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Buckminsterfulleride(1−) Salts: Synthesis, EPR, and the Jahn–Teller Distortion of C_{60}^-

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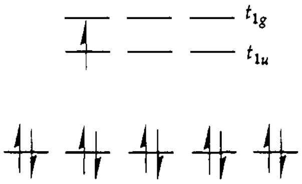
Abstract: Synthetic methods are reported for the isolation of a number of buckminsterfulleride(1−) salts. Counterions include cobaltocenium ion, Na(dibenzo-18-crown-6)$^+$, and bis(*N*-methylimidazole)(tetraphenylporphinato)tin(IV)$^{2+}$. The EPR spectrum of C_{60}^- in frozen solution shows two unusual features. First, there is a counterion-dependent anisotropy observed at low temperatures. This is ascribed to an ellipsoidal distortion induced by ion pairing. It is consistent with, but not directly ascribable to, a static Jahn–Teller distortion. Second, there are two components to the high-temperature spectrum: the broad essentially isotropic, major signal and a narrower "spike". The narrower signal is ascribed to thermal population of a low-lying excited state, a natural consequence of the distortion that splits the $^2T_{1u}$ state into closely spaced ^2E and ^2A states. In contrast to intuition and to *ab initio* calculations, the ^2E state is lowest in most systems studied to date.

Introduction

Buckminsterfullerene readily accepts electrons to form fulleride anions. Evidence for this electronegativity came early in the microscale era of C_{60} from estimates of its high gas-phase electron affinity and small HOMO–LUMO gap.[1,2] The macroscale era of C_{60} began in 1990,[3] and there was immediate confirmation of anion formation in condensed media via reductive voltammetry.[4] Since then, electrochemical methods have demonstrated formation of C_{60}^{n-} for n up to 6.[5-8] The synthesis and isolation of fulleride salts has moved much more slowly, with only two $n = 1$ compounds reported to date: the double salt $[Ph_4P^+]_3[C_{60}^-][Cl^-]_2$[9] and the chromium(III) tetraphenylporphyrin salt $[Cr(TPP)(THF)_2^+][C_{60}^-]\cdot$ THF.[10,11] Discrete fulleride lattices corresponding to $n = 2, 3, 4$, and 6 have been identified in connection with the exploration of superconductivity in alkali metal-doped C_{60}.[12] A fulleride salt isolated from the reaction of tetrakis(dimethylamino)ethane and C_{60} has been characterized; it shows an unusual molecular ferromagnetism.[13] The paucity of isolated fullerides derives mainly from limitations in the amount of C_{60} available for conventional synthesis, a situation that has been rectified in recent months.[14-19]

In this paper, we report a number of new isolated salts of the buckminsterfulleride(1−) ion. They are important for addressing two interesting questions about this unique anion radical. The first concerns the nature and extent of the Jahn–Teller distortion requiried by the $(t_{1u})^1$ degeneracy upon occupation of the LUMO of C_{60}. The second concerns the need to understand the EPR spectrum of C_{60}^- which shows many distinctive and peculiar features.

The very high symmetry of C_{60}, a truncated icosahedron of point group I_h, gives rise to an extraordinary hierarchy of degenerate orbitals[2] which are in many ways reminiscent of the hydrogen atom. In fulleride chemistry, the important region of the molecular orbital energy level diagram involves the low-lying LUMOs. These are the triply degenerate t_{1u} and t_{1g} orbitals, about 1 eV apart, and about 2.6 eV above the $(h_u)^{10}$ HOMO:



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(11) Abbreviations used in this paper: TPP = tetraphenylporphyrinate, THF = tetrahydrofuran, TpTP = tetra-*p*-tolylporphyrinate, crown = dibenzo-18-crown-6, *N*-MeIm = *N*-methylimidazole, Cp = cyclopentadienide ($C_5H_5^-$).

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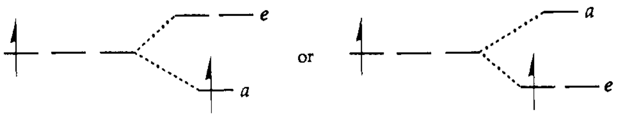
The Jahn–Teller theorem requires a splitting of the $(t_{1u})^1$ degeneracy, and this could occur in either of two ways:



Intuitively, one might expect the former configuration to prevail since the latter configuration is itself subject to a further Jahn–Teller splitting. There are PPP[20] and UHF[21] calculations on the Jahn–Teller effect in C_{60}^- but little in the way of definitive experimental verification of its nature and magnitude. The broad NIR spectrum of C_{60}^- has been suggested to arise from a Jahn–Teller distortion.[22,23] From the isotropic nature of the EPR signal of C_{60}^- in 13X molecular sieves the distortion was suggested to be dynamic, even at 4 K.[24]

Early reports on the EPR spectrum of C_{60}^- noted several features, many of which have yet to be fully explained. The *g* value is less than the free electron value typical of organic radicals.[9] This has been treated theoretically.[22] The line width is large (>45 G) at room temperature and decreases markedly with decreasing temperature to 77 K.[9,25,26] A highly *an*isotropic signal was observed near liquid helium temperatures in one case[10] but not in another.[24] High-temperature spectra typically show a minor component that appears as a relatively sharp spike. Its origin is unknown. Conjecture that it arises from electron exchange[27] with free C_{60} or from disproportionation[25] to C_{60}^{2-} are discounted in the present work. We propose instead that it arises from thermal population of an excited state, a natural consequence of the distortion which splits the ^2T state into closely spaced ^2E and ^2A states. We show that there is a marked cation dependence on the low-temperature EPR spectrum which is probably best interpreted in terms of a facile environmental enhancement of a Jahn–Teller distortion.

Experimental Section

General Methods. All manipulations of fullerides were carried out under inert atmosphere in a Vacuum Atmospheres Drybox under helium (H_2O, O_2 < 1 ppm). C_{60} was prepared and purified by literature methods.[14] $[Cr(TPP)(THF)_2][C_{60}]$[10] and Sn(TpTP)[28] were prepared as reported. Elemental analyses were performed by Oneida Research Services Inc. or U. C. Berkeley Microanalytical Laboratory and typically showed carbon somewhat lower than expected. This presumably arises from incomplete combustion of these high carbon content species. EPR spectra were recorded on a Bruker ER 200D-SRC spectrometer equipped with an Oxford Instruments ESR 900 cryostat, and *g*-values were determined by calibration to DPPH affixed to the outside of the tube. NIR spectra were recorded anaerobically on a Cary 17 spectrometer. Tetrahydrofuran, 2-methyltetrahydrofuran, hexanes, and toluene were distilled from sodium/benzophenone inside the drybox. Benzonitrile was purified and degassed by vacuum distillation from sodium. All other materials were used as commercially available (Aldrich).

$[CoCp_2^+][C_{60}^-]\cdot PhCN$. Cobaltocene (4 mg, 0.021 mmol) and C_{60} (21 mg, 0.029 mmol) were stirred together in benzonitrile (2 mL) for 2 min to form a deep red solution. After filtration, hexane was added to effect precipitation of the product as a dark brown solid. This solid was washed with hexane, toluene, and hexane again and finally allowed to dry (20 mg, 94%): λ_{max} (THF) 261 nm ($CoCp_2^+$), 336 nm (C_{60}^-); IR (CsI) 3100, 2918, 2849, 1474, 1463, 1413, 1008, 730, 720, 576, 460 cm^{-1}. Anal. Calcd for $C_{77}H_{15}NCo$: C, 91.31; H, 1.49; N, 1.38; Co, 5.81. Found: C, 84.32; H, 1.62; N, 1.34; Co, 5.56. The low solubility of this compound in 2-methyltetrahydrofuran led us to record its EPR spectrum in tetrahydrofuran.

$[Na(dibenzo\text{-}18\text{-}crown\text{-}6)(THF)_2^+][C_{60}^-]\cdot THF$. A freshly cut piece of sodium (ca. 0.2 g) was added to a suspension of C_{60} (0.1 g, 0.14 mmol) and dibenzo-18-crown-6 (0.051 g, 0.14 mmol) in THF (60 mL). The solution was warmed and stirred until dissolution of C_{60} was complete (ca. 2 h). The dark reddish-purple solution was filtered to remove excess sodium, and hexane was added to effect crystallization of the dark brown crystalline product (0.12 g, 80%): λ_{max} (THF) 337, 507 nm (C_{60}^-); IR (CsI) 3070, 2929, 2875, 1596, 1505, 1454, 1395, 1330, 1254, 1215, 1129, 1059, 951, 910, 780, 576, 526 cm^{-1}. Anal. Calcd for $C_{92}H_{48}O_9Na$: C, 83.69; H, 3.66; Na, 1.69. Found: C, 83.21; H, 3.37; Na, 1.78.

$[Sn(TpTP)(N\text{-}MeIm)_2^{2+}][C_{60}^-]_2$. *N*-Methylimidazole (1 mL) was added to a toluene solution (70 mL) of Sn(TpTP) (0.079 g, 0.1 mmol) and C_{60} (0.159 g, 0.22 mmol). After 1 h the purple crystalline product was filtered off, washed with toluene, and allowed to dry (0.18 g, 70%): λ_{max} (THF) 430 Soret, 563, 607 nm; 336 nm (C_{60}^-); IR (CsI) 3130, 3023, 2919, 2855, 1710, 1610, 1517, 1464, 1395, 1232, 1212, 1182, 1108, 1076, 1031, 1014, 946, 847, 804, 723, 695, 662, 616, 576, 526, 465, 428 cm^{-1}. Anal. Calcd for $C_{176}H_{48}N_8Sn$: C, 88.34; H, 2.02; N, 4.68; Sn, 4.96. Found: C, 83.64; H, 3.27; N, 4.93; Sn, 4.4. Integration of the ^1H NMR signals of an oxidized sample confirmed the ratio of imidazole to porphyrin to be 2:1.

Results and Discussion

Synthesis. Given that the first and second reduction potentials of C_{60} are ca. −0.45 and −0.90 V (vs SCE), respectively, in low dielectric media, the logical approach to the synthesis of fulleride(1−) species is to react C_{60} with reducing agents that lie within this range. Cobaltocene (E_0 −0.9 V)[29] is one of the more convenient reagents for reduction of C_{60} because it is readily available, it is soluble in a wide variety of organic solvents, its reduction potential is not particularly sensitive to counterion, and it is oxidized cleanly by one electron to form the robust cobaltocenium ion. As indicated by NIR spectroscopy (Figure 1), the 1:1 reaction proceeds cleanly in benzonitrile. Bands due to C_{60}^{2-} at 954 and 830 nm[23] are absent. However, as might be expected from a reagent whose reduction potential is close to that of C_{60}^{2-}, NIR spectroscopy indicates that excess cobaltocene can drive the reduction part way to the 2− state.[30]

Alkali metals are very strong reducing agents and have been widely used with C_{60}. However, the degree of reduction is driven by lattice energies such that the C_{60}^{2-}, C_{60}^{3-}, C_{60}^{4-}, and C_{60}^{6-} salts are the typically isolable products.[12] On a small scale it is difficult to control the precise stoichiometry for lower levels of reduction, but we find that the addition of an equivalent of a crown ether overcomes this problem. When a suspension of C_{60} in THF is stirred with 1 equiv of dibenzo-18-crown-6 and excess sodium, the solution turns increasingly reddish-purple over a period of about an hour due to the formation of C_{60}^-. Dissolution of the solid C_{60} signals completion of the one-electron reduction, and excess sodium is immediately filtered off to prevent further reduction. The extent of reduction was confirmed to be 1− by NIR spectroscopy (Figure 1).

We previously reported that (tetraphenylporphinato)chromium(II), Cr(TPP), can be used as a reducing agent for C_{60} in a toluene/THF solvent mixture.[10] This warrants a second mention to make two observations, one regarding redox potentials, the other regarding the very weakly coordinating ability of the C_{60}^- anion. The literature measurement[31] of the reduction potential of $Cr^{III}Cl(TPP)$ places E_0 ca. −0.9 V, apparently quite negative enough for $Cr^{II}(TPP)$ to reduce C_{60} (E_0 = −0.45 V). The

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octaethylporphyrin analogue, Cr^{II}(OEP), has an even more negative potential (–1.1 V) raising initial concern that a two-electron reduction of C_{60} might occur. In fact, neither Cr(TPP) nor Cr(OEP) react at all with C_{60} in toluene solution, despite an apparent driving force of 0.45 and 0.65 V, respectively. The problem is not kinetic. Rather, the actual $Cr^{II/III}$ redox potentials in toluene are vastly different from those measured under typical literature conditions of electrolyte, coordinating anion and polar solvent. The literature values are measured *in situ* by reduction of the chromium(III) porphyrin chlorides, CrCl(porphyrin). The presence of chloride ion as well as a donor solvent such as DMSO and/or the anion of the electrolyte (often PF_6^- or ClO_4^-) means that the positive charge on the chromium(III) porphyrin is readily stabilized by coordination of Cl^-, DMSO, PF_6^-, or ClO_4^-. The $Cr^{II/III}$ redox potentials will be very negative under these conditions. However, under our conditions of C_{60} and Cr^{II}(porphyrin) in toluene, redox does not occur, presumably because C_{60}^- is unable to stabilize the $[Cr^{III}(porphyrin)]^+$ cation. The $Cr^{II/III}$ redox potential has been shifted in a positive direction by more than half a volt. This suggests that C_{60}^- is a very weakly coordinating anion, possibly the weakest known for hard centers such as Cr(III). Of course, the $C_{60}^{0/1-}$ redox potential is also expected to show some shift in toluene compared to more polar solvents, but indications are that this is a relatively small effect.[5–8]

In a conceptually similar manner, strongly reducing tin(II) porphyrins[32] are *in*effective in reducing C_{60} in toluene. Even in THF the reaction is incomplete (UV–vis spectroscopy: λ_{max} Soret 397, 490 nm (Sn^{II}); 430 nm (Sn^{IV})) and impractical synthetically because C_{60} rather than the C_{60}^- salt is the least soluble component of this kinetically labile system. The addition of a good ligating base such as *N*-methylimidazole (*N*-MeIm) drives the reaction and allows isolation of $[Sn(TpTP)(N\text{-}MeIm)_2^{2+}][C_{60}^-]_2$. The successful isolation of the redox product probably has more to do with its low solubility than particularly favorable redox thermodynamics. NIR spectroscopy again confirms the presence of C_{60}^- and absence of C_{60}^{2-} (Figure 1).

Aerobic Sensitivity. In the course of this work with a variety of salts of C_{60}^- we have noticed marked differences in their sensitivity to aerobic oxidation. The chromium(III) porphyrin salt is the most sensitive, being instantly converted to C_{60} and a mixture of chromium(III) and -(IV) porphyrins upon exposure to just traces of air. Both the solid and its solutions are very air sensitive. The tin(IV) porphyrin salt is also very sensitive to air exposure, the sodium crown ether salt less so, and the cobaltocenium salt is spectroscopically stable for several minutes upon air exposure of an initially dry THF solution. This dependence of the rate of oxidation of C_{60}^- upon the nature of the cation can be rationalizied by a mechanism involving superoxide ion, where the rate depends upon how well the cation stabilizes the charge on O_2^-:

$$C_{60}^- + O_2 \rightleftarrows C_{60} + O_2^-$$

The outer-sphere electron-transfer reaction of the above equation is thermodynamically disfavored by ca. ~0.4 V because the O_2/O_2^- reduction potential is ca. –0.8 V in aprotic media.[33] It will proceed only if a proton or a cation can stabilize the charge on O_2^- and initiate eventual reduction to the peroxidic or aquo level. Thus, metal centers such as chromium(III), which are known to form superoxide complexes,[31] and tin(IV), which might be expected to bind O_2^-, will drive the reaction. The accessibility of Cr(IV) chemistry[34] probably helps to complete the reduction of O_2 and the spectroscopic identification of Cr^{IV}(O)(TPP) in the air-exposed solution has already been noted.[10] Na(crown)$^+$ is reasonably expected to form a good ion pair with O_2^- in low dielectric media, thereby offering some driving force, while the buried charge and lack of a vacant coordination site in the cobaltocenium ion make it the least stabilizing cation for O_2^-. Of course, the overall redox reaction probably involves further reduction of superoxide to peroxide and finally to hydroxide ion, a process that requires cations or protons to proceed at a significant rate.[33] Most of the literature reports on C_{60}^- mention significant air sensitivity, a property that can now be associated with traces of water and high concentrations of electrolyte.

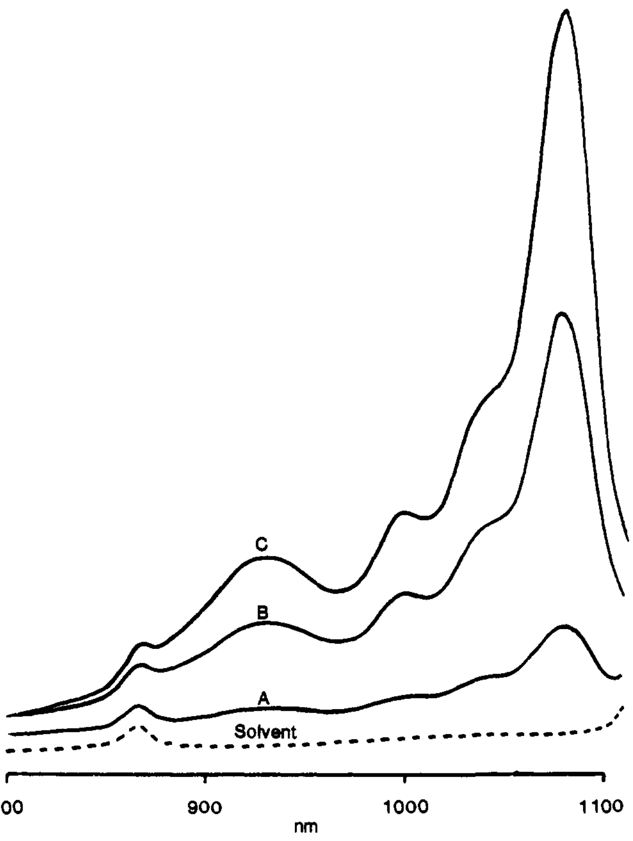

Figure 1. NIR spectra of C_{60}^- salts in benzonitrile: (A) $Sn(TPP)(N\text{-}MeIm)_2^{2+}$, (B) $CoCp_2^+$, and (C) Na(crown)$^+$ salts. The vertical scale is arbitrary.

Anisotropy in Low-Temperature EPR. The temperature dependence of the EPR spectrum of C_{60}^- is illustrated in Figure 2 for two of the salts in frozen solution. The salient features are (1) a broad, essentially isotropic signal at high temperatures with *g* values and line widths comparable to literature reports (recently summarized in ref 26), (2) a large decrease in line width of the major signal with decreasing temperature as originally observed by Wudl[9] and recently quantified by Jones & Kadish[25] and by Schell-Sorokin et al.,[26] (3) a narrower spike in the high-temperature spectrum which disappears as the temperature approaches liquid helium temperatures, and (4) a marked anisotropy in the low-temperature spectrum of the Na(crown)$^+$ salt but not the cobaltocenium salt. This anisotropy is similar to that reported earlier for the $Cr(TPP)(THF)_2^+$ salt[10] and is a separate and distinct feature from the above-mentioned spike. The illustrated examples represent the extremes of anisotropy and isotropy that we have observed to date.

We first discuss the low-temperature anisotropy. Most of the literature reports of the EPR of C_{60}^- concern the temperature region above 77 K so the anisotropy has not been commonly observed. Moreover, in those cases where liquid helium temperature spectra have been reported, there is rather little anisotropy. These environments have included 13X molecular sieves[24] and tetra-*n*-butylammonium as counterion.[26,35] If ion

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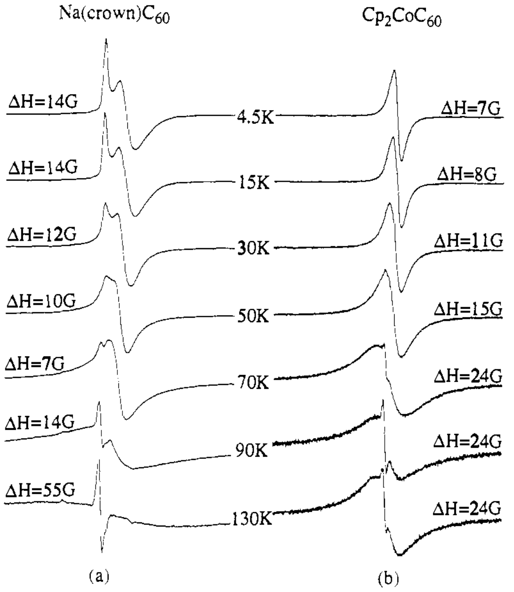

Figure 2. Temperature dependence of the X-band EPR spectrum of C_{60}^- as a function of counterion: (a) $Na(crown)^+ C_{60}^- (10^{-4}$ M) in 2-MeTHF and (b) $CoCp_2^+ C_{60}^-$ (10^{-4} M) in THF. Spectra were recorded at modulations of 1.25 and 1.0 G for (a) and (b), respectively, at a 126-mW power level. The vertical scale does not reflect spectral amplitude. ΔH values (G) are peak-to-peak separations, using the outermost peaks in cases of anisotropy.

pairing is the cause of anisotropy, the lack of marked anisotropy for R_4N^+ salts is understandable. The molecular sieve environment is unknown, and, in fact, we have a different explanation to offer for its isotropy (see below). Evidence for ion pairing effects has recently come from the cation dependence of the C_{60}/C_{60}^- redox potential[36] although van der Waals interactions are probably more important than electrostatic forces.

We ascribe the anisotropy to a distortion of C_{60}^- away from I_h symmetry induced by interaction with the cation. It is consistent with the manifestation of a static Jahn–Teller effect. As the temperature is increased, the effect appears to becomes dynamic on the EPR time scale and an isotropic signal is observed. For the $Na(crown)^+$ salt (see Figure 2a), this occurs over the temperature range 4–70 K. The "line width" of the signal, measured as the outer peak-to-peak width, varies from 14 to 7 G over this range. This is consistent with a static-to-dynamic change but may include thermal sampling of additional distorted structures. The dramatic increase in line width above 70 K must arise from a different, as yet unidentified, effect associated with the orbitally degenerate ground state.

The anisotropy in the 4.5 K spectrum of the $Na(crown)^+$ can be simulated by an axial spectrum with $g_\perp = 1.9968$ and $g_\parallel = 2.0023$ (see Figure 3a). The line widths of the Lorentzian fits are 4.5 and 1.1 G, respectively. The fit is reasonably good but not perfect, particularly in the extended wings of the signal. A rhombic fit with three g values is only marginally better. The lack of a precise fit probably arises from so-called g-strain, the signal broadening effect that arises from a distribution of slightly different structures induced by microscopically different sites in the frozen solvent/cation matrix. Saturation recovery data have been interpreted in terms of a distribution of structures with different relaxation times.[26] The wings of the signal are not consistent with unresolved ^{13}C hyperfine interactions.[26] Possible ^{23}Na hyperfine coupling is also unlikely since the $Na(crown)^+$ salt and the $Cr(TPP)(THF)_2^+$ salt have essentially the same spectrum. That the paramagnetic chromium cation has no detectable spin coupling effect on the EPR spectrum of C_{60}^- suggests that the cation interaction, whatever its true nature, is rather weak and is solvent separated. The cobaltocenium C_{60}^- spectrum at 4.5 K can be simulated quite well by an isotropic Lorentzian with $g = 1.9969$ and $\Delta H = 6.0$ G. This is illustrated in Figure 3b.

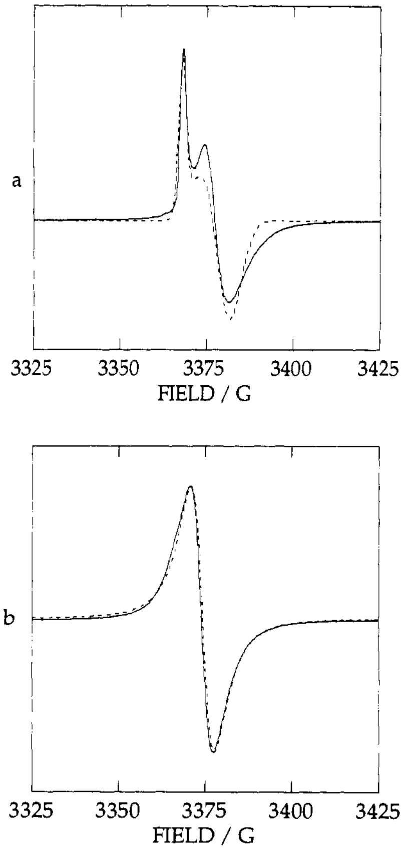

Figure 3. Simulation (- • -) of the 4.5 K EPR spectrum of (a) $Na(crown)^+ C_{60}^-$ in 2-MeTHF and (b) $CoCp_2^+C_{60}^-$ in THF. Fitting parameters are given in the text.

The axial nature of the anisotropic signal is consistent with an ellipsoidal distortion or one that is nearly so when probed by EPR spectroscopy. Support for this kind of a distortion comes from the calculations of Morokuma[21] which, under imposed D_{5d}, D_{3d}, or D_{2h} symmetry, predict in each case a Jahn–Teller distortion which somewhat localizes the unpaired electron in the equatorial region of a structure that is slightly stretched along the principal axis. As attractive as this model appears, it predicts a ground state that is the inverse of that observed (see later) and suggests that the distortion may be better described as a compression, rather than an elongation, along the principal axis. Since the Jahn–Teller degeneracy originates in T_{1u} symmetry, the distortion must occur along normal modes of H_g symmetry. In an attempt to calculate the magnitude of the distortion in C_{60}^- Negri et al.[20] identified the low-frequency mode at ~270 cm^{-1} as the major contributor. This is a mode that produces an ellipsoidal distortion of C_{60}. In addition, the high frequency "pentagonal pinch" A_g mode at ~1460 cm^{-1} was identified as a major component of the distortion. Interestingly, this latter mode, along with H_g modes in the 700-cm^{-1} region, is greatly enhanced in the Raman spectroscopy of C_{60}^- on gold.[37] It is also the mode that is most sensitive to the nature of the adsorbed counterion. A structural model for C_{60}^- ion pairing might therefore be one where the cation associates with a pentagonal or hexagonal face, stabilizing an approximately ellipsoidal distortion along a 5- or 3-fold axis. This would rationalize the predominantly axial nature of the anisotropic EPR spectrum, while at the same time acknowledging that other, less idealized structure(s) may also contribute. Indeed,

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(36) Dubois, D.; Moninot, G.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1992**, *96*, 7137.

(37) Zhang, Y.; Du, Y.; Shapley, J. R.; Weaver, M. J. *Chem. Phys. Lett.* **1993**, *205*, 508.

1:1 ion pairing should induce a formally rhombic distortion rather than a purely axial one, the true shape of an egg rather than an proper ellipsoid. This example, however, is just one of four possible structural models for the distortion depending upon whether the cation associates with polar or equatorial regions of an elongated (prolate) or flattened (oblate) ellipsoid.

The low thermal energy required to convert the static distortion into a dynamic one on the EPR time scale is readily understood. Firstly, the distortion is, by all accounts, small. None of the vibrational modes of C_{60} change by more than 18 cm^{-1} upon reduction to C_{60}^-; most change by only 1 or 2 cm^{-1}.[37] Calculations of bond length changes in C_{60}^- show differences of no more than 0.0016 Å between icosahedral and Jahn–Teller distorted ellipsoidal structures.[21] Secondly, because of the diffuse charge on C_{60}^-, ion pairing probably involves mostly weak van der Waals forces rather than strong electrostatic forces. Thirdly, C_{60} is known to spin rapidly, even in the solid state.[38] There is every reason to expect this will also be a property of C_{60}^- and this has been discussed with respect to the large temperature dependence of the line width of the EPR signal at higher temperatures.[26] If cations (or particular arene portions of cations) do in fact associate preferentially with a particular face of C_{60}^- anion, a rotation which effects exchange with the symmetry-equivalent faces may occur with a very small activation energy.

Origin of the Spike. Most reports of the high-temperature EPR spectrum of C_{60}^- include the observation of a minor, sharp signal superimposed on the familiar broad signal (see Figure 2). The *g* value of this spike is close to 2.000 suggesting it arises from C_{60} rather than an organic radical impurity (~2.002). The line width is not particularly narrow (~3 G), again suggestive of C_{60} origin. The two signals, sharp and broad, have such different responses to the power and modulation settings of the spectrometer, that a precise integration of signal intensity has not been possible. One estimate puts the spike at <1% of signal intensity.[25] Relative intensities of the two signals have been reported to vary with sample preparation[26] suggesting that whatever gives rise to this signal is sensitive to environmental effects. Importantly, the spike diminishes with temperature and cannot be discerned much below 50 K in the spectra shown in Figure 2. Unlike the broad signal, the line width does not show a large temperature dependence in the 4–130 K range. It remains at 2–3 G for both sets of spectra displayed in Figure 2.

There have been two proposals made regarding the origin of the spike. Greaney and Gorun[27] noticed a similarity of the room temperature spectrum of C_{60}^- to that of electron-exchanging sodium naphthalide/naphthalene and suggested that the broad signal arise from ion-paired C_{60}^-/C_{60} undergoing slow exchange, the sharp signal from free C_{60}^-/C_{60} in fast exchange. There are a number of problems with this explanation, not the least of which is the essential absence of C_{60} in anaerobically prepared samples made up from isolated fulleride(1−) salts. Moreover, the spike is present in frozen solution where C_{60}, even if present in realistic amounts, would not be physically mobile toward electron exchange on the EPR time scale. Purposeful addition of excess C_{60} to solutions of $[Na(crown)^+][C_{60}^-]$ does not cause significant changes in the observed spectrum, and there is little response to changes in concentration from ca. 10^{-3}–10^{-5} M in 2-methyltetrahydrofuran.

Jones and Kadish[25] have suggested that the spike is due to a small amount of C_{60}^{2-} arising from thermodynamically required disproportionation:

$$2C_{60}^- \rightleftarrows C_{60} + C_{60}^{2-}$$

Evidence cited in favor of this proposal included signal characteristics which are roughly comparable to those observed for the central signal of authentic C_{60}^{2-}, prepared electrochemically under similar conditions. In addition, the Nernst equation was used in conjunction with the difference in first and second reduction potentials (~400 mV) to calculate the equilibrium percentage of C_{60}^{2-} in bulk solutions. The calculations produced a figure of ca. 0.5% which was suggested to correlate with the relative signal intensity of the spike, quoted at no more than 1%. However, the calculation is in error by an order of magnitude. The correct percentage is <0.04% at 295 K.[39] Given the problems alluded to earlier of obtaining reliable relative intensities, it is difficult to quantify the spike. Nevertheless, if the relative intensity is approaching 1% at room temperature (our own estimates vary up to several percent), disproportionation cannot rationalize the existence of the spike. Additional evidence offered by Jones and Kadish in support of the disproportionation proposal included experiments with partially electrolyzed solutions of C_{60}. The relative intensity of the spike was reported to increase with the extent of reduction, in keeping with bias of the disproportionation equilibrium. However, when we add 15 equiv of C_{60} to a pyridine solution of $CoCp_2^+C_{60}^-$ we do not observe a significant suppression of the spike. Occasional changes in the apparent relative intensities are sometimes observed, but these are related more to the normal problems of reproducibility of EPR spectra from sample to sample under "identical" conditions than to systematic effects.

We propose that the spike arises from thermal population of a low-lying excited state. If we idealize the distortion of C_{60}^- as an axial elongation along the principal axis in D_{5d} symmetry (i.e., a prolate ellipsoid), the ^2T_u state in I_h symmetry splits into $^2A_{2u}$ and $^2E_{1u}$ states corresponding to the orbital configurations illustrated in Figure 4a.[21,23] Alternatively, if we idealize the distortion as an axial compression along the principal axis in D_{5d} symmetry (i.e., an oblate ellipsoid), the splitting is inverted (Figure 4b). The choice between these two is straightforward because broad EPR signals are associated with degenerate ground states.[40] The predominant, broad signal is assigned to a ^2E ground state. The narrower spike, which grows in as the temperature is raised, is assigned to the ^2A excited state of Figure 4b. The population of the excited state is related to the energy gap and the temperature by the Boltzmann relationship. A 1 kcal gap would give ~8% excited state population at 295 K. A 2 kcal gap would give ~3%, a 3 kcal gap would give ~0.6%. These are reasonable numbers for both the energy gap and the percentage of the EPR signal in the spike. Although the levels are inverted, Morokuma has calculated that the Jahn–Teller distorted ground state is ~2 kcal below the spherical ^2T_u state and that the energy gap is ~6 kcal.[21] In other calculations, concerning the low *g* value, Kato et al.[22] find the energy gap to be at least 70 cm^{-1} (~0.3 kcal). A possible indication of the energy gap comes from NIR spectroscopy where two bands, both with vibronic fine structure, appear at 1073 and 927 nm.[22,23,27,41] Reasonable assignments for these bands are transitions from the ^2E ground state to ^2E_g and ^2A_g Jahn–Teller split excited states of $^2T_{1g}$ origin. The excited-state energy gap is 1430 cm^{-1}, i.e., ~4 kcal. While the excited-state splitting in the NIR is not necessarily related to the ground-state splitting

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

(39) The disproportionation equilibrium constant *K* is given by

$$K = \frac{[C_{60}^{2-}][C_{60}]}{[C_{60}^-]^2}$$

Assuming a 400-mV window between C_{60}^- and C_{60}^{2-}

$$\log_{10}K = \frac{nFE_{\mathrm{disp}}}{2.303RT} = \frac{-0.4F}{2.303RT}$$

At 295 K, $K = 10^{-6.8327}$, but $[C_{60}] = [C_{60}^{2-}]$; therefore

$$\frac{[C_{60}^{2-}]}{[C_{60}^-]} = 10^{-3.4163}$$

i.e., $[C_{60}^{2-}] < 0.04\%$.

(40) Townsend, M. G.; Weissman, S. I. *J. Chem. Phys.* **1960**, *32*, 309.

(41) Heath, G. A.; McGrady, J. E.; Martin, R. L. *J. Chem. Soc., Chem. Commun.* **1992**, 1272.

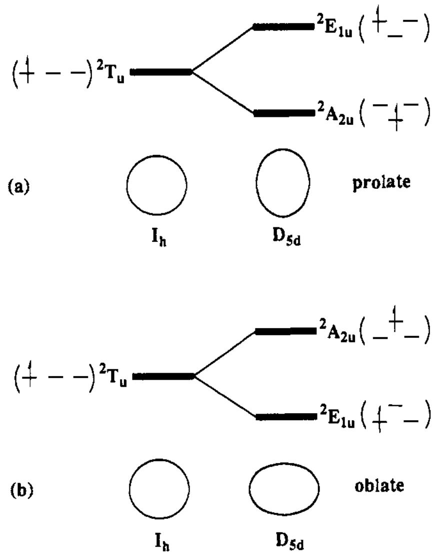

Figure 4. Splitting of the ^2T_u state upon (a) prolate or (b) oblate distortion from I_h to D_{5d} symmetry. The corresponding electronic configurations are indicated in parentheses.

in the EPR, it does suggest that ~1 kcal is of the correct order of magnitude to account for these types of splitting. This is close to the value of a few hundred wavenumbers very recently suggested by Dinse et al.[42]

We have chosen to illustrate the concept of a low-lying excited state in Figure 4 by idealizing the distortion along a 5-fold symmetry axis in D_{5d} point group symmetry. We could equally well have chosen an ellipsoidal distortion along a 3-fold axis in D_{3d} symmetry or along a 2-fold axis in D_{2h} symmetry. The result in D_{3d} symmetry is identical to that in D_{5d}. A prolate distortion produces a ^2A ground state and a ^2E excited state. In D_{2h} symmetry, strictly speaking there are three discrete ^2B_u levels, but a grouping of these into singly degenerate ($^2B_{1u}$) and essentially doubly degenerate levels ($^2B_{2u}$, $^2B_{3u}$) is likely.[21] It may eventually be possible to decide between these idealized alternatives once the precise nature of the ion pairing and/or solvent interaction becomes known. If it is associated primarily with a pentagonal face, the distortion may in fact approximate D_{5d} symmetry. On the other hand, a primary interaction with a hexagonal face would induce D_{3d} symmetry. A specific interaction at the olefinic double bond of C_{60}^- (i.e., that fusing two six-membered rings) would induce D_{2h} symmetry. Whether the distortion approximates a prolate or an oblate ellipsoid is an interesting question. Our suggestion that it is oblate rather than prolate as deduced for the "gas phase" free ion by *ab initio* calculations[21] is offered guardedly because the EPR signal reflects the nature of the half-filled molecular orbital rather than the total electron distribution.

The strongest evidence that the spike arises from population of a thermally accessible excited state is its disappearance as the temperature is decreased. The disappearance should follow a Boltzmann relationship, but because of the difficulties discussed earlier of quantifying the relative intensities of the sharp versus broad signal we have not been able to rigorously establish this. Another point concerns variations of the relative intensity of the spike as a function of the matrix. These can be rationalized by environmental effects on the distortion of C_{60}^- which will in turn perturb the nature and extent of the splitting of the ^2A and ^2E electronic levels. It is quite possible that the ordering of the levels can be inverted by environmental effects. This would explain the rather puzzling observation of a narrow isotropic signal for C_{60}^- in 13X molecular sieves at 4 K.[24] The line width of the signal is only 3.5 G, consistent with the idea that it originates from a ^2A ground state rather than the ^2E of the present work. The line width of the cobaltocenium salt in THF, although nearly isotropic at 4 K, remains >6 G throughout the accessible temperature range. The tetra-*n*-butylammonium salt in CH_2Cl_2 has line widths in the range 5.3–7.0 G between 77 and 2 K.[35] These compare to a line width of only 3.0 G for the ^2A spike. Not only does the 4 K line width help identify a signal with a ^2A or ^2E state, but the temperature dependence of the line width appears also to be diagnostic. Thus, while signals originating from ^2E states broaden extensively above about 70 K, the line width of the spike (measured as peak-to-peak separation) changes very little, at least up to 130 K.[43]

Summary and Conclusion. A number of the unusual features of the EPR spectrum of C_{60}^- are seen to arise as a natural consequence of a ground-state distortion which splits the ^2T state into ^2E and ^2A levels. This is consistent with a Jahn–Teller effect, but because it is sensitive to environmental effects, it cannot be rigorously ascribed to this origin. Any distortion due solely and intrinsically to the Jahn–Teller effect can only be assessed by studying C_{60}^- in a totally symmetric environment. The present work suggests that it is relatively easy to induce small distortions away from icosahedral symmetry. However, these distortions represent rather shallow energy minima, and it is likely that a wider exploration of environmental effects will in the future identify different types of structural and electronic distortions. With regard to the possibility of inverting the ^2E and ^2A splitting, we are intrigued by the preliminary observation that a nearly perfectly isotropic signal of only 3 G line width is observed when the EPR spectrum of $[CoCp_2^+][C_{60}^-]$ is recorded in frozen benzonitrile at 4 K.[30] This may reflect a ^2A ground state and is under detailed investigation. Another environmental effect that may eventually be observed is the production of a rhombic signal and/or a further splitting of the ^2E state. This state is, after all, formally subject to a degeneracy-lowering Jahn–Teller distortion and ion-pairing might induce a C_{nv} distortion rather than a strictly ellipsoidal D_{nd} or D_{nh} one. Nevertheless, to a first approximation, the EPR properties of C_{60}^- can now be understood in terms of a simple $^2E/^2A$ ground-state splitting.

The synthetic methods developed in this work lend themselves to the isolation and characterization of fullerides of higher charge and higher molecular weight. In this regard we note that the concept of a low-lying excited state provides a ready explanation for the otherwise puzzling observation[25] of two major components in the EPR spectrum of C_{60}^{2-} and an additional minor component in the spectrum of C_{60}^{3-}. It also suggests an approach to understanding the EPR spectrum of C_{70}^-. To a first approximation it is axial in nature,[7] making it a model for the ellipsoidal distortion of C_{60}^- proposed in the present work.

Note Added in Proof: Kato et al. have recently published further investigations on electrochemically generated C_{60}^-: Kato, T.; Kodama, T.; Shida, T. *Chem. Phys. Lett.* **1993**, *205*, 405.

Acknowledgment. We thank Professors Philip Stephens and David Bocian for helpful discussions, Professor Tatsuhisa Kato for sharing unpublished data with us, Dr. Frank Devlin, Gerard Jensen, and Bruno Reyntjens for assistance with the EPR and NIR measurements and Professor Michael Weaver for a preprint of ref 37. This work was supported by the National Science Foundation and the National Institutes of Health.

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(42) Ruebsam, M.; Dinse, K.-P.; Plueschau, M.; Fink, J.; Kraetschmer, W.; Fostiropoulos, K.; Taliani, C. *J. Am. Chem. Soc.* **1992**, *114*, 10059.

(43) As pointed out by a referee, a signal broadening effect from close-lying states (Orbach relaxation) should be observable at higher temperatures. However, reliable spectra are not easy to obtain at room temperature, making a quantitative treatment difficult.