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Synthesis and Electronic Characterization of Discrete Buckminsterfulleride Salts: C_{60}^{2-} and C_{60}^{3-}

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Exceptional ball-to-ball interactions between fulleride ions are the basis of superconductivity[1] in alkali-metal-doped C_{60} and of ferromagnetism[2] in [TDAE][C_{60}]. It is therefore of fundamental interest to study discrete fulleride ions and to explore the nature of weaker or less extended interactions between them in a variety of well-characterized salts. The electrochemical generation of C_{60}^{n-} for $n = 1$–6 has been well established[3] along with a growing EPR,[4,5] NIR,[6–9] and Raman[10,11] characterization, but the synthesis, isolation, and characterization of discrete fulleride salts has progressed well only for $n = 1$.[5,12] One preliminary report on a route to isolable $n = 2$ and $n = 3$ salts has recently appeared.[13] Theoretical predictions of the electronic ground states have been prudently tentative.[14]

The synthesis of C_{60}^{n-} 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 ~0.45-V window of stability appropriate to each C_{60}^{n-} ion. Product solubility is also an important consideration. The interplay of these factors is seen in the observations that stoichiometric cobaltocene is useful[5] for forming C_{60}^{1-}, excess leads to C_{60}^{2-} (NIR $\lambda_{max} = 810, 957$ nm), and decamethylcobaltocene leads to C_{60}^{3-}, but in our hands, a practical synthesis of C_{60}^{2-} and C_{60}^{3-} salts uses stoichiometric control of reduction with sodium, via judicious choice of cation. Thus, stirring a suspension of C_{60} in tetrahydrofuran with excess sodium and 2 and 3 equiv of dibenzo-18-crown-6 (crown) leads to precipitation of the fulleride(2–) salt $[Na(crown)(THF)_2]_2[C_{60}]$ (**1**) and the fulleride(3–) salt $[Na(crown)(THF)_2]_3[C_{60}]$ (**2**), respectively, in good yield. Cation metathesis with bis(triphenylphosphine)iminium chloride, [PPN]Cl, leads to the less soluble, more analytically pure, brown, crystalline salts $[PPN]_3[C_{60}][Cl]\cdot CH_3CN$ (**3**) and $[PPN]_3[C_{60}]\cdot 2CH_3CN$ (**4**), respectively. Full synthetic details, elemental analyses, and NIR and NMR data are available as supplementary material.

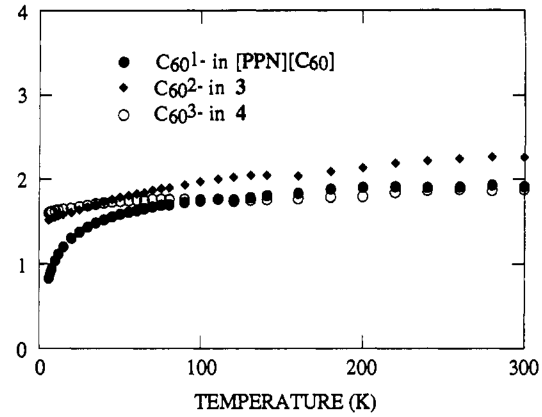

Figure 1. Magnetic susceptibility data for C_{60}^{1-} in $[PPN][C_{60}]\cdot[PhCN]\cdot[THF]$, C_{60}^{2-} in **3**, and C_{60}^{3-} in **4** at 10 kG.

Since the large cations in these salts should lead to magnetically dilute fulleride ions, their magnetic susceptibilities are expected to unambiguously define their ground spin states. Figure 1 shows representative data for analytically pure C_{60}^{1-}, C_{60}^{2-}, and C_{60}^{3-} salts. Data on the C_{60}^{1-} salt tend to plateau at $\mu_{eff} \approx 1.8\ \mu_B$, consistent with an $S = 1/2$ state (spin-only value = 1.73 μ_B). The C_{60}^{3-} salt shows very similar behavior, demonstrating its $S = 1/2$ ground state. This is in contrast to theoretical predictions[14] and highlights the importance of extensive configuration interaction and spin–spin (and/or spin–orbit) coupling in destabilizing the $S = 3/2$ state that might otherwise be expected from filling of the t_{1u} LUMO of C_{60} according to Hund's rule. The excess spin[15] and deficient spin[13] reported for related C_{60}^{1-} and C_{60}^{3-} salts, respectively, are intriguing if they are not artifactual. The fall-off of μ_{eff} at low temperature in the C_{60}^{1-} salt probably arises from ball-to-ball *antiferro*magnetic coupling. This contrasts with the *ferro*magnetic behavior observed in [TDAE][C_{60}].[2] Spin coupling is essentially absent in **4**, as expected for C_{60}^{3-} ions that are well isolated by the presence of three large cations.

The magnetic susceptibility data for the C_{60}^{2-} salt are intriguing. They show an unusual temperature dependence (Figure 1) and are slightly field-dependent (not shown). Both **1** and **3** show the same behavior, suggesting that these features are an intrinsic property of discrete fulleride(2–) ions. It is notable that the high-temperature moment is asymptotically approaching ~2.5 μ_B, not 2.9 μ_B as expected for an isolated spin triplet ($S = 1$). This suggests a small singlet–triplet energy gap. The distinctive gradual decrease in moment with decreasing temperature suggests that a singlet state is, in fact, lower in energy. However, since there is still a significant magnetic moment at 6 K, the gap is probably less than a wavenumber or so. Also, EPR signals can still be observed at 4 K. Preference for a singlet ground state is found in QCFF/PI calculations[14] ($^1A_g < {}^1A_u < {}^3T_{1g} < {}^1H_g$), although it may be possible to develop an alternative model based on an analogy to d^2 systems (e.g., V^{3+}) in high-symmetry ligand fields.

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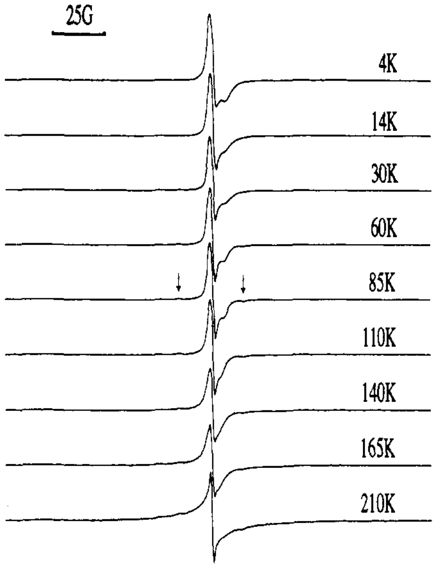
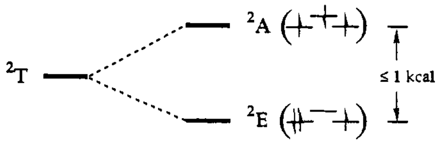
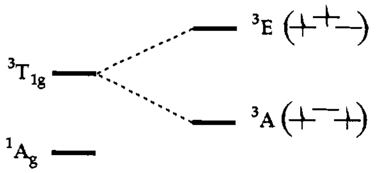


Figure 2. *X*-band EPR spectrum of C_{60}^{2-} in **3** in frozen benzonitrile solution (1 mM) as a function of temperature (modulation 0.25 G, microwave power 200 μW). The arrows identify the so-called "winged triplet" signal; under high gain, an outer pair of signals at twice the separation can be detected. The *g* values of this signal and the crossing point of the strong signal are coincident at 2.0000 ± 0.0002 at 85 K.

The EPR spectrum of C_{60}^{3-} in **3** in frozen DMSO solution (supplementary material) is almost indistinguishable from that[5] of C_{60}^{1-}, strongly supporting the interpretation[4] of a spin doublet ground state. There is both a cation dependence at low temperature (sometimes with anisotropy), ascribable to weak ion-pairing, and the ingrowth of a "spike" with increasing temperature. Rather than ascribe this spike to traces of C_{60}^{2-} arising from disproportionation or incomplete reduction,[4] we suggest that it arises from thermal population of a close-lying ^{2}A excited state:



The EPR spectrum of C_{60}^{2-} in **3** in frozen benzonitrile solution is shown in Figure 2. A puzzling feature has been the appearance of two signals at liquid nitrogen temperatures:[4] the strong central line (ΔH = 1–2 G) and the "winged triplet" (ΔH = 11–30 G). With liquid helium temperature spectra now available, it is apparent that the winged triplet spectrum actually grows in with increasing temperature (see arrows in 85 K spectrum). We therefore assign it to the thermal population of a low-lying ^{3}E excited state arising from Jahn–Teller splitting of the $^3T_{1g}$:



Both signals are assigned triplet origins, the narrower signal to the higher symmetry state. One physical interpretation of the C_{60}^{2-} data is that the odd electrons behave nearly like those of an uncoupled diradical. Spectrometer gain settings are always higher for the dianion than for the mono- or trianion (at equivalent concentrations), consistent with the idea that less than half of the C_{60}^{2-} ions are in a triplet state. Application of the simple dipole–dipole model for isolated spins to the winged triplet spectrum (ΔH = 30 G) places the two electrons 9.7 Å apart. This is not an unreasonable value given the 7.1-Å nuclear diameter and 10.1-Å van der Waals diameter expected of C_{60}^{2-}. Nevertheless, a point charge model remains rather unrealistic because of the delocalized nature of the molecular orbitals in which the unpaired electrons are expected to reside.

In summary, the synthesis and magnetic characterization of discrete fulleride salts is leading to interesting new insight into the rather complex electronic structures that result from sequential filling of the t_{1u} LUMO of C_{60}. Hund's rule is not obeyed in either C_{60}^{2-} or C_{60}^{3-} because of the density of low-lying excited states which remain to be described in detail. The preference for a consistent A/E splitting of the T_{1u} level upon filling with one, two, or three electrons is notable, particularly because in each case there are elements of the configuration that are counter-intuitive with respect to the Jahn–Teller theorem.

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Supplementary Material Available: Synthesis and characterization details (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.