Synthesis and isolation of an all-carbon tetraanion; a discrete C_{60}^{4-} fulleride salt

Yongping Sun and Christopher A. Reed*

Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0744, USA

The highly reduced, all-carbon tetraanion, C_{60}^{4-}, earlier identified as a discrete ion in solution by electrochemical and spectroscopic methods, can be synthesized and isolated as an analytically pure, sodium cryptand salt.

There is considerable current experimental and theoretical interest in the high negative charge states attainable in small aromatic molecules.[1] The first isolable tetraanion of a π hydrocarbon (rubrene, $C_{42}H_{28}$) has recently been reported[2] and the all-carbon π frameworks of fullerenes present further interesting targets for the study of anionic charge buildup.

The electron accepting ability of C_{60} is its most characteristic chemical property and the maximal extent of charge buildup is an intriguing phase-dependent question. In the gas phase, two electrons can bind to give the rare example of a stable dianion.[3] In the solid state, the heavier alkali- or alkaline-earth cations can interstitially stabilize negative valencies at least as large as 8 in the so-called superfullerides.[4] Intercalated lithium stabilizes the C_{60}^{12-} state, presumably with some degree of covalency.[5] In solution, the highest C_{60}^{n-} fullerides known are $n = 6$ on the electrochemical timescale[6] and $n = 5$ for low-temperature spectroscopic identification.[7] In synthetic chemistry, discrete fulleride salts have only been isolated up to $n = 3$.[8,9] We now report the successful synthesis and isolation of a discrete salt of the highly reduced tetraanion, C_{60}^{4-} ion.

The nature of the C_{60}^{4-} ion is of interest for a number of reasons. For alkali-metal intercalated C_{60}, it is not well understood why A_4C_{60} salts are insulating while A_3C_{60} salts are metallic and superconducting.[10] A detailed knowledge of the electronic structure of the discrete repeating units, namely C_{60}^{4-} and C_{60}^{3-}, may be instructive. With its t_{1u}^4 configuration, C_{60}^{4-} is the electron–hole equivalent of the C_{60}^{2-} ion, whose electronic structure is controversial.[11,12] Mirrored properties would be interesting. The question of a singlet *vs.* a triplet ground state for C_{60}^{4-} is particularly intriguing because unexpectedly, neither C_{60}^{2-} nor C_{60}^{3-} obeys Hund's rule.[9,11] For C_{60}^{3-}, it is presently unknown whether there is a relationship between Cooper pairs of superconducting electrons and the unanticipated tendency of localized spins on C_{60}^{n-} fullerides to attain minimum multiplicity.

The synthesis of an analytically pure salt of C_{60}^{4-} was achieved in an inert-atmosphere glovebox by stirring a suspension of C_{60} (20.0 mg, 0.0278 mmol) in tetrahydrofuran (thf) (35 ml) with a piece of freshly cut sodium in the presence of 4.2 equiv. of cryptand 222 (44.0 mg, 0.117 mmol).† The reaction proceeds *via* successive reductions with [Na-(crypt)⁺]₄[C_{60}^{4-}] precipitating as a dark brown, microcrystalline solid. The product was filtered off, the ball of excess sodium removed as completely as possible with tongs, and the product washed with thf and dried under vacuum (90%). Anal. calc. for $C_{132}H_{144}N_8Na_4O_{24}$: C, 68.38; H, 6.26; N, 4.83; Na, 3.97. Found: C, 67.69, 66.80; H, 6.16, 6.17; N, 4.88, 5.25; Na, 5.25%. Integration of the NOE-suppressed ¹³C NMR signals (15 s pulse delay) of the cryptand (δ 67.9, 66.9, 52.1) *vs.* fulleride (see below) gives the expected 4:1 ratio of cation to anion. The product is exceedingly air sensitive, oxidizing initially to C_{60}^{3-} as the major product. It dissolves without immediate decomposition in scrupulously dried, deoxygenated dimethyl sulfoxide. Electrochemical estimates[13] of the pK_a of the conjugate acid, $C_{60}H^{3-}$ ($pK_a = 37$), suggest that C_{60}^{4-} is a sufficiently powerful base to remove a proton from Me_2SO ($pK_a = 31$). That this does not occur within a day or so indicates either that this reaction is very slow or that the pK_a estimate is incorrect for electrolyte-free solvent. Traces of protonic solvents (*e.g.*, water) in the Me_2SO cause immediate oxidation to C_{60}^{3-}, presumably *via* fullerene hydrocarbon formation. Attempted cation metathesis reactions with NBu_4Cl and with $[N(PPh_3)_2]Cl$ both led to oxidation to C_{60}^{3-}, presumably due to acidity of the α-methylene protons in NBu_4^+ and redox instability[14] of $[N(PPh_3)_2]^+$, respectively.

The fingerprint region for the absorption spectrum of fullerides is in the near-IR region and corresponds to t_{1u}–t_{1g} transitions of *ca.* 1 eV.[7,15] The VIS–NIR spectrum of [Na-(crypt)⁺]₄[C_{60}^{4-}] in Me_2SO is shown in Fig. 1. The absence of a band at 780 nm indicates the absence of C_{60}^{3-}. Maxima at 730 and 1195 nm are consistent with those reported for electrochemically generated C_{60}^{4-} in benzonitrile (728, 1209 nm)[15] and rubidium-reduced C_{60}^{4-} in liquid ammonia (715, 1175 nm).[7]‡

We have recently shown that for $n = 1$, 2 and 3, the C_{60}^{n-} fullerides have broad, downfield-shifted resonances in their solution ¹³C NMR spectra, the result of paramagnetism.[11,17] The same is true for C_{60}^{4-}, indicating that it too has significant paramagnetism at room temperature. The spectrum in $(CD_3)_2SO$ is shown in Fig. 2. The chemical shift of δ 185 is essentially the same as that of C_{60}^- (δ 186) and C_{60}^{2-} (δ 184) but different from that of C_{60}^{3-} (δ 197). An integrity check on the NMR sample was run after measurement and, within the limits of VIS–NIR detection (*ca.* 5%), it indicated no decay to C_{60}^{3-} ($\lambda_{max} = 780$ nm). Interestingly, the chemical shift of the discrete C_{60}^{4-} ion (δ 185) is not very different from that in solid-state K_4C_{60} (δ 180) and Rb_4C_{60} (δ 182).[18] The interpretation of ¹³C chemical shifts in fullerides is complex, but to a first approximation, the *ca.* 40 ppm downfield shift can be equated with an average spin density of about one unpaired electron per buckyball. This suggests that like C_{60}^{2-}, the singlet ($S = 0$) and triplet ($S = 1$) states are close in energy. Fast intersystem crossing and/or electron transfer would average the signal to that approximating an $S = 1/2$ system. Efforts to quantify the singlet–triplet splitting for C_{60}^{4-} and C_{60}^{2-} by NMR methods
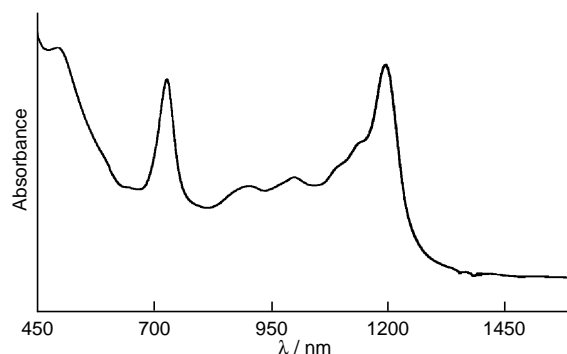

Fig. 1 VIS–NIR spectrum of C_{60}^{4-} in Me_2SO

are ongoing. The present results are in qualitative agreement with those on Rb_4C_{60} where a localized singlet ground state is proposed with a close-lying triplet a few hundred cm^{-1} higher in energy.[19]

EPR spectroscopy has been widely used to investigate the spin states of fullerides but interpretations have been bedeviled by problems of sensitivity to impurities, the difficulty of quantifying overlapping signals with widely differing line-widths, aggregation uncertainties in frozen solution, *etc.*[11,12] Preliminary results on C_{60}^{4-} salts fare no better. Fig. 3 shows the low-temperature EPR spectrum of C_{60}^{4-} in frozen Me_2SO solution. Comparison to the spectrum of C_{60}^{3-} under identical conditions of cation and solvent (also shown in Fig. 3) indicates the presence of C_{60}^{3-} in the C_{60}^{4-} sample even though this is undetectable by NIR. The additional, sharper signals are potentially ascribable to C_{60}^{4-}, but it would be premature to make such an assignment in view of the difficulties[11,12] associated with assigning the spectrum of C_{60}^{2-}, of which C_{60}^{4-} is the electron–hole equivalent. Since these signals appear to have integrated intensities that are less than the trace C_{60}^{3-} signal, the simplest interpretation is that C_{60}^{4-} is EPR silent at 4 K because of a singlet ground state.§ However, a close-lying, thermally accessible triplet state is indicated by the paramagnetically shifted ^{13}C NMR signal seen at room temperature.

In summary, despite its exceedingly strong reducing nature (−2.35 V *vs.* ferrocene),[6] the discrete C_{60}^{4-} ion can be isolated with an 'innocent' cation. This opens the way to deeper studies of its electronic and molecular structure and to studies of its chemical reactivity, particularly with electrophiles.[20]

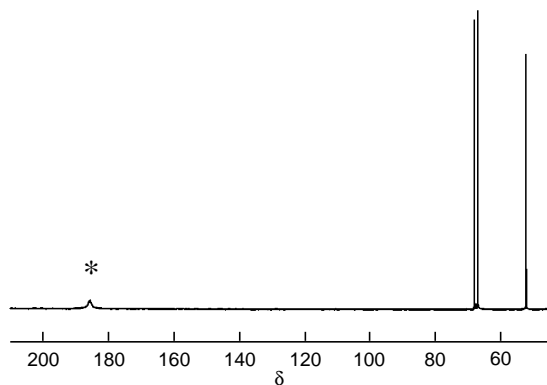**Fig. 2** ^{13}C NMR spectrum of C_{60}^{4-} in $(CD_3)_2SO$ (34196 scans, 125.8 MHz) Peak marked * at δ 185 is from C_{60}^{4-}; the others are from Na(cryptand 222)$^+$

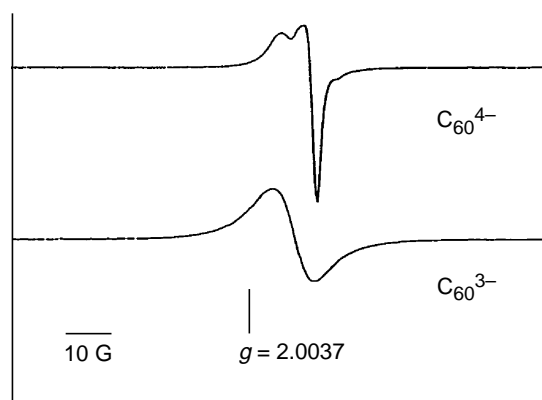**Fig. 3** EPR spectra of C_{60}^{4-} and C_{60}^{3-} in frozen Me_2SO solution at 5 K

Footnotes

References

1 M. Baumgarten, L. Gherghel, M. Wagner, A. Weitz, M. Rabinovitz, P.-C. Cheng and L. T. Scott, *J. Am. Chem. Soc.*, 1995, **117**, 6254.

2 H. Bock, K. Gharagozloo-Hubmannm, C. Nather, N. Nagel and Z. Havlas, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 631.

3 M. K. Scheller, R. N. Compton and L. S. Cederbaum, *Science*, 1995, **270**, 1160.

4 A. J. Maxwell, P. A. Brühwiler, S. Andersson, N. Martensson and P. Rudolf, *Chem. Phys. Lett.*, 1995, **247**, 257; W. Andreoni, P. Giannozzi, J. F. Armbruster, M. Knupfer and J. Fink, *Europhys. Lett.*, 1996, **34**, 699 and references therein.

5 Y. Chabre, D. Djurado, M. Armand, W. R. Romanow, N. Coustel, J. P. McCauley, Jr., J. E. Fischer and A. B. Smith III, *J. Am. Chem. Soc.*, 1995, **114**, 764; J. Kohanoff, W. Andreoni and M. Parrinello, *Chem. Phys. Lett.*, 1992, **198**, 472.

6 Q. Xie, E. Perez-Cordero and L. Echegoyen, *J. Am. Chem. Soc.*, 1992, **114**, 3978.

7 W. K. Fullagar, I. R. Gentle, G. A. Heath and J. W. White, *J. Chem. Soc., Chem. Commun.*, 1993, 525.

8 C. Bossard, S. Rigaut, D. Astruc, M.-H. Delville, G. Félix, A. Février-Bouvier, J. Amiell, S. Flandrois and P. Delhaès, *J. Chem. Soc., Chem. Commun.*, 1993, 333.

9 P. Bhyrappa, P. Paul, J. Stinchcombe, P. D. W. Boyd and C. A. Reed, *J. Am. Chem. Soc.*, 1993, **115**, 11004.

10 M. J. Rosseinsky, *J. Mater. Chem.*, 1995, **5**, 1497; J. E. Fischer, in *The Chemical Physics of Fullerenes: 10 (and 5) Years Later*, ed. W. Andreoni, NATO ARW Series E316, Kluwer, Dordrect, 1996, p. 359; R. Kerkoud, P. Auban-Senzier, D. Jerome, S. Brazovskii, I. Luk'yanchuk, N. Kirova, F. Rachdi and C. Goze, *J. Phys. Chem. Solids*, 1996, **57**, 143 and references therein.

11 P. D. W. Boyd, P. Bhyrappa, P. Paul, J. Stinchcombe, R. D. Bolskar, Y. Sun and C. A. Reed, *J. Am. Chem. Soc.*, 1995, **117**, 2907.

12 P. C. Trulove, R. T. Carlin, G. R. Eaton and S. S. Eaton, *J. Am. Chem. Soc.*, 1995, **117**, 6265.

13 M. E. Niyazymbetov, D. H. Evans, S. A. Lerke, P. A. Cahill and C. C. Henderson, *J. Phys. Chem.*, 1994, **98**, 13093.

14 M. Tilset, A. A. Zlota, K. Folting and K. G. Caulton, *J. Am. Chem. Soc.*, 1993, **115**, 4113.

15 D. R. Lawson, D. L. Feldheim, C. A. Foss, P. K. Dorhout, C. M. Elliott, C. R. Martin and B. Parkinson, *J. Electrochem. Soc.*, 1992, **139**, L68.

16 M. Baumgarten, A. Gügel and L. Gherghel, *Adv. Mater.*, 1993, **5**, 458.

17 Confirmation has been recently provided by J. Chen, F.-Y. Cai., Q.-F. Shao, Z.-E. Huang and S.-M. Chen, *Chem. Commun.*, 1996, 1111.

18 J. Reichenbach, F. Rachdi, I. Luk'yanchuk, M. Ribet, G. Zimmer and M. Mehring, *J. Chem. Phys.*, 1994, **101**, 4585.

19 G. Ruani, P. Guptasarma, C. Taliani and J. Fischer, *Physica C*, 1994, **235**, 2477; I. Lukyanchuk, N. Kirova, F. Rachdi, C. Goze, P. Molinie and M. Mehring, *Phys. Rev. B*, 1995, **51**, 3978.

20 Alkylation of C_{60} has been reported *via* the reaction of alkyl halides with fullerides: J. W. Bausch, G. K. S. Prakash and G. A. Olah, *J. Am. Chem. Soc.*, 1991, **113**, 3205; C. Caron, R. Subramanian, F. D'Souza, J. Kim, W. Kutner, M. T. Jones and K. M. Kadish, *J. Am. Chem. Soc.*, 1993, **115**, 8505; J. Chen, R.-F. Cai, Q.-F. Shao, Z.-E. Huang, H.-M. Wu, S.-K. Jiang and Q.-F. Shao, *J. Chem. Soc., Chem. Commun.*, 1995, 1553; P. L. Boulas, Y. Zuo and L. Echegoyen, *Chem. Commun.*, 1996, 1547; K.-M. Mangold, W. Kutner, L. Dunsch and J. Fröhner, *Synth. Met.*, 1996, **77**, 73.