenylphosphonium-)$^+$ $(\mathrm{TCNQ})_2^-$ single crystal, the line shape of the $\Delta m = \pm 1$ transsitions is dependent upon the concentration of the magnetic entities. In this case the $\Delta m = \pm 2$ transition has also been observed; its intensity drops off rapidly as the exchange interaction sets in. Therefore, it is conceivable that the reason why we could not observe the $\Delta m = \pm 2$ transition over the accessible temperature range in our cases may be due to couplings among the magnetic entities.

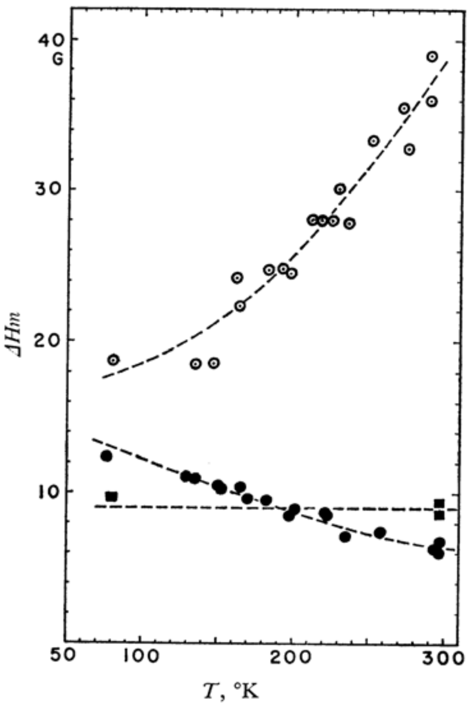

Fig. 5. Temperature dependence of the line width of the electron spin resonance absorption of the salts: full circle, ●, Bp-K(830); full square, ■, Bp-Rb; dotted open circle, ⊙, Bp-Cs.

The line-width variation of the sample as a function of the temperature is shown in Fig. 5. Because of the powdered sample, the line is considered to be a superposition of the lines of all the orientations. However, this can also be interpreted by means of the exchange interaction between dimer clusters whose concentrations vary as:

$$\mathcal{N} = \mathcal{N}_0 \cdot \frac{3}{3 + e^{\delta/kT}}\,, \qquad (2)$$

that is, the zero-field splittings of a certain orientation of the cluster are narrowed by the exchange interaction as the temperature increases in the range of:[17]

$$(\nu_1 - \nu_2)^2 < 8\nu_e{}^2\,,$$

where ν_1 and ν_2 are two characteristic absorption frequencies and ν_e is a transition frequency from one resonance to the other and is the function of the concentration expressed by Eq. (2). Therefore, the envelope consisting of the zero-field splittings of all the orientations (powder) is also narrowed by the exchange interaction. On the contrary, the $\Delta m = \pm 2$ transition is considered to be smeared out by the increase in line width because of the large concentration of the magnetic entities.

Secondly, the EPR spectrum of Bp-Rb at the temperature of liquid nitrogen exhibited two lines similar to that of Bp-K(709) in Fig. 4. If one takes into account the susceptibility in Fig. 2, it is conceivable that T_c is in the vicinity of, perhaps just below, 77°K, which leads to a singlet-triplet separation of $\delta = 0.01$ eV. It is, however, more difficult to interpret the fact that Bp-Cs salt exhibits a broad single resonance line around $g = 2.002$ over the accessible temperature range. Furthermore, it is striking that the line width increases with the temperature up to 37 gauss. It is not known at present what species is responsible for this line.

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[17] D. B. Chesnut and N. D. Phillips, *J. Chem. Phys.*, **35**, 1002 (1961).