Spectroscopic Properties of Dicyclopentadienylberyllium and Its Complexes with Aromatic Solvents[1]

G. L. Morgan and G. B. McVicker

Contribution from the Department of Chemistry, The University of Wyoming, Laramie, Wyoming 82070. *Received August 17, 1967*

Abstract: Evidence is presented for a molecular complex of 2 moles of dicyclopentadienylberyllium with 1 mole of benzene or toluene. Although this complex could not be isolated as a solid, interactions in solution were strong enough to induce paramagnetism in the system. This paramagnetism caused large shifts in the aromatic resonance signals in the nmr spectra and was observed directly by esr spectroscopy.

Many attempts have been made to describe a structure for dicyclopentadienylberyllium, $(C_5H_5)_2Be$, which would be consistent with its properties.[2-4] One such property is the large dipole moment, 2.24 D in cyclohexane and 2.46 D in benzene.[3] An electron diffraction study[4] has shown $(C_5H_5)_2Be$ to be monomeric in the gas phase with the cyclopentadienyl rings parallel to each other but with the beryllium ion nearer to one ring than the other (1.48 and 1.98 Å, respectively). Fritz[5] has claimed that infrared spectral data support such a model, although his data were not taken on the vapor but on the solid and solutions.

Preliminary microwave spectral data[6] seem to indicate that $(C_5H_5)_2Be$ is more complicated than a symmetric-top molecule, although it may appear so as an average. In addition, very intense lines suggest a large dipole moment.

Dissolution of colorless crystals of $(C_5H_5)_2Be$ in benzene or toluene results in slightly yellow solutions. The aromatic solvent is removed with difficulty, but with repeated sublimations, colorless crystals of $(C_5H_5)_2Be$ are once again obtained. Dissolution in cyclohexane produces colorless solutions, but when the crystals are removed and redissolved in benzene or toluene, a slight yellow color is again observed. In carrying out further studies on $(C_5H_5)_2Be$ we have obtained evidence of complex formation with aromatic solvents.

Experimental Section

Materials. Dicyclopentadienylberyllium was prepared by the reaction of cyclopentadienylsodium with beryllium chloride in both ether and benzene solutions.[7] Sample preparations were carried out in an inert atmosphere enclosure[8] with spectroscopic samples being doubly sublimed *in vacuo* immediately before use.

Solvents were purified and dried using standard methods. Purity was monitored by glpc and infrared spectroscopic techniques.

Nmr and Esr Spectra. Proton magnetic resonance spectra were measured on a Varian Associates HA-100 spectrometer using degassed and sealed sample tubes. Beryllium resonance spectra were obtained using a Varian V-4311 radiofrequency unit at 14.05 MHz with a field of 23.5 kG. Chemical shifts were measured by replacing an audio-modulated reference sample of aqueous beryllium nitrate with the analytical sample without interrupting the field sweep.

Electron spin resonance spectra were obtained using quartz sample tubes on a Varian Associates E-3 spectrometer. The quartz tubes fitted into nmr tubes to obtain nmr spectra which were used to check the purity of the samples.

Fluorescence and Phosphorescence Spectra. These were measured on an Aminco-Bowman spectrophotofluorometer manufactured by American Instrument Co., Inc., Silver Springs, Md.

Molecular Weight Determination. Although molecular weight data are very desirable to confirm complex formation, we did not have a cryoscopic apparatus that could easily be used in our inert atmosphere enclosures. A rough measurement was carried out in a vacuum line using Raoult's law according to the method employed by Brown.[9] The data all indicated that $(C_5H_5)_2Be$ in toluene was nearer to a dimer than a monomer, but the data varied over 28 molecular weight units. Fischer[7] reported that $(C_5H_5)_2Be$ was monomeric in benzene from cryoscopic data, but no data were given.

Results

Nmr Spectra. The major absorption in the proton resonance of $(C_5H_5)_2Be$ in toluene is a singlet (τ 4.12) which does not shift with temperature. Two other signals are observed in the spectrum in addition to the aromatic ring and methyl protons of the solvent, toluene. The first varies in chemical shift from 110 to 140 Hz to *higher field* from the aromatic ring proton signal of free toluene, moving to higher field with decreasing temperature. The ratio of intensity of this moving signal to the $(C_5H_5)_2Be$ signal is 1:4. At lower temperatures this signal begins to broaden. The second signal is present on the *low-field* side of the methyl proton signal of the solvent toluene, but these signals were only separated by 10 Hz so good intensity measurements could not be obtained. The 1:4 intensity ratio would imply that a complex, $2(C_5H_5)_2Be$–toluene, exists if the moving signal is attributed to complexed toluene (*vide infra*).

In benzene solution the main $(C_5H_5)_2Be$ signal appears at a τ value of 4.19, and there is a second signal which has a very similar temperature dependence to the extra peak seen in the $(C_5H_5)_2Be$–toluene solution spectrum. The corresponding intensity ratio is 1:3.3, which is consistent with a $2(C_5H_5)_2Be$–benzene complex. Fluorobenzene solutions of $(C_5H_5)_2Be$ gave the same behavior, but intensities could not be measured accurately because of the width of the complexed fluorobenzene signals.

---

[1] (a) This paper was presented, in part, at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967. (b) This research was supported by Grant GP-5072 from the National Science Foundation.

[2] H. P. Fritz and R. Schneider, *Ber.*, **93**, 1171 (1960).

[3] E. O. Fischer and S. Schreiner, *ibid.*, **92**, 938 (1959).

[4] A. Almenninger, O. Bastiansen, and A. Haaland, *J. Chem. Phys.*, **40**, 3434 (1964).

[5] H. P. Fritz and D. Sellmann, *J. Organometal Chem.* (Amsterdam), **5**, 501 (1966).

[6] E. A. Rinehart and G. L. Morgan, unpublished results.

[7] E. O. Fischer and H. P. Hofmann, *Ber.*, **92**, 482 (1959).

[8] T. L. Brown, D W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instr.*, **33**, 491 (1962).

[9] S. U. Choi and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 903 (1966).

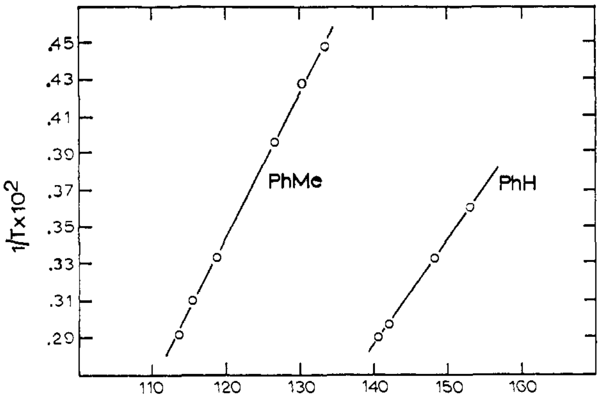

Figure 1. Upfield shift of complexed aromatic protons from free aromatic protons (cps).

No signals other than a sharp singlet for $(C_5H_5)_2Be$ itself at τ values of 4.25, 4.26, and 4.43 were observed in the nonaromatic solvents TMS, cyclohexane, and methylcyclohexane, respectively.[10] These measurements were also made over a wide range of temperatures.

Chemical-shift data for the complexed aromatic solvent molecules with respect to free solvent molecules, Figure 1, indicate a linear relationship with $1/T$. Chemical shifts for complexed fluorobenzene, though not included in the graph, are much smaller. Assuming that the shift of the complexed solvent from free solvent is a measure of the strength of these complexes, the relative strength increases in the order fluorobenzene < toluene < benzene.

These systems were also studied in other concentration ranges. When nearly equal concentrations ($\sim$2%) of $(C_5H_5)_2Be$ and aromatic solvent were placed in cyclohexane solution, no complexed solvent signals were observed. Saturated solutions of $(C_5H_5)_2Be$ in benzene and toluene show temperature-dependent complexed solvent signals, but the intensities were no longer in the ratios 3.3:1 and 4:1, respectively, but were ranged in intensity ratio from 6:1 to 10:1.

The beryllium resonance spectrum of $(C_5H_5)_2Be$ in toluene was a singlet 18.5 ppm upfield from the saturated beryllium nitrate resonance. In methylcyclohexane solution the chemical shift was 18.3 ppm. This is a very large shift compared to all other reported compounds[11] which include only inorganic complexes with oxygen, chloride, and fluoride ligands. This large shift can be attributed to the dominance of ring current effects from the associated cyclopentadienide rings.

Esr Spectra. The nmr results strongly indicated that the very large chemical shifts of the complexed solvents either were due to very strong bonding (which seemed unlikely from our dilution studies) or were indicative of an effect analogous to paramagnetic contact shifts. Although the system seemed to consist of purely diamagnetic species, an esr investigation was initiated. No esr signal was observed for solid $(C_5H_5)_2Be$ over the temperature range +60 to −100° nor for its solutions in cyclohexane.

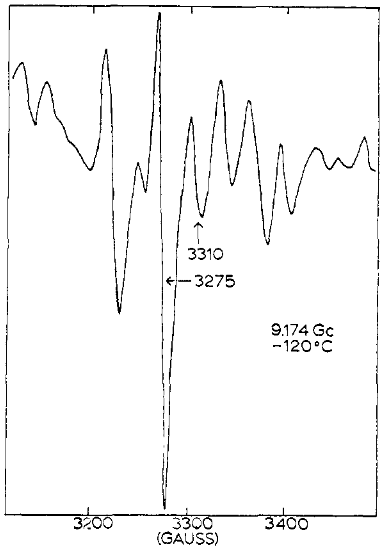

Figure 2. Esr spectrum observed for a toluene solution of $(C_5H_5)_2$-Be at −120°.

Two very weak, superimposed signals are observed in toluene solutions at the temperatures used in the nmr experiment (approximately +60 to −50°), a very broad signal and a somewhat sharper one at $g = 2.00$. At much lower temperatures (below −100°), the $g = 2.00$ signal becomes sharper and fine structure emerges from the very broad signal (Figure 2). Although this spectrum cannot be definitely assigned, three distinct features can be noted and reasonably described. (a) The wing peaks with a separation of 370 G are strongly indicative of electron correlation. Such interactions are indicative of triplet states but are more likely, in this case, due to two monoradicals in close proximity. (b) The intense peak at 3275 G ($g = 2.00$) may be attributed to a toluene monoradical. This peak is about 20.5 G wide and contains further fine structure when the scale is expanded.[12] (c) Seven peaks (the third from the left being obscured by the peak described in feature b centered at 3310 G ($g = 1.98$) with a hyperfine splitting of 30 G are attributed to splitting by two equivalent beryllium nuclei, each with a spin of $^3/_2$. The splitting of 30 G is near the 24-G hyperfine coupling constant for ^{11}B in BH_3^-.[13] Both ^{11}B and ^9Be have the same spin and very nearly equal quadrupole moments.

This system was studied in the temperature range +40 to −140°. Figure 3 is a plot of the peak to peak signal intensity for the $g = 2.00$ peak *vs.* $1/T$. Such a linear relationship can be attributed to a Curie law dependence and implies that there is a zero activation energy to form the radical.[14] It is also possible that our intensity measurements on this weak signal were not accurate enough to demonstrate any curvature, especially since the peaks broaden at higher temperatures.

---

[10] Methylcyclohexane was selected because of its freezing point of −126°; 3–5% solutions of $(C_5H_5)_2Be$ in this solvent were observed to freeze in the form of a clear glass at approximately −35°. No impurities were present in the solvent so that one may suspect that, even in this nonaromatic solvent, some sort of interaction is occurring with $(C_5H_5)_2Be$.

[11] J. C. Kotz, R. Schaeffer, and A. Clouse, *Inorg. Chem.*, **6**, 620 (1967).

[12] J. R. Bolton and A. Carrington, *Mol. Phys.*, **4**, 497 (1961).

[13] M. C. R. Symons and H. W. Wardale, *Chem. Commun.*, 758 (1967).

[14] R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *J. Am. Chem. Soc.*, **89**, 1112 (1967).

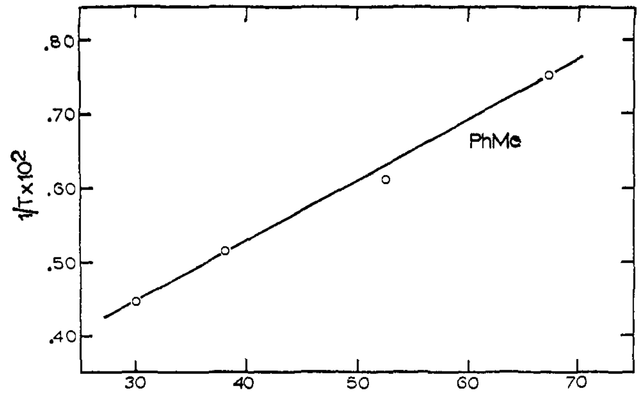

Figure 3. Esr peak-to-peak intensity of absorption signal (arbitrary units).

Benzene solutions of $(C_5H_5)_2Be$ also have an absorption signal but no fine structure could be resolved.

Fluorescence and Phosphorescence Spectra. The magnetic resonance spectral data strongly suggest that either a triplet state or diradical is being stabilized in the complex. To test this theory, qualitative fluorescence and phosphorescence studies were carried out. Dilute solutions of $(C_5H_5)_2Be$ in cyclohexane and benzene gave rise to an intense fluorescence emission at 415 mμ at room temperatures. At liquid nitrogen temperatures the compound was found to fluoresce at 420 mμ in cyclohexane and 405 mμ in benzene. Since only approximate weight percentages in these solutions were known, a similar concentration of benzene in cyclohexane was prepared. This solution gave rise to a fluorescence emission at 320 mμ with an intensity of about 0.01 that of the $(C_5H_5)_2Be$ solution in cyclohexane.

Our sample of benzene exhibited a phosphorescence emission at 440 mμ with $\tau = 0.625$ sec.[15] A small amount of $(C_5H_5)_2Be$ shifted the phosphorescence maximum in benzene to 470 mμ (shoulder at 440 mμ) with $\tau = 1.56$ sec. Diluting this solution by one-half resulted in a phosphorescence maximum at 465 mμ (shoulder at 440 mμ) and a τ of 3.12 sec. The excitation maximum is centered at 250 mμ which corresponds to the absorption maximum of benzene. No phosphorescence was observed in a cyclohexane solution of $(C_5H_5)_2Be$. All phosphorescence spectra were recorded at liquid nitrogen temperatures.

Discussion

The results of our investigation lead us to conclude that complexes exist between $(C_5H_5)_2Be$ and aromatic solvent molecules as shown in Figure 4. The tendency of beryllium to form electron-deficient bonds is indicative of the strong acidic nature of beryllium. The existence of monomeric $(C_5H_5)_2Be$ in the gas phase and in certain solvents is thus interesting as the beryllium cannot easily be "satisfied" with either a pure ionic or σ-covalent formulation. Aromatic molecules are well-known donor species and have been shown to exhibit triplet states in certain donor-acceptor complexes.[16] Stable compounds were isolated when phenyllithium, *p*-tolyllithium, and *o*-tolyllithium were prepared in benzene solution in the presence of dioxane. Analytical data showed the compounds to have the composition $2ArLi \cdot 2C_4H_8O \cdot C_6H_6$, which were described as having the benzene molecule sandwiched between two lithium atoms.[17]

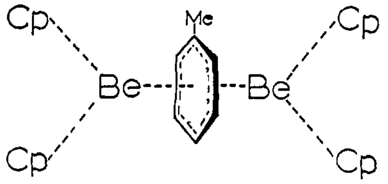

Figure 4. Proposed structure of toluene–$(C_5H_5)_2Be$ complex.

For this system we tentatively propose a bonding scheme in which the beryllium atom is sp^3 hybridized with two of these orbitals directed toward the cyclopentadienyl rings and two toward the complexed aromatic solvent molecule. Symmetry considerations permit a bond with the vacant E_2 orbitals on the aromatic molecule. In order to form a bond, electrons can be excited into this E_2 orbital[18] and then "stabilized" in a new molecular orbital. The esr spectrum can then be rationalized as resulting from one electron in a molecular orbital constructed from four beryllium orbitals plus the E_2 orbital of the complexed aromatic solvent molecule resulting in splitting by the berylliums in an equivalent spin state of 3,[19] with the second electron localized on the complexed aromatic solvent molecule. The wing peaks result from the correlation term. This description does not elucidate the nature of the bond with the cyclopentadienyl rings. Some inferences can be drawn, however, from the chemical-shift data.

While chemical-shift data for these solutions cannot be rigorously applied to infer the nature of the bonding, it can be generalized that σ covalent cyclopentadienyl compounds, such as $(C_5H_5)_2Sn$ and $(C_5H_5)_2Hg$, have τ values of 4.2 to 4.3, whereas ionic derivatives such as C_5H_5Li and C_5H_5Na have resonance signals slightly toward higher fields at τ values of about 4.5 to 4.6.[20,21] Thus if any interpretation of the observed shifts for $(C_5H_5)_2Be$ solutions is at all justifiable, it would seem that the σ covalent character is increasing in aromatic solvents, whereas the chemical shift in nonaromatic solvents, being toward higher fields, would indicate more ionic character.

The large shift of the complexed solvent can be attributed to paramagnetic contact shifts[22] and interpreted using the equation

$$\frac{\Delta H}{H} = \frac{\Delta \mathrm{Hz}}{\mathrm{Hz}} = -Q\frac{\gamma_e}{\gamma_H}\frac{g\beta S(S+1)F}{6KT}$$

where ΔHz is the shift of complexed solvent from free solvent, 134 Hz at 223°K; Hz is the resonance frequency, 100 MHz; Q for phenyl groups is -22.5 gauss; S is 1 for a triplet state, but if one assumes the above model in which one electron remains on the

---

[15] τ is the time required for phosphorescence to fall to $1/e$ of its initial value.

[16] L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, Chapter V.

[17] B. M. Mikhailov and N. G. Chernova, *Zh. Obshch. Khim.*, **29**, 8 (1959).

[18] J. A. Pople, *Proc. Roy. Soc.* (London), **A239**, 541 (1967).

[19] B. Bleaney and K. D. Bowers, *ibid.*, **A214**, 451 (1952).

[20] G. Fraenkel, R. E. Carter, A. McLachlan, and J. Y. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960).

[21] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 38 (1965).

[22] D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).

aromatic ring while the second is delocalized into a molecular orbital containing the two beryllium atoms, S can be considered as $^1/_2$; F is then a weighting factor estimating the spin density centered on the p orbitals of carbon of the coordinated solvent. Calculating F from these data gives 0.012% for the spin density on aromatic ring carbon atoms where $S = {}^1/_2$. This value seems qualitatively reasonable, being consistent with the low intensity of the esr spectrum and with other reported contact shift ranges. Figure 1 demonstrates that the shift is linear with $1/T$ as required by the equation but also implies (as does Figure 3) that there is a zero activation energy to form the diradical. This may be quite the opposite effect, however, and means that the activation energy is so large that there is no significant change in F in the range of temperatures studied. The presence of the methyl resonance of complexed toluene on the *low*-field side of the free solvent signal is also consistent with paramagnetic contact-shift phenomena since Q for methyl groups is of opposite sign.

The line widths of the nmr and esr signals are quite compatible. In order to observe contact shifted resonances, electronic relaxation times must be short, whereas electronic relaxation times must be relatively long to observe sharp esr signals. As noted above, the nmr contact shifted peak begins to broaden at lower temperatures (−50°) while the esr spectrum is unresolvable until the temperature is about −120°.

Further confirmation of complexation to form stabilized triplet states or diradicals was obtained from the phosphorescence emission study. Small amounts of $(C_5H_5)_2Be$ in benzene caused the lifetime of the triplet state of benzene to increase markedly. The lifetime is even longer in more dilute solutions, indicating that concentration quenching is decreasing. This may also be the reason for the anomalous and lower intensity ratios in the nmr spectra of saturated solutions. The shift of the phosphorescence maximum from 440 to 470 mμ upon addition of $(C_5H_5)_2Be$ to benzene indicates, further, that the triplet state is arrived at more easily *via* complex formation.

Finally, vapor pressure measurements over toluene solutions of $(C_5H_5)_2Be$ indicate that this interaction is strong enough to manifest itself as apparent association in solution.

Magnesium(II) in Aqueous Acetone and the Kinetics of Proton Exchange

R. G. Wawro and T. J. Swift[1]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio. *Received October 17, 1967*

Abstract: Magnesium nitrate and magnesium perchlorate solutions in aqueous acetone were prepared, and the proton magnetic resonance spectra were recorded between *ca.* −40 and *ca.* −90°. Below *ca.* −60° the water resonance signal is resolved into two components, one from bulk water and one from water in the primary hydration spheres of magnesium ions. These doublets were treated by a complete line-shape analysis technique based on the Bloch equations, and the values of τ_A, the average lifetime of a given proton in the primary hydration sphere of Mg^{2+}, were obtained as a function of temperature. Spectra obtained above *ca.* −60° were also analyzed by a somewhat different technique to obtain values of τ_A between *ca.* −60 and *ca.* −40°. The value of τ_A at a given temperature is a function of the concentration of added $HClO_4$ and HNO_3, indicating that the acid-catalyzed proton-transfer reaction observed previously for paramagnetic metal ions in aqueous solution is also operable for diamagnetic nontransition metal ions in aqueous acetone.

Considerable effort has been devoted in recent years to the study of the solvation of simple metallic cations in pure and mixed solvents,[2] principally through the application of magnetic resonance techniques. These cations may be separated into two distinct classes for a given solvent system, namely those ions for which a separate resonance signal (or signals) is observable (at least in theory) for those solvent molecules in the cationic primary solvation sphere in solution and those ions for which all observables such as line widths and chemical shifts are inseparable averages of the respective parameters for primary sphere solvent and bulk solvent.

The differentiation between these two classes arises from the wide variation between various ion–solvent systems of the rate constant for solvent exchange between the cationic primary solvation sphere and the bulk. For an ion such as Al^{3+}, the exchange rate may be made sufficiently slow in any of a variety of solvents[3,4] so that a separate resonance signal is readily observable for primary sphere solvent molecules, and Al^{3+} clearly belongs in the first of the two classes for these solvents.

At the opposite extreme is Na^+, an ion for which the solvent exchange rate is extremely rapid in all solvents for which measurements have been attempted.

In any such array there must obviously be borderline cases, and one of particular interest in this

---

[1] Author to whom inquiries should be addressed.

[2] J. F. Hinton and E. S. Amis, *Chem. Rev.*, **67**, 367 (1967).

[3] (a) R. E. Connick and D. N. Fiat, *J. Chem. Phys.*, **39**, 1349 (1963); (b) S. Thomas and W. L. Reynolds, *ibid.*, **44**, 3148 (1966).

[4] H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *J. Am. Chem. Soc.*, **89**, 3065 (1967).