

Structural Evidence for the Expected Jahn–Teller Distortion in Monoanionic C₆₀: Synthesis and X-ray Crystal Structure of Decamethylnickelocenium Buckminsterfulleride

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The electronic and structural properties of fulleride anions are of considerable interest due to the discovery of superconductivity in the alkali metal intercalated fullerenes¹ and ferromagnetism in [TDAE][C₆₀].² Reductions in symmetry of the fullerene anions, such as the expected Jahn–Teller (JT) distortion in the C₆₀ⁿ⁻ (n = 1–5) anions, are of particular interest due to the possible role of cooperative symmetry-breaking vibrations in electron–phonon mechanisms of superconductivity in the M₃C₆₀ phases.³ However, relatively few examples of structurally well-characterized fulleride salts have been reported. Reed and coworkers have reported evidence for distortion of the C₆₀ dianion in [PPN⁺]₂[C₆₀²⁻],⁴ but at present there is no structural evidence for the JT distortion expected in the C₆₀ monoanion. Among the increasing number of discrete fulleride salts that have been isolated and characterized,^{5–8} two single-crystal X-ray structures of C₆₀⁻ salts⁸ have been reported; however, both structures exhibit disorder in the C₆₀ monoanion.

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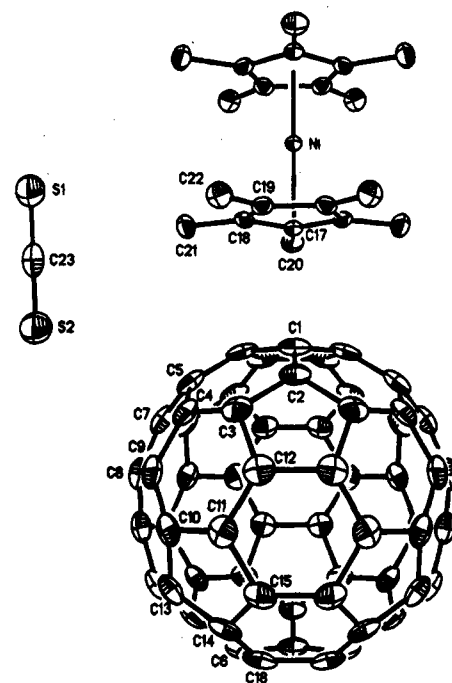


Figure 1. ORTEP drawing of **1** showing 50% thermal ellipsoids and the atom-labeling scheme. The hydrogen atoms have been omitted for clarity.

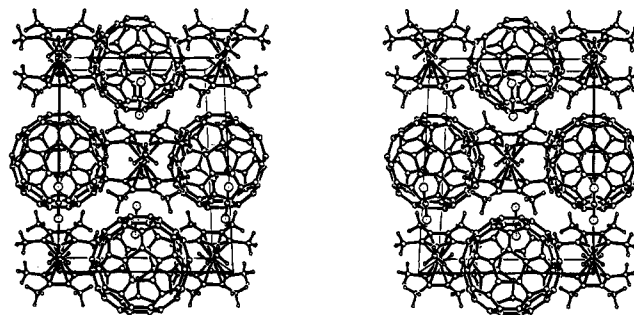


Figure 2. Stereoscopic packing diagram for **1** viewed down the *c* axis.

We have approached the synthesis of discrete fulleride salts, as have others,^{5b,f,6} through the use of strongly reducing organometallic species such as metallocenes, which allow precise control of stoichiometry for the production of C₆₀ⁿ⁻ species.⁷ Decamethylnickelocene, Ni(C₅Me₅)₂, is a selective reductant ($E_{1/2}^{+/0} = -0.65$ V vs SCE)⁹ for the production of the C₆₀ monoanion ($E_{1/2}^{0/1-} \approx -0.45$ V and $E_{1/2}^{1-/2-} \approx -0.9$ V vs SCE)¹⁰ and yields a crystalline 1:1 salt when combined with C₆₀ in CS₂. The structure of this 1:1 salt, [Ni(C₅Me₅)₂]⁺[C₆₀]⁻CS₂ (**1**), is highly ordered and is the first example of a non-disordered monoanionic C₆₀ structure. The metrical parameters of the C₆₀⁻ anion in **1** reveal a modest but statistically significant distortion from icosahedral symmetry. We report here the synthesis and single-crystal X-ray structure of **1** and structural evidence for the expected JT distortion in the C₆₀ monoanion.

1 was prepared under anaerobic conditions by the addition of Ni(C₅Me₅)₂⁹ (46 mg, 0.14 mmol) in CS₂ (20 mL) to C₆₀¹¹

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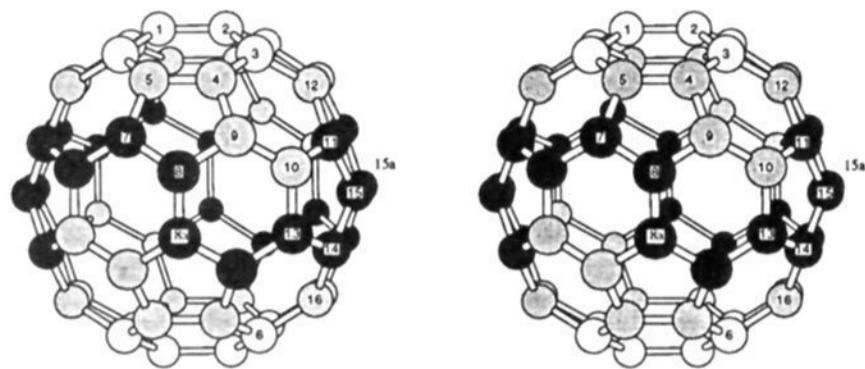


Figure 3. Stereoscopic visualization of the distortion of the C_{60}^- in **1**. C_{60}^- atom-to-atom diameters >0.02 Å longer than the mean diameter are represented in black, and those >0.02 Å shorter than the mean are represented in white. Atom-to-atom diameters near the mean are represented by gray-shaded carbon atoms. Atom-to-atom diameters (in Å) through the 16 unique carbon atoms: C1–C1a, 7.018(6); C2–C2a, 7.015(6); C3–C3b, 7.052(5); C4–C4c, 7.062(5); C5–C5c, 7.061(5); C6–C6a, 7.042(4); C7–C7c, 7.098(5); C8–C8c, 7.099(5); C9–C9c, 7.086(5); C10–C10c, 7.081(6); C11–C11c, 7.097(6); C12–C12b, 7.065(6); C13–C13c, 7.099(5); C14–C14c, 7.104(5); C15–C15c, 7.113(5); C16–C16b, 7.062(4).

(100 mg, 0.14 mmol) in CS_2 (40 mL) with stirring. After the volume was reduced to ~ 15 mL, the dark microcrystalline product was collected by filtration, washed with CS_2 , and dried under vacuum, yielding 141 mg of **1** (90%).¹² Dark red parallelepiped crystals suitable for X-ray analysis were obtained by recrystallization from CS_2 .

In the structure of **1**,¹³ the Ni atom is found at (0,0,0), and the C_{60}^- anion is centered about the mirror plane at $(\frac{1}{2}, 0, \frac{1}{2})$, with carbons C1 and C2 located directly on the crystallographic mirror plane (Figure 1). The $[Ni(C_5Me_5)_2]^+$ cation is found directly over a pentagonal ring of the C_{60}^- anion, with the closest C_5Me_5 ring staggered relative to the C_{60}^- ring (Figures 1 and 2). The C_5Me_5 and C_{60} five-membered rings are nearly parallel (dihedral angle, 0.3°), with an average interplanar distance of 3.17 Å. The packing diagram (Figure 2) shows that the C_{60}^- anions and Ni cations alternate along the (1,0,1) direction. The close interaction of the methyl group C–H bonds of the cations with the hexagonal rings of the C_{60}^- anions is believed to be responsible for the ordered nature of the C_{60}^- anion in **1**.

The C_{60}^- anion in **1** is slightly distorted from I_h symmetry, displaying an apparent axial compression centered about the midpoint of the C1–C2 bond. The diameter along the axis bisecting C1–C2 is the shortest (6.878(6) Å, midpoint of C1–C2 to midpoint of C1a–C2a), and the two longest axes, bisecting C8–C8a (6.965(5) Å) and C15–C15a (6.976(5) Å), are found in the equatorial plane perpendicular to the short C1–C2 axis (Figure 3). The axial nature of the distortion can also be viewed in Figure 3, wherein the carbon atoms have been shaded according to whether the atom-to-atom diameter is >0.02 Å longer (black) or shorter (white) than the mean (7.076(5) Å).

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(12) $[Ni(C_5Me_5)_2][C_{60}]$ was also prepared using benzonitrile as the solvent. Anal. Calcd for $[Ni(C_5Me_5)_2][C_{60}]\cdot PhCN$ ($C_{87}H_{35}NNi$): C, 90.63; H, 3.06; N, 1.21. Found: C, 89.40; H, 3.15; N, 1.21.

(13) Crystallographic data: $C_{81}H_{30}S_2Ni$, $M = 1125.88$; monoclinic, $C2/m$; $a = 16.527(7)$ Å; $b = 11.805(7)$ Å; $c = 14.286(6)$ Å; $\beta = 116.30(3)^\circ$; $V = 2499(2)$ Å³; $Z = 2$; $\rho_{calcd} = 1.50$ g cm⁻³; $\mu = 5.2$ cm⁻¹. The structure was solved by Patterson and Fourier techniques in SHELXTL PLUS 4.11. Full-matrix least-squares refinement of 209 parameters gave $R(F) = 0.051$ and $R_w(F) = 0.045$ for 2029 observed reflections, with $F^2 > 4\sigma(F^2)$ measured between $3^\circ \leq 2\theta \leq 55^\circ$ at -123 °C (Mo K α radiation, $\lambda = 0.71073$ Å).

All of the short diameters are found in the polar region, and the longest diameters are located in the equatorial region. The C_{60}^- anion is ~ 0.1 Å larger in diameter around the equator, with the shortest atom-to-atom diameter being C2–C2a (7.015(6) Å) and the longest diameter C15–C15c (7.113(5) Å). This difference in diameter is slightly larger than that observed for C_{60}^{2-} (0.086 Å)⁴ and significantly larger than the greatest variation in the diameter of C_{60} (0.026 Å).¹⁴

The mean 6:6 and 6:5 ring juncture bond distances in **1**, 1.389(3) and 1.449(3) Å, respectively, fall between the corresponding distances for C_{60} (1.355(9) and 1.467(21) Å)¹⁴ and C_{60}^{2-} (1.399(2) and 1.446(2) Å).⁴ The trend of increasing 6:6 bond lengths and decreasing 6:5 bond lengths in the series $C_{60} \rightarrow C_{60}^- \rightarrow C_{60}^{2-}$ is consistent with successive additions of electrons to the t_{1u} LUMO of C_{60} . As with the LUMO of other conjugated hydrocarbons, the t_{1u} orbital is generally bonding with respect to the “single” (6:5) bonds and antibonding with respect to the “double” (6:6) bonds.¹⁵

A linear approximation method applied to the T_{1u} state of an I_h system shows that D_{5d} and D_{3d} distorted structures are maxima and minima (or vice versa) of the associated potential energy surface and that a D_{2h} structure is a saddle point.¹⁶ Calculations by Koga and Morokuma on C_{60}^- under D_{5d} , D_{3d} , or D_{2h} symmetries predict that JT distortions occur in each case by ellipsoidal elongation along the C_5 , C_3 , or C_2 axes, respectively, with the singly occupied MO located mainly in the equator.¹⁵ The crystallographic symmetry of the C_{60} monoanion in **1** is C_{2h} ; however, the distortion can be described as D_{2h} symmetric within one esd of the atom-to-atom diameters. The axial compression observed for C_{60}^- in **1** is inconsistent with the theoretical prediction of axial elongation,¹⁵ as well as the observed prolate distortion for C_{60}^{2-} .⁴ However, the results presented here for **1** are consistent with the EPR evidence reported by Reed and co-workers for an oblate distortion in $[Co(Cp)_2]^+[C_{60}^-]$.^{6a}

Intermolecular interactions such as crystal packing effects or electronic interactions between C_{60}^- anions may play a role in the distortion in **1**; however, the interaction of the $[Ni(C_5Me_5)_2]^+$ cation with the C_{60}^- would be expected to produce a D_{5d} distortion in the C_{60}^- , since the $[Ni(C_5Me_5)_2]^+$ sits directly over a pentagonal ring of the C_{60}^- (vide infra). Electronic interactions between the C_{60}^- in **1** appear to be significant, since **1** is a fairly good conductor, with $\sigma_{RT} \sim 0.01$ Ω^{-1} cm⁻¹ (pressed pellet), and the role these interactions may have in effecting the observed distortion cannot be ignored. Further studies on this interesting fulleride salt, such as EPR, magnetic susceptibility, and single-crystal conductivity measurements, are underway and will be reported elsewhere.

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Supporting Information Available: Tables of crystallographic details, fractional coordinates, isotropic and anisotropic thermal parameters, atom-to-atom C_{60}^- diameters, and bond lengths and angles for **1** (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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