The C_{60}^{2-} Fulleride Ion

Peter D. W. Boyd,[†] **P. Bhyrappa, Parimal Paul,**[‡] **John Stinchcombe, Robert D. Bolskar, Yongping Sun, and Christopher A. Reed***

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90089-0744

Received November 4, 1994[⊗]

Abstract: Synthetic, structural, and magnetic aspects of discrete C_{60}^{2-} salts have been investigated to bring coherence to conflicting descriptions of the electronic structure of the Buckminsterfulleride(2−) ion. The ^{13}C NMR chemical shift in DMSO solution appears as a broad signal at 184 ppm indicative of a ∼40 ppm downfield paramagnetic shift relative to C_{60}. Variable-temperature magnetic susceptibility studies are consistent with essentially equi-energy singlet ($S = 0$) and triplet ($S = 1$) spin states. The EPR spectrum of C_{60}^{2-} at 4 K consists of two signals. One signal is a typical axial triplet with $2D \sim 25$ G. The second is a narrower, doublet-like signal proposed to arise from a triplet with $2D$ too small to be resolved. A further axial triplet signal is observed at higher temperatures and is ascribed to thermal occupation of a low-lying excited state. The presence of three triplet states is a natural consequence of the reduction of the symmetry of C_{60}^{2-} from I_h to C_i as required by the Jahn−Teller theorem and observed in the X-ray crystal structure of $[PPN^+]_2[C_{60}^{2-}]$ ($PPN^+ = $ bis(triphenylphosphine)iminium). Collectively, the NMR, magnetic susceptibility, and EPR data show that, contrary to indications from recent EPR studies, C_{60}^{2-} is paramagnetic.

The discovery of C_{60} is the closest thing this century to the discovery of a new main-group element.[1] It is truly remarkable that a new allotrope of carbon, especially one of such structural elegance, should appear this late in the exploration of the chemistry of the stable elements.

In many ways, C_{60} behaves like a large, electronegative atom. Of 10 Å diameter and nearly spherical, it readily adds electrons to form anions called fullerides, C_{60}^{n-}. Values of $n = 1$ and 2 have been established in the gas phase.[2,3] Discrete values of $n = 1$ through 6 have been established in solution by electrochemical methods[4] and even more negative "oxidation states" ($n > 6$) seem to be accessible in the presence of stabilizing metal cations.[5,6] The analogy to an atom is also seen in the remarkable similarity of the hierarchy of filled Hückel molecular orbitals of C_{60} to the familiar s, p, d, f, g, and h orbitals of atoms. The lowest unoccupied molecular orbitals (LUMOs) are the relatively low-lying triply degenerate t_{1u} and t_{1g}, and this has led to the suggestion that C_{60} can accept up to 12 electrons.[7]

Of the known C_{60}^{n-} fulleride ions, C_{60}^{2-} is one of the most interesting. It is the rare case of a dianion that is stable in the gas phase;[2,3] the electron affinity of C_{60} is notably high.[8] Its electronic state has been the source of much conjecture and uncertainty. The 3-fold degeneracy of the LUMO of C_{60}, and the analogy to an atom, leads to the expectation that Hund's rule will be obeyed, i.e., that C_{60}^{2-} might have a $(t_{1u})^2$ spin triplet ground state:
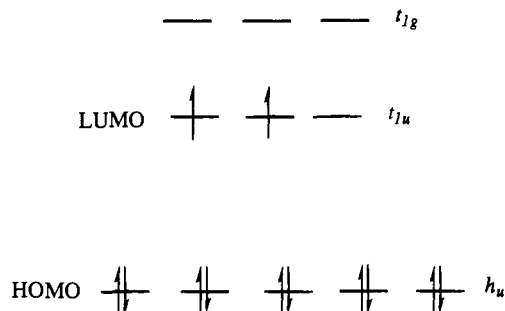
The first experimental information on the spin state of C_{60}^{2-} was interpreted along these lines. The 77 K EPR spectrum of an electrochemically generated sample showed triplet character[9] although other features of the spectrum could not be readily explained.[10] Numerous calculations have been performed to probe the electronic structure of C_{60}^{2-}.[11−19] Most come out in favor of a singlet ground state. However, all admit to small

† On leave from the Chemistry Department, The University of Auckland, Auckland, New Zealand.

‡ On leave from the Central Salt and Marine Chemials Research Institute, Bhavnagar, India.

⊗ Abstract published in *Advance ACS Abstracts*, February 15, 1995.

(1) The last stable non-metallic elements to be isolated were the noble gases, by Ramsey and Travers in the late 1890s. Ironically, if C_{60} were to be viewed as a new element ($Z = 720$) it would most logically be placed in the same group of the periodic table as the noble gases.

(2) Limbach, P. A.; Schweikhard, L.; Cowen, K. A.; McDermott, M. T.; Marshall, A. G.; Coe J. V. *J. Am. Chem. Soc.* **1991**, *113*, 6795−6798.

(3) Hettich, R. L.; Compton, R. N.; Ritchie, R. H. *Phys. Rev. Lett.* **1991**, *67*, 1242−1245.

(4) The first reports were: (a) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634−8636. (b) Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050−1051. For reports of reductions to C_{60}^{6-} see: (c) Xie, Q.; Pérez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978−3980. (d) Ohsawa, Y.; Saji, T. *J. Chem. Soc., Chem. Commun.* **1992**, 781−782. For further references, see citations within.

(5) See for example: Chabre, Y.; Djurado, D.; Armand, M.; Romanow, W. R.; Coustel, N.; McCauley, J. P., Jr.; Fischer, J. E.; Smith, A. B., III *J. Am. Chem. Soc.* **1992**, *114*, 764−766.

(6) Jiang, L. Q.; Koel, B. E. *Chem. Phys. Lett.* **1994**, *223*, 69−75 and references therein.

(7) Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* **1986**, *125*, 459−464.

(8) (a) Zhang, Q. L.; O'Brian, S. C.; Heath, J. R.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. *J. Phys. Chem.* **1986**, *90*, 525. (b) Wang, L. S.; Conceicao, J.; Jin, C.; Smalley, R. E. *Chem. Phys. Lett.* **1991**, *179*, 449.

(9) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364.

(10) Dubois, D.; Jones, M. T.; Kadish, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 6446−6451.

(11) Corongiu, G.; Clementi, E. *Int. J. Quantum Chem.* **1992**, *42*, 1185−1208.

(12) Negri, F.; Orlandi, G.; Zerbetto, F. *J. Am. Chem. Soc.* **1992**, *114*, 2909−2913.

(13) de Coulon, V.; Martins, J. L.; Reuse, F. *Phys. Rev. B* **1992**, *45*, 671−675.

(14) Martins, J. L.; Troullier, N. *Phys. Rev. B* **1992**, *46*, 1766−1772.

(15) Saito, R.; Dresselhaus, G.; Dresselhaus. M. S. *Chem. Phys. Lett.* **1993**, *210*, 159−164.

(16) Hutter, J.; Lüthi, H. P. *Int. J. Quantum Chem.* **1993**, *46*, 81−86.

(17) Larsson, S.; Rodriguez-Monge, L. *Int. J. Quantum Chem.: Quantum Chem. Symp. 27* **1993**, 655−665.

singlet—triplet energy gaps such that there is real uncertainty about whether a singlet or a triplet state is lowest in energy. The essential theoretical problem is one of configuration interaction. With a small HOMO-LUMO gap, open-shell configurations, a multiplicity of low-lying states, and Jahn—Teller instabilities, high-level calculations on fullerides present formidable challenges. Recent magnetic susceptibility measurements on isolated crystalline salts of C_{60}^{2-} gave the first bulk assessment of the ground spin state.[20] These salts show a similar amount of paramagnetism to their C_{60}^{1-} or C_{60}^{3-} counterparts. The ca. 2 μ_B magnetic moment, which decreases slightly with decreasing temperature, indicates nearly equi-energetic singlet and triplet states. This is consistent with the fact that triplet EPR signals can still be observed at temperatures as low as 4 K.[20] Nevertheless, even more recent work takes the position that C_{60}^{2-} is diamagnetic and that the EPR signals arise from impurities at the <10% level.[21] The present work does not support this conclusion.

C_{60}^{2-} is also interesting for structural reasons. Regardless of the true nature of the ground spin state, its electronic configuration is orbitally degenerate in I_h symmetry and subject to a Jahn—Teller splitting. In fact, it is now recognized that all C_{60}^{n-} for $n = 1-5$ are subject to Jahn—Teller distortions.[20] The $n = 2$ ion is the first, and to date the only, fulleride to reveal the nature of these distortions. The precision of the X-ray structure determination of [PPN$^+$]$_2$[C_{60}^{2-}] (PPN$^+$ = bis-(triphenylphosphine)iminium ion)[22] is among the highest of any C_{60}-containing structure and reveals quasi-ellipsoidal distortions in the C_{60}^{2-} ion. Consistent with the Jahn—Teller theorem, icosahedral symmetry is lost and only C_i point group symmetry is retained.

A further interest in C_{60}^{2-} is its reactivity as a nucleophile. It can be protonated with triflic acid to form $C_{60}H_2$.[23] It can be dimethylated in about 50% yield with methyl iodide, a reaction which apparently does not occur with the (−1) ion.[24]

In addition, C_{60}^{2-} is of interest as an isolable, structurally-characterizable model for the photoexcited triplet state of neutral C_{60}. Both C_{60}^{2-} and $^3C_{60}$ are two electrons different from a filled shell configuration and might therefore be expected to show certain gross structural and electronic similarities, even though the specific orbital occupations are obviously quite different.

In the present paper we address synthetic, structural, and magnetic aspects of well-characterized C_{60}^{2-} salts to bring coherence to the basic description of its electronic structure. In particular, the complementary application of NMR, EPR, and magnetic susceptibility allows us to corroborate our earlier assertion that C_{60}^{2-} is paramagnetic, that Hund's rule is not obeyed, and that the lowest singlet and triplet states of C_{60}^{2-} are almost equal in energy.

Experimental Section

All manipulations of fullerides were carried out under the inert atmosphere conditions of a Vacuum Atmospheres glovebox under

helium (H$_2$O, O$_2$ < 1 ppm). C_{60} was prepared and purified as previously described.[25] Decamethylcobaltocene (CoCp*$_2$) was prepared by a literature method[26] and all other reagents were used as purchased from Aldrich. Tetrahydrofuran, hexanes, and toluene were distilled from sodium—benzophenone inside the glovebox. Acetonitrile was distilled from P$_2$O$_5$, and then distilled from CaH$_2$ inside the glovebox and passed through dry alumina before use. Benzonitrile was distilled from P$_2$O$_5$, and then vacuum distilled from sodium inside the glovebox. Pyridine was distilled from NaOH, and then distilled from Na inside the glovebox. Acetone was distilled from anhydrous K$_2$CO$_3$ inside the glovebox. Aniline, DMSO, and DMF were vacuum distilled inside the glovebox from CaH$_2$.

Elemental analyses were performed by the U.C. Berkeley Microanalytical Laboratory. EPR spectra were recorded on a Bruker ER 200D-SRC spectrometer equipped with an Oxford Instruments ESR 900 cryostat. NIR spectra were recorded on a Cary 17 spectrometer. NMR spectra were recorded at room temperature on a Bruker AM-360 or 500-MHz spectrometer and shifts were calibrated against internal solvent values. Magnetic susceptibility data were collected on 30-mg samples on an SHE Model 905 Squid Susceptometer. Samples were routinely run at two or more applied magnetic fields (2, 10, or 40 kG) to check for the presence of trace amounts of ferromagnetic impurities. These were frequently observed (up to about 10% of signal at low temperatures) and the data presented herein have been corrected accordingly. The source of the ferromagnetic impurity, undetectable by elemental analysis, is unknown. It may arise from microscopic particulates of iron, nickel, etc. in the environment of the glovebox or in the reducing agents (e.g. sodium).

[Na(dibenzo-18-crown-6)(THF)$_2$]$_2$[C$_{60}$]. A piece of sodium (0.1 g) was added to a warmed suspension of C$_{60}$ (0.020 g, 0.028 mM) and dibenzo-18-crown-6 (0.021 g, 0.059 mM) in tetrahydrofuran (25−35 mL). The mixture was gently stirred at near reflux until the brown coloration of the solvent faded (6−8 h) and the brown precipitate was filtered off. The excess sodium was removed and the product washed with THF. Recrystallization was effected from acetonitrile—toluene to give a dark brown microcrystalline solid (0.030 g, 75%). Anal. Calcd for C$_{123}$H$_{88}$O$_{16}$Na$_2$: C, 78.45; H, 4.54; Na, 2.60; N, 0.00. Found for several independent preparations: C, 77.49−78.22; H, 4.92−5.08; Na, 2.63−3.09; N, <0.03. The crown/THF ratio was determined by ^{1}H NMR: calcd for aryl/aliphatic 8:8, found 8:7.3.

[PPN]$_2$[C$_{60}$]. Freshly isolated [Na(dibenzo-18-crown-6)]$_2$[C$_{60}$] (0.050 g, 0.0313 mmol) was dissolved in dry acetonitrile (10 mL) and filtered. PPNCl (0.160 g, 0.279 mmol, ~5 times molar excess) was dissolved in acetonitrile (ca. ~30 mL). Black shiny crystals of the [PPN]$_2$[C$_{60}$] salt were grown by slow diffusion of the PPNCl solution into the [Na-(dibenzo-18-crown-6)]$_2$[C$_{60}$] solution through a medium or fine frit (1 to 2 days). Sometimes, colorless crystals form as a crusty film on the walls of the crystallizing flask, but with careful collection of the black [PPN]$_2$[C$_{60}$] crystals these do not interfere. The product was washed with acetonitrile. Anal. Calcd for C$_{132}$H$_{60}$P$_4$N$_2$: C, 88.19; H, 3.36; P, 6.89; N, 1.56. Found: C, 88.01; H, 3.71; P, 6.67; N, 1.62.

[CoCp*$_2$]$_2$[C$_{60}$]. Accurate weighing of pure, dry starting materials is critical to avoid under- or overreduction. C$_{60}$ (0.020 g, 0.0277 mmol) was dissolved in toluene (15 mL) and filtered to remove any trace particulates. To this filtrate CoCp*$_2$ (0.0183 g, 0.0555 mmol) dissolved in toluene (2 mL) was added dropwise. The reaction mixture was stirred for 1 h at room temperature. The resulting brown precipitate was filtered off and washed 3 times with toluene (3 mL) and allowed to dry. Anal. Calcd for C$_{100}$H$_{60}$Co$_2$: C, 87.07; H, 4.38; Co, 8.54. Found: C, 86.38; H, 4.97; Co, 8.48.

Results and Discussion

Synthesis. The synthesis of discrete C_{60}^{2-} salts from C_{60} requires either good stoichiometric control of a strong reducing agent and/or the selection of a reducing agent that is specific for the ca. 0.45-V window of redox stability that lies between C_{60}^{1-} and C_{60}^{3-}. The kinetic and thermodynamic solubilities of the reagents and products also come into play in developing

(18) Bergomi, L.; Jolicoeur, Th. *C. R. Acad. Sci., Ser. 2* **1994**, *318*, 283−288.

(19) Yamaguchi, K.; Hayashi, S.; Okumura, M.; Nakano, M.; Mori, W. *Chem. Phys. Lett.* **1994**, *226*, 372−380.

(20) Bhyrappa, P.; Paul, P.; Stinchcombe, J.; Boyd, P. D. W.; Reed, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 11004−11005.

(21) Khaled, M. M.; Carlin, R. T.; Trulove, P. C.; Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1994**, *116*, 3465−3474.

(22) Paul, P.; Xie, Z.; Bau, R.; Boyd, P. D. W.; Reed, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 4145−4146.

(23) (a) Cliffel, D. E.; Bard, A. J. *J. Phys. Chem.* **1994**, *98*, 8140−8143. (b) Niyazymbetov, M. E.; Evans, D. H.; Lerke, S. A.; Cahill, P. A.; Henderson, C. C. *J. Phys. Chem.* **1994**, *98*, 13093−13098.

(24) Caron, C.; Subramanian, R.; D'Souza, F.; Kim, J.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Am. Chem. Soc.* **1993**, *115*, 8505−8506.

(25) Bhyrappa, P.; Pénicaud, A.; Kawamoto, M.; Reed, C. A. *J. Chem. Soc., Chem. Commun.* **1992**, 936−937.

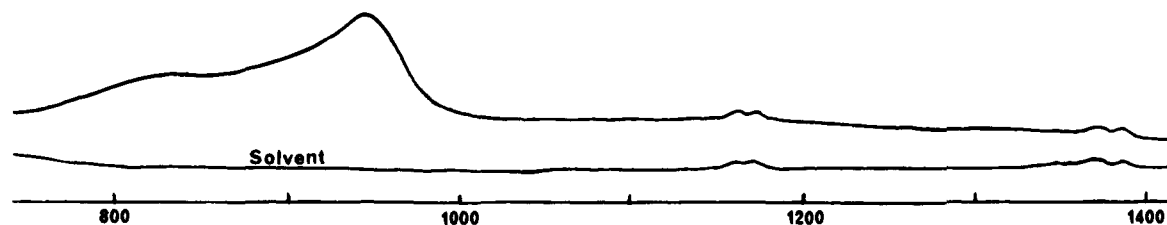(26) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882−1893.

Figure 1. Near-IR spectrum of $[PPN^+]_2[C_{60}{}^{2-}]$ in acetonitrile. Peaks near 1170 and 1370 nm are from the solvent.

good chemical reduction methods. Given the clean, stepwise nature of the electrochemical reduction of C_{60}, synthetic scale electrocrystallization methods would also appear to be potentially useful. They have been successfully applied to the problem of obtaining crystalline salts of the fulleride$(1-)$ ion, but in all cases reported to date double salts and/or nonstoichiometric compounds are formed.[4b,27-31] Some of the nonstoichiometric compounds produced with overvoltage conditions may contain $C_{60}{}^{2-}$ but electrochemical methods have yet to developed for synthesizing pure, discrete $C_{60}{}^{2-}$ salts.

Our present method of choice is to use excess sodium in tetrahydrofuran. The reagents are readily available and are not expensive. Overreduction is prevented by the trick of adding 2 equiv of a commonly available crown ether. This stops the reaction at the $(2-)$ stage because of essentially quantitative precipitation of the product, $[Na(crown)(THF)_2]_2[C_{60}]$. The piece of excess sodium metal is simply removed. Underreduction is easily avoided; the brown $(1-)$ salt is soluble in THF. Indeed, the end-point of the reaction is readily observed by following the disappearance of brown coloration from the solvent.

An alternative synthetic method uses decamethylcobaltocene. Earlier we had shown that cobaltocene is a very convenient reducing agent for preparing the $(1-)$ salt.[32] The decamethyl analogue is a stronger reducing agent by ca 0.5 V and can in fact be used to prepare $C_{60}{}^{n-}$ for $n = 1$, 2, or 3 depending primarily on stoichiometric control. Nevertheless, solvent choice is also important in obtaining clean products. Toluene is the preferred solvent for the $C_{60}{}^{2-}$ preparation.

The $Na(crown)^+$ salt of $C_{60}{}^{2-}$ has reasonably good solubility in acetonitrile so that cation metathesis can be readily achieved by precipitation of less soluble salts. Because it gives nicely crystalline material suitable for single-crystal X-ray diffraction, we have tended to work mostly with the bis(triphenylphosphine)iminium cation, PPN^+. Thus, shiny black crystals of $[PPN]_2[C_{60}]$ can be grown by slow diffusion ($\sim$1 day) of an acetonitrile solution of [PPN]Cl into an acetonitrile solution of $[Na(crown)]_2[C_{60}]$. The crystals are somewhat air sensitive but with proper anaerobic storage they appear to be stable indefinitely.

All three isolated salts gave good elemental analyses and their reduction state was readily established in solution by NIR spectroscopy.[33] A typical spectrum is shown in Figure 1. The lack of a band at 1080 nm indicates the absence of $C_{60}{}^{1-}$ and

the lack of bands at 780 and 1380 nm indicates the absence of $C_{60}{}^{3-}$. This type of spectral analysis was routinely used as an integrity check on samples before and after making other physical measurements (NMR, EPR, and magnetic susceptibility). Once absorption bands of the solvent are taken into account, we do not find the bands at $\sim$1400 nm that sometimes appear in electrochemically prepared samples.[21] The most sensitive test for $C_{60}{}^{1-}$ impurity in the $C_{60}{}^{2-}$ salts was found to be EPR spectroscopy. As discussed below, the signal from $C_{60}{}^{1-}$ is of greater peak intensity than $C_{60}{}^{2-}$ and has a distinctly lower g value under most conditions.

^{13}C NMR Spectroscopy. C_{60} has a single sharp ^{13}C resonance at about 143 ppm downfield of TMS in its NMR spectrum.[34] Similarly, $C_{60}{}^{n-}$ fullerides are expected to show a single resonance but, if paramagnetic, should also show considerable broadening and shifting. ^{13}C NMR measurements have been reported for alkali metal reduced C_{60} salts in the solid state,[35,34] but to our knowledge there are no reports of ^{13}C chemical shifts of discrete fullerides in solution.[36]

We have determined ^{13}C chemical shifts of $C_{60}{}^{n-}$ for $n = 1$, 2, and 3 in deuterated dimethyl sulfoxide solution. They appear as broad peaks (up to a few ppm wide) at 186, 184, and 197 ppm, respectively. The values are reproducible and independent of cation to within 2–3 ppm. NIR spectra before and after the NMR measurements were used to establish sample integrity. Mixtures of $C_{60}{}^{2-}$ and $C_{60}{}^{3-}$ salts gave single peaks with shift values intermediate between 184 and 197. This shows that electron exchange is fast on the NMR time scale.

The interpretation of ^{13}C chemical shifts in C_{60} is complex.[37] Nevertheless, a first-order interpretation of the chemical shifts of the present fullerides is that all three anions experience similar 40–55 ppm downfield paramagnetic shifts relative to C_{60} as a result of similar unpaired spin densities. The $C_{60}{}^{1-}$ and $C_{60}{}^{3-}$ ions have almost identical EPR spectra and magnetic susceptibilities.[20] Both are spin-doublet $S = \frac{1}{2}$ systems and the similar magnitude of their ^{13}C shifts is therefore not too surprising. More importantly for the present work, the near identity of the $C_{60}{}^{2-}$ shift to that of $C_{60}{}^{1-}$ (and the similarity with $C_{60}{}^{3-}$) is conclusive evidence that $C_{60}{}^{2-}$ is paramagnetic in solution and that the average spin state is similar. This is consistent with our earlier conclusion that the ground spin triplet and singlet states of $C_{60}{}^{2-}$ are essentially equal in energy. Under the time-averaged conditions of an NMR experiment this would lead to about one unpaired electron per sixty carbon atoms, just as in $C_{60}{}^{1-}$ and $C_{60}{}^{3-}$.

Magnetic Susceptibility. We have been puzzled that the variable-temperature magnetic susceptibility data for salts of

(27) Moriyama, H.; Kobayashi, H.; Kobayashi, A.; Watanabe, T. *J. Am. Chem. Soc.* **1993**, *115*, 1185–1187.

(28) Pénicaud, A.; Peréz-Benítez, A.; Gleason, R.; Muñoz, E.; Escudero, R. *J. Am. Chem. Soc.* **1993**, *115*, 10392–10393.

(29) Miller, B.; Rosamilia, J. M. *J. Chem. Soc., Faraday Trans.* **1993**, 273–276.

(30) Bilow, U.; Jansen, M. *J. Chem. Soc., Chem. Commun.* **1994**, 403–404.

(31) Kobayashi, H.; Tomita, H.; Moriyama, H.; Kobayashi, A.; Watanabe, T. *J. Am. Chem. Soc.* **1994**, *116*, 3153–3154.

(32) Stinchcombe, J.; Pénicaud, A.; Bhyrappa, P.; Boyd, P. D. W.; Reed, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 5212–5217.

(33) Lawson, D. R.; Feldheim, D. L.; Foss, C. A.; Dorhout, P. K.; Elliott, C. M.; Martin, C. R.; Parkinson, B. *J. Electrochem. Soc.* **1992**, *139*, L68–71.

(34) Johnson, R. D.; Bethune, D. S.; Yannoni, C. S. *Acc. Chem. Res.* **1992**, *25*, 169–175.

(35) Tycko, R.; Dabbagh, G.; Rosseinsky, M. J.; Murphy, D. W.; Fleming, R. M.; Ramirez, A. P.; Tully, J. C. *Science* **1991**, *253*, 884–886.

(36) A ^{13}C shift of 157 ppm reported for C_{60} treated with excess lithium probably arises from Li_6C_{60}: Bausch, J. W.; Prakash, G. K. S.; Olah, G. A.; Tse, D. S.; Lorents, D. C.; Bae, Y. K.; Malhotra, R. *J. Am. Chem.* **1991**, *113*, 3205–3206.

(37) Pasquarello, A.; Schlüter, M.; Haddon, R. C. *Phys. Rev. A* **1993**, *47*, 1783–1789.

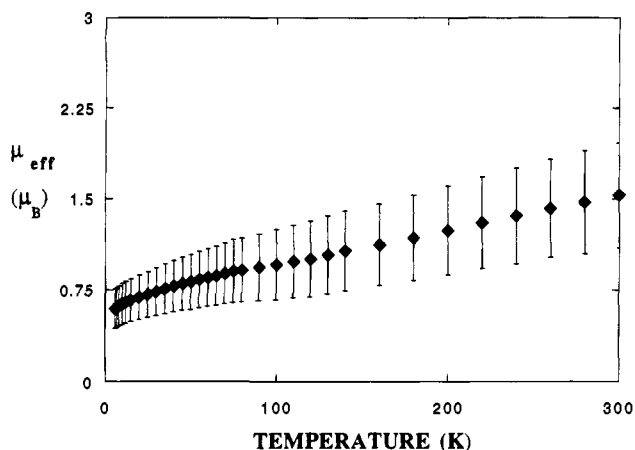**Figure 2.** Plot of magnetic moment versus temperature for [PPN$^+$]$_2$-[C$_{60}^{2-}$].

C$_{60}^{2-}$ vary considerably with counterion and sample history. All samples show significant paramagnetism but the room temperature magnetic moment among all samples studied to date varies from 1.0 to 2.3 μ_B. To illustrate this phenomenon, we show data in Figure 2 for the best characterized salt, [PPN$^+$]$_2$[C$_{60}^{2-}$]. Seven different data sets on seven different samples have been averaged and standard deviations are shown as error bars.

The ground state of C$_{60}^{2-}$ could be either a triplet or a singlet state depending on the relative importance of Hund's rule-like exchange energy versus spin-pairing forces (from Jahn–Teller splitting or mixing of the ground state with singlet excited states). Calculations at the QCFF/PI level[12] find three low-lying states, all sufficiently close in energy that a reliable prediction of the ground state cannot be made. These three states are ^1A_g, ^1A_u, and $^3T_{1g}$ and the magnetic susceptibility data are consistent with their near equivalence. The slight fall-off of magnetic moment with decreasing temperature suggests that one (or both) of the singlet states is lowest in energy but the observation of triplet EPR signals at 4 K (see below) means that if this is true, the singlet–triplet energy gap is very small (perhaps less than a wavenumber or so). The spin-only magnetic moment for a spin triplet is 2.83 μ_B. The leveling off of the high-temperature μ_{eff} plot at values substantially below this is therefore inconsistent with an isolated ground state triplet state. The spin-only magnetic moment for a two-state system with equi-energy $S = 0$ and $S = 1$ states is 2.45 μ_B. The spin-only moment for a three-state $S = 0$, $S = 0$, $S = 1$ equi-energy system is 2.19 μ_B. In either case, if a singlet state is lowest, the moments will be further reduced. The experimental data are more compatible with these descriptions, but given the unknown number of low-lying singlet and triplet states, let alone their separations, it is unwise to attempt any further interpretation at this time. The variability of the susceptibility data with counterion and sample history probably reflects the sensitivity of the state energies to the crystal environment of the C$_{60}^{2-}$ ions. Increased grinding of the samples leads to lower susceptibility.

We have considered the possibility that ball-to-ball spin coupling should be considered in the interpretation of the magnetic susceptibility data. However, by restricting our data set to the PPN$^+$ salt this possibility appears remote. The two large cations should be sufficient to separate the anions and render them magnetically dilute. The van der Waals surfaces of the C$_{60}^{2-}$ ions in the X-ray crystallographically characterized [PPN]$_2$[C$_{60}$][22] are separated by >2.0 Å, and the closest center-to-center separation of buckyballs is 12.7 Å. For comparison,

there are many cases of organic radicals in van der Waals *contact* (i.e. separation 0.0 Å) where magnetic coupling is weak.[38]

In summary, the ^{13}C NMR data and the magnetic susceptibility data offer convincing evidence that C$_{60}^{2-}$ is paramagnetic in both solution and the solid state. The C$_{60}^{2-}$ ions are magnetically dilute in both phases. The conclusion that C$_{60}^{2-}$ is diamagnetic, based upon integrated intensities of EPR signals,[21] is probably in error. Low integrated intensities could arise from a lack of magnetic dilution when 4:1 toluene–acetonitrile is used as solvent. It is possible that in this low dielectric medium, aggregation of the ions and consequent antiferromagnetic coupling from ball-to-ball contact makes a significant fraction of the material EPR silent. In fact, aggregation is a potential problem when freezing any solution, particularly with the non-glassing solvents that must be used for dissolution of C$_{60}^{2-}$. As alluded to above, there is an additional problem of interpreting quantified spin. The existence of one or more low-lying singlet states, and their apparent environmental sensitivity, greatly complicates the prediction of expectation values. When expressed as a percentage of the value expected for an isolated ground state triplet, a value of ~10% spin intensity has been measured.[21] This value must be raised to >12% to accommodate material loss during electrolytic preparation of the sample (measured by NIR)[21] and could easily be doubled to ~25% if , for example, half of the C$_{60}^{2-}$ ions were in singlet states. Thus, there is significant paramagnetism detected by EPR spectroscopy even without considering losses of signal from aggregation, much more than can be ascribed to impurities. We now discuss these EPR signals.

EPR Spectroscopy. The EPR spectrum of the C$_{60}^{2-}$ ion is not well understood. It consists primarily of two signals, a relatively sharp (1−3 G) doublet-like signal of unknown origin and a pair of signals ($\Delta H = 10-15$ G) readily assigned to the perpendicular portion of a typical axial triplet. The g value for the narrow signal is slightly greater than that of the triplet, both being less than the free electron value. This is consistent with a fulleride origin of the signals (as opposed to impurities). These features were first reported by Jones and Kadish et al. for electrochemically-generated material in benzonitrile.[9,10] Figure 3 shows the 4 K spectrum of C$_{60}^{2-}$ (as the Na(crown)$^+$ salt) in seven different solvents. Frozen dimethyl sulfoxide is the only solvent that forms anything approaching a good glass. Nevertheless, the same qualitative spectral features are seen in each solvent. This suggests that the low-temperature C$_{60}^{2-}$ spectrum is much less sensitive to media influence than is C$_{60}^{1-}$ where marked anisotropy is observed under a variety of conditions.[31] Not shown are spectra of C$_{60}^{2-}$ as a function of the cation. These reveal some sensitivity to the nature of the cation but no more than that seen as a function of solvent. Eaton[21] has suggested that all of the signals ascribed to C$_{60}^{2-}$ arise from impurities. However, the constancy of the above observations (Figure 3), made on different occasions with different samples under a variety of conditions of concentration, solvent, and cation, leaves little doubt that the signals arise from C$_{60}^{2-}$. Moreover, the same general features can be detected in the low-temperature solid-state EPR spectrum of analytically pure [PPN]$_2$[C$_{60}$], a salt whose structure has been established by X-ray crystallography.[22] This EPR spectrum is shown in Figure 4. The signals are understandably broader than in frozen solution because of weak dipolar coupling effects, but the large PPN$^+$ cations apparently render the C$_{60}^{2-}$ anions sufficiently magnetically dilute that their spectrum approaches that of frozen solution

(38) See for example: Song, H.; Orosz, R. D.; Reed, C. A.; Schedit, W. R. *Inorg. Chem.* **1990**, *29*, 4274−4282.
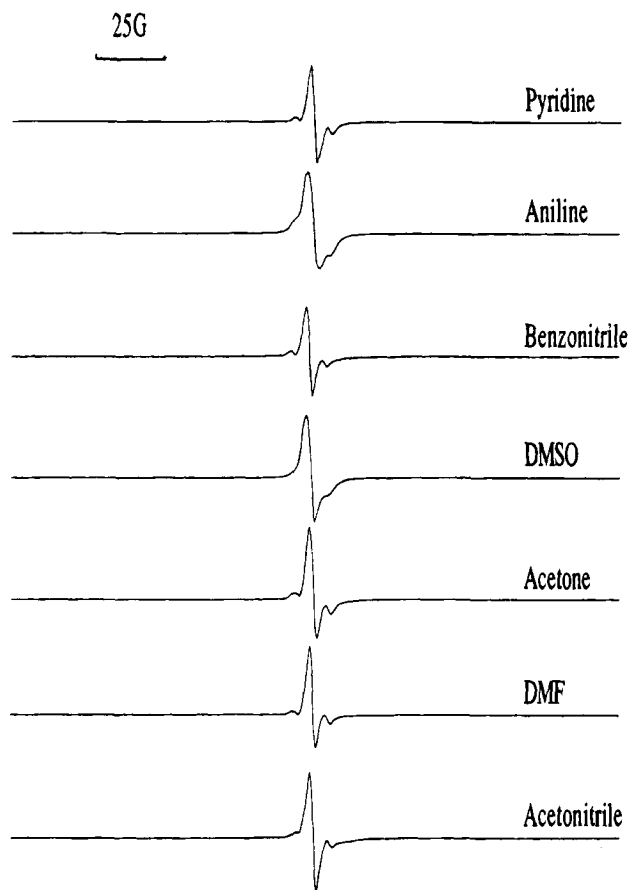
Figure 3. X-band EPR spectra of [Na(crown)(THF)₂]₂[C_{60}^{2-}] in seven different solvents (~10^{-3} M) recorded at 4 K (modulation 0.25 G, microwave power 200 μW).

conditions. The central "doublet-like" line dominates the spectrum. On the high-field (right-hand) side there are features attributable to the same triplet observed at low temperature in frozen solution.[39] The peaks marked A and B correspond to perpendicular and parallel components of a triplet state spectrum with $2D \sim 19$ G.

The question might be raised as to whether the sharp doublet-like central line of the C_{60}^{2-} spectrum is due to the presence of some C_{60}^{1-} or C_{60}^{3-}. After all, either of these ions could be present if under- or overreduction had occurred during the synthesis or handling, and both have doublet spectra with similar *g* values. However, by surveying solvents, we have found conditions where the three ions have sufficiently distinct *g* values and line widths that we can rule out this possibility. Figure 5 illustrates this point for Na(crown)$^+$ salts of the three C_{60}^{n-} anions in frozen DMSO solution. Each ion has a distinctive spectrum. Moreover, the power saturation characteristics of the signals differ, the C_{60}^{2-} signal being the most easily saturated. As indicated earlier, EPR is particularly sensitive to the presence of traces of C_{60}^{1-} because of its high peak height at low *g* value. By EPR, we were able to detect C_{60}^{1-} contamination of C_{60}^{2-} samples that were "pure" by NIR criteria.

In order to better reveal the nature of the low-temperature triplet spectrum we have measured EPR spectra at high microwave powers where the overlapping center line is markedly saturated. Figure 6 shows a typical power saturation study. The relative intensity of the central line diminishes with increasing microwave power. Figure 7 shows a vertical expansion of the highest power spectrum. It clearly reveals the
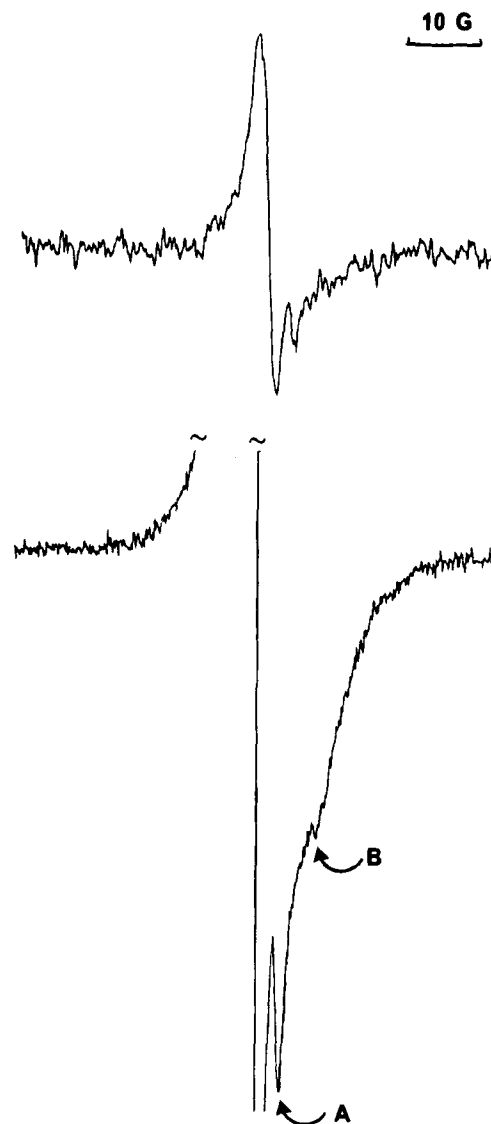
(39) In samples containing large bundles of needle-like crystals, some anisotropy with respect to orientation is observed for the triplet features.


Figure 4. X-band EPR spectrum of crystalline [PPN$^+$]₂[C_{60}^{2-}] at 4 K (modulation 1 G, microwave power 0.2 μW, gain 8 × 10^5, frequency 9.4377 GHz). The lower spectrum is a vertical scale expansion of the upper spectrum with a very slow scan rate.

two pairs of signals expected for a triplet of axial symmetry. The outer peak-to-peak separation is 22 G and it is equated with $2D$ for the parallel portion of the spectrum. The inner signals are influenced by the presence of the incompletely saturated central line, but the familiar shape and position of this perpendicular portion of the axial triplet is readily discernible.

We have studied the temperature dependence of the EPR signal of C_{60}^{2-} in a variety of frozen solvents. In general, the appearance of the central, doublet-like signal is unaffected by temperature. The triplet lines typically broaden and become more diffuse with increasing temperature and, depending on the solvent, can become indiscernible above ca. 100 K. A typical set of data is illustrated in Figure 8, in this case for the Na(crown)$^+$ salt in DMSO.

In most solvents we see a *new* triplet begin to grow in with increasing temperature. As indicated by the arrows in Figure 8, a new pair of signals with 29 G separation are just discernible at 30 K and are clearly visible all the way up to 155 K. Similar observations were reported for the PPN$^+$ salt in acetonitrile in our earlier communication.[20] The new peaks are also seen in the Na(crown)$^+$ salt in DMF, CH₂Cl₂, aniline, and pyridine. In a vertical scale expansion, the parallel portion of this new triplet becomes visible. These outer peaks, which have not been

2912   *J. Am. Chem. Soc., Vol. 117, No. 10, 1995*

Boyd et al.
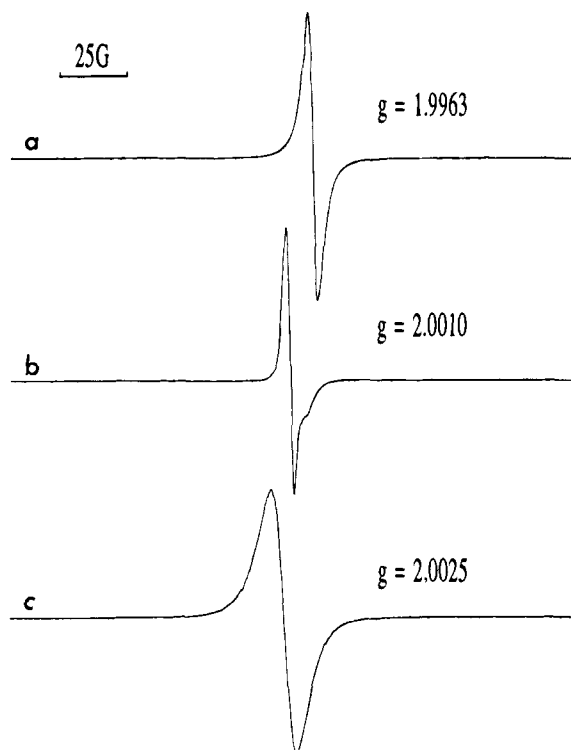
Figure 5. EPR spectra of (a) C_{60}^{1-}, (b) C_{60}^{2-}, and (c) C_{60}^{3-} as their [Na(crown)]$^+$ salts in DMSO at 4 K.
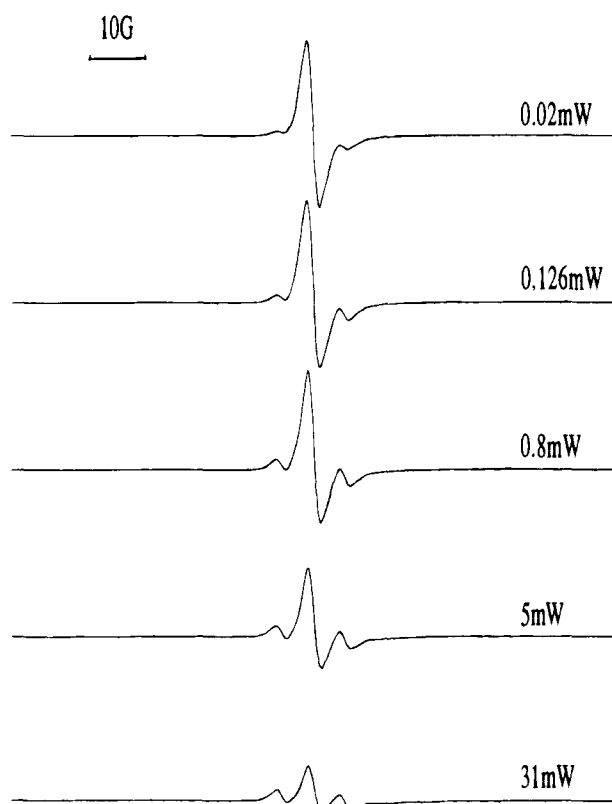

Figure 6. Microwave power dependence of the EPR spectrum of 10^{-3} M [Na(crown)(THF)$_2^+$]$_2$[C_{60}^{2-}] in pyridine at 4 K showing gradual saturation of the central signal (gain 1.25×10^2 except at 31 mW where it is 1.25×10^4; frequency 9.4345 GHz).

reported before, are marked with asterisks in Figure 9. Their separation of 58 G is equated with $2D$. We refer to this new signal as the "high-temperature triplet" to distinguish it from the aforementioned triplet which we now refer to as the "low-temperature triplet". These two triplets differ in g value and
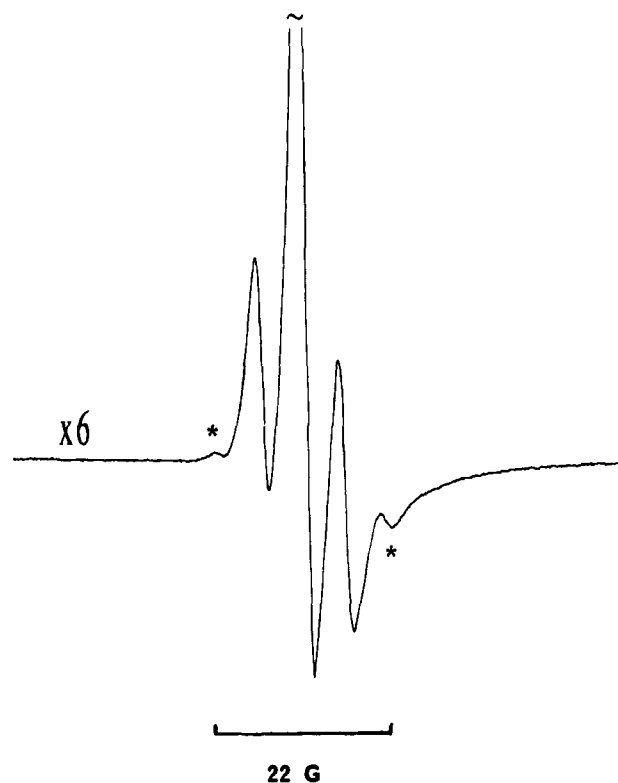

Figure 7. Vertical expansion ($\times 6$) of the highest power spectrum of Figure 6. The outer peaks marked with an asterisk are the parallel portion of the low-temperature triplet ($2D = 22$ G).
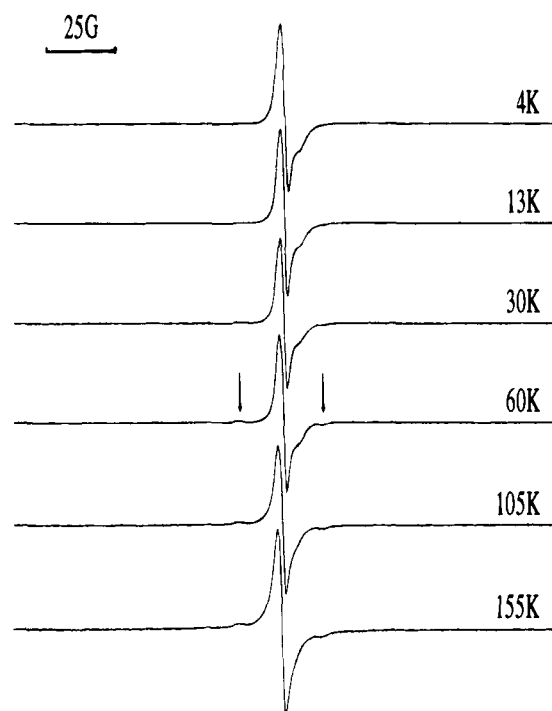

Figure 8. Temperature dependence of the EPR spectrum of C_{60}^{2-} as the Na(crown)$^+$ salt in frozen 2×10^{-3} M DMSO solution showing the appearance of the perpendicular portion of the high-temperature triplet (marked with arrows). Frequency 9.4318 GHz, modulation 0.25 G, gain 6.3×10^2 at 4 K and 3.2×10^4 at 155 K.

$2D$ splitting, the high-temperature triplet having the slightly lower g value and approximately double the splitting (58—60 G versus 19—29 G depending on conditions).

The appearance of two distinct triplets at liquid N$_2$ temperatures enables us to explain the observation of Jones and Kadish[10]

The C_{60}^{2-} Fulleride Ion
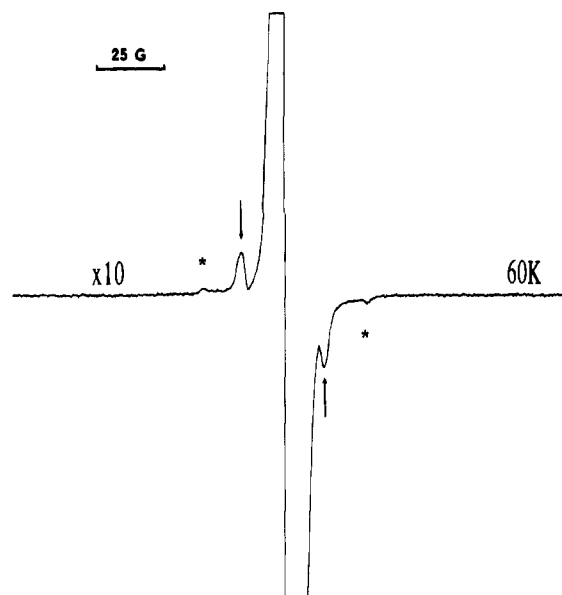
J. Am. Chem. Soc., Vol. 117, No. 10, 1995 2913

Figure 9. Vertical expansion ($\times 10$) of the 60 K spectrum of Figure 8 revealing the parallel portion of the high-temperature triplet, marked with asterisks. As in Figure 8, the perpendicular portion is marked by arrows.

that the separation of the outer peaks of their triplet ($2D$) was not exactly twice the spacing of the inner lines (D) as required by theory. Under their experimental conditions (benzonitrile, Bu_4N^+ salt, $123-226$ K) the two triplet signals have quite similar g values and their splittings are nearly a factor of 2 different. As a result, the perpendicular portion of one signal is fortuitously nearly coincident with the parallel portion of the other. In the higher field region the spacings are distorted by overlap of the peaks. In the lower field region, two separate peaks can in fact be seen in their spectrum (see Figure 4a in ref 10).

We assign the high-temperature triplet signal to the thermal occupation of a low-lying triplet state. This is conceptually closely related to our proposal that the sharp spike that grows into the EPR spectrum of C_{60}^{1-} as the temperature is raised is due to thermal occupation of a low-lying excited state.[32] That it appears in some solvents but not others is consistent with the idea that the energy gap is sensitive to the solvent environment. The situation was complicated in the C_{60}^{1-} case by the overlap of the proposed excited state signal with an intense ground state signal. However, in the present case of the C_{60}^{2-} ion there is no such overlap. The proposed high-temperature signal grows in directly from an essentially flat baseline (see Figure 8).

To summarize, the EPR of C_{60}^{2-} shows three signals: (a) a narrow doublet-like central line (~ 2 G), (b) a "low-temperature" triplet ($2D \simeq 25$ G), and (c) a thermally populated triplet ($2D \simeq 60$ G). A typical spectrum showing all three signals is presented in Figure 10. We now consider an electronic energy level diagram consistent with the observation of three signals.

Energy Level Diagram. As discussed above with regard to the magnetic susceptibility data, the ground state of C_{60}^{2-} could be either a singlet or a triplet. Regardless of the particular state that is actually lowest, the observation of more than one EPR signal at 4 K requires that there is more than one triplet state at or very near the ground state energy level. Under icosahedral symmetry, the $(t_{1u})^2$ configuration gives rise to a low-lying triplet state ($^3T_{1g}$) corresponding to the spin-parallel state
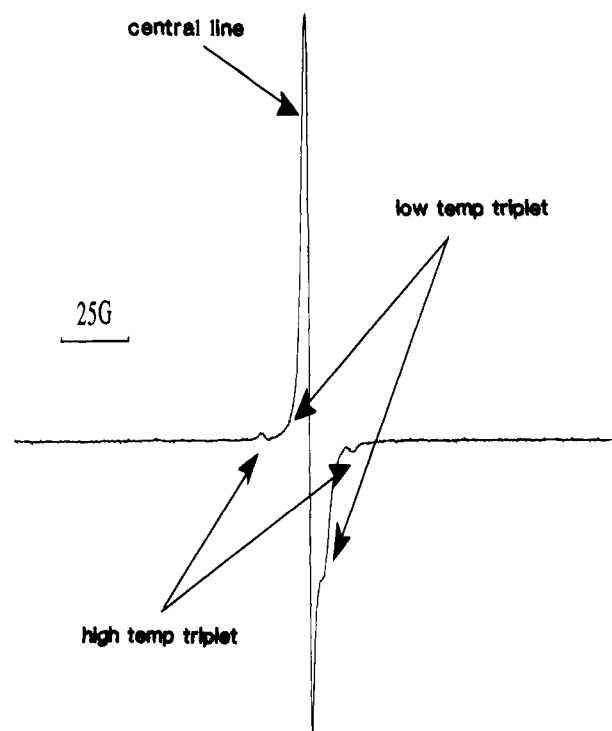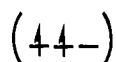
$$\left(\uparrow\uparrow - \right)$$

Figure 10. A representative EPR spectrum of C_{60}^{2-} showing the three typical signals. The spectrum was recorded at 85 K for the [PPN$^+$] salt in benzonitrile (modulation 0.25 G, microwave power 200 μW).
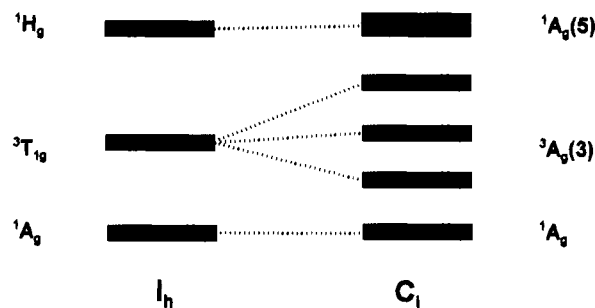
Figure 11. Qualitative energy level diagram for the states of C_{60}^{2-} under I_h symmetry (left) and C_i symmetry (right).

and two singlets (^1A_g and ^1H_g).[12] Upon lowering the symmetry to C_i (i.e. to the symmetry of C_{60}^{2-} seen in the X-ray structure), the $^3T_{1g}$ state will split into three ^3A states. The degenerate H_g state will also split into singly degenerate singlet states. This is shown in Figure 11. The precise order of these states is difficult to determine. For example, a limited configuration interaction calculation ($t_{1u} - t_{1g}$ manifold) under I_h symmetry within the AM1 model[40] gives the state ordering $^1A < {}^3T_{1g} < {}^1H_g$. A similar calculation using the geometry of C_{60}^{2-} seen in the X-ray structure shows a significant splitting of states ($^1A < {}^3A < {}^3A' < {}^1A' < {}^1A'' < {}^3A$). All of these states are calculated to be within 2400 cm^{-1} of the ground state! For the purposes of the present discussion, the relevant point is that the splitting of the $^3T_{1g}$ state may be quite significant and it provides an explanation for the observation of EPR signals from different triplet states.

The "low-temperature triplet" signal is ascribed to one of the lowest lying of the triplet states, having zero-field splitting $D \simeq 13$ G. The narrow "central line" is ascribed to a second low-lying state with an unresolved low zero-field splitting, i.e. $D \simeq 0$ G. Physically, this corresponds to a triplet state where at

(40) AM1-CI molecular orbital calculations were carried out using AMPAC 4.5, Semichem Inc., 1994.

least conceptually the two unpaired electrons have parallel spins but can be viewed as sufficiently remote from each other that no interaction is measurable by EPR. In other words, the electrons behave much like independent spins and have doublet-like EPR character. The "high-temperature triplet" ($D \simeq 30$ G) is ascribed to thermal occupation of the third ^3A state at somewhat higher energy. These assignments provide a reasonable point of departure for developing a more quantitative model of the electronic structure of C_{60}^{2-} and a target for assessing the merits of theoretical approaches. At this time, we note only that although the symmetry of C_{60}^{2-} has presumably been reduced to C_i, the triplet EPR signals are axial not rhombic. This suggests that the rhombic anisotropy is time-averaged by some dynamic process to give the appearance of axial symmetry.

Comparison to Triplet C_{60}. It is notable that the photoexcited triplet state of (neutral) C_{60} is not only EPR detectable but has been interpreted in terms of at least two signals.[41] At low temperatures, the triplet character of these signals is readily seen. At higher temperatures there is a dynamic process which averages the magnetic axes and leads to a very narrow doublet-like signal. Fast interconversion between different distorted structures (referred to as pseudorotation or a dynamic Jahn−Teller effect) is proposed to account for this observation. Thus, there are certain parallels between triplet C_{60} and C_{60}^{2-} and the question arises, could pseudorotation account for the narrow signal in C_{60}^{2-}? Certainly, from the X-ray structure, we know that C_{60}^{2-} is distorted from icosahedral symmetry in crystals of the PPN$^+$ salt.[22] The extent of the distortion is small; no atom is displaced by more than 0.02 Å from icosahedral symmetry. So dynamic interconversion between different "distortomers" would seem feasible. However, there is no evidence in the X-ray structure for any distribution of structures. Rather, the X-ray structure is very precise and ordered.

It is easier to conceive of the existence of discrete populations of distortomers in a frozen solvent matrix. Cation interactions might also affect structure. However, the EPR signals from C_{60}^{2-} at low temperatures (see Figure 3) are much less sensitive to solvent or counterion than might be expected if C_{60}^{2-} was being trapped by medium interactions into two (or more) substructures. Also, it seems unlikely that seven different

solvents would trap similar ratios of distortomers. In addition, the solid state EPR spectrum of crystals of the PPN$^+$ salt shows both types of EPR signals and is qualitatively similar to the frozen solution spectra. Moreover, it is significant that both the sharp central line and the triplet are present at temperatures as low as 4 K and they change rather little upon increasing the temperature through several decades of degrees Kelvin. The thermal onset of a dynamic process, although a viable explanation for the narrow signal in $^3C_{60}$, does not seem to be consistent with the data on C_{60}^{2-}. The same comments apply to the "high-temperature triplet". If this signal was the result of some thermally activated dynamic process (which occurred in some of the C_{60}^{2-} ions that had the low-temperature triplet signal) the zero-field splitting would be expected to decrease as the effective symmetry increases. In fact, the line width of the high-temperature triplet is *larger* than that of the low-temperature triplet. Thus, although there are superficial parallels between the EPR of $^3C_{60}$ and C_{60}^{2-}, the differences in their low-temperature dependencies suggest that they have quite different electronic state behavior. This is consistent with the different orbital occupations: $(t_{1u})^2$ for C_{60}^{2-} and $(h_u)^{-1}(t_{1u})^1$ for $^3C_{60}$.

Conclusion. The basic electronic description of C_{60}^{2-} is now clear. It is paramagnetic. The ground triplet and singlet states are very close in energy, so close in fact that it is difficult to establish experimentally which is lower. The EPR spectrum of C_{60}^{2-} has two major signals, a rather typical axial triplet and a narrow doublet-like line which can also be assigned to a triplet state. Future investigations are likely to be directed toward a deeper understanding of these signals and the electronic and molecular structure which gives rise to them. The gross physical picture of C_{60}^{2-} that emerges is one where the two added electrons reside in molecular orbitals that are spatially quite segregated. The closest parallel may be to diradical anions of oligomeric pyrenyl aromatics.[42]

(41) For representative papers on the EPR of $^3C_{60}$ see: (a) Wasielewski, M. R.; O'Neil, M. P.; Lykke, K. R.; Pellin, M. J.; Gruen, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 2774−2776. (b) Closs, G. L.; Gautam, P.; Zhang, D.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Phys. Chem.* **1992**, *96*, 5228−5231. (c) Terazima, M.; Hirota, N.; Shinohara, H.; Saito, Y. *Chem. Phys. Lett.* **1992**, *195*, 333−338. (d) Bennati, M.; Grupp, A.; Mehring, M.; Dinse, K. P.; Fink, J. *Chem. Phys. Lett.* **1992**, *200*, 440−444. (e) Regev, A.; Gamliel, D.; Meiklyar, V.; Michaeli, S.; Levanon, H. *J. Phys. Chem.* **1993**, *97*, 3671−3679. (f) Zhang, D.; Norris, J. R.; Krusic, P. J.; Wasserman, E.; Chen, C-C.; Lieber, C. M. *J. Phys. Chem.* **1993**, *97*, 5886−5889.

(42) Kreyenschmidt, M.; Baumgarten, M.; Tyntyulkov, N.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1957−1959.