

Electrocrystallizing C₆₀: Synthesis, Single Crystal X-ray Structure, and Magnetic (ESR, SQUID) Characterization of [(C₆H₅)₄P]₂[C₆₀][I]_x

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Despite the explosion of research¹ on C₆₀^{2,3} mostly due to its novel chemical nature and the discovery of superconductivity⁴ and ferromagnetism⁵ in fulleride salts, there still exist only a few families of well-characterized C₆₀-based materials.

We report here on the synthesis by electrocrystallization of high quality single crystals of volume up to 1 mm³ of a salt of formula [(C₆H₅)₄P]₂[C₆₀][I]_x (0 < x < 1), the description of its crystal and molecular structure, and its characterization by NIR, EPR, and SQUID magnetic measurements.

Surprisingly, the electrocrystallization, so successful in growing bulk single crystals of pre-C₆₀ organic superconductors, has received little attention to date in the field of fullerene chemistry. Wudl et al. first described the synthesis by electrocrystallization of a C₆₀⁻ salt of formula [(C₆H₅)₄P⁺]₃[C₆₀][Cl⁻]₂⁶ but only of microcrystalline form. More recently, microcrystals of [Ru(bpy)₂]-[C₆₀] were synthesized by electrocrystallization,⁷ and Kobayashi et al. reported the synthesis of single crystals of PPN-C₆₀⁸ (PPN = [(C₆H₅)₃P=]₂N⁺), but to date, no report of the crystal structure has appeared.

To fully characterize the C₆₀ⁿ⁻ species, it is highly desirable to obtain single crystals. The first single-crystal X-ray structure of a salt of C₆₀, that of Co(cp)₂C₆₀, has recently been determined.⁹ We decided to explore the synthetic power of the electrocrystallization technique to generate new bulk *single-crystal* salts of C₆₀ of varied charges whose structure and physical properties could thus be fully characterized. Furthermore, by electrocrystallizing C₆₀ in the presence of cations of varied charge, length, and shape, fine-tuned new materials of varied architectures and hence physical properties might be synthesized.¹⁰

C₆₀ was either produced by the Krätschmer–Huffman technique³ and purified by column chromatography¹¹ or bought from MER corporation. (C₆H₅)₄PI was purchased from Aldrich

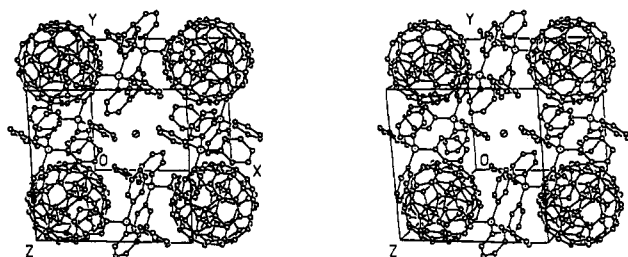


Figure 1. Stereoscopic view of the unit cell. For the sake of clarity, iodide anions at the corners of the unit cell and C₆₀⁻ anions at (1/2,1/2,0) and (1/2,1/2,1) have been omitted. Both orientations of the C₆₀⁻ anions are represented.

corporation. Solvents were of HPLC grade (% water < 0.05) and passed over a column of activated alumina prior to use. In an H-cell with Pt electrodes and two sintered glasses separating the anodic and cathodic compartments, a solution of 8 mg of pure C₆₀ and 45 mg of (C₆H₅)₄PI was electrolyzed at constant current (I = 3 μA, dI ≈ 5 μA·cm⁻²) in a degassed CH₂Cl₂/toluene (17.5 mL/15 mL) mixture at 43 °C for 3 days (50% of the time necessary to reduce all C₆₀ to C₆₀⁻). Black shiny single crystals of [(C₆H₅)₄P]₂[C₆₀][I]_x were harvested on the cathode.¹² As expected for monoanionic salts of C₆₀, no air sensitivity was observed.¹³

During resolution of the structure, the iodide site appeared to be only partially populated. The occupancy factor was allowed to vary and converged to a value of 0.35, in agreement with the elemental analysis.¹⁴ The NIR spectrum was recorded from 800 to 1200 nm in KBr pellets. It shows an intense band around 1100 nm and several minor bands at 1060, 1015, and 950 nm. Overall, it is identical to the solution spectrum of the monoanionic species recently reported but with a 25-nm red shift.¹³ It shows absolutely no bands due to C₆₀²⁻ (954 and 830 nm).¹⁵

A stereoscopic view of the unit cell is shown in Figure 1. I⁻ anions are located at the origin of the unit cell. Tetraphenylphosphonium cations are located on $\bar{4}$ centers at (0,1/2,1/4). The C₆₀⁻ anions are centered around ⁴/m centers at (0,0,1/2). The I_h point group has no element of 4-fold symmetry. Hence, two orientations at 90° relative to each other were refined with 50% occupancy factor (Figure S1). Attempts to lower the symmetry to space group I_{2/m} failed. [(C₆H₅)₄P]₂[C₆₀][I]_x is a truly ionic salt with each anion surrounded by cations and vice versa. Specifically, there are no short contacts between C₆₀⁻ anions (shorter center to center distance 12.588 Å, Σ_{vdw} = 10 Å) nor C₆₀⁻ and I⁻ anions (shorter center-to-center distance = 8.90 Å, Σ_{vdw} = 7 Å). C₆₀⁻ anions, as well as I⁻ anions, are surrounded by a tetragonally distorted cube of tetraphenylphosphonium cations. In turn, each phosphonium cation is surrounded by two interpenetrating tetragonally distorted tetrahedra, one formed by C₆₀⁻ anions, the other by I⁻ anions.

There are eight equivalent short contacts H...I (d = 2.82 Å, Σ_{vdw} = 3.40 Å) between I⁻ anions and tetraphenylphosphonium cations. The shortest contact C...C between C₆₀ and a phenyl group is between atoms C2 and C13 (d = 3.49 Å). There are

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

(12) Crystal data for [(C₆H₅)₄P]₂[C₆₀][I]_{0.35}: formula C₁₀₈H₄₀I_{0.3462}P₂ (FW = 1443.3), crystal size 0.30 × 0.40 × 0.65 mm³, space group I_{4/m}, a = 12.588(2) Å, c = 20.134(2) Å, V = 3190.5(7) Å³, Z = 2. Room temperature, Mo Kα radiation (λ = 0.710 73 Å), R = 4.68, R_w = 5.48 for 145 parameters refined and 1006 reflections with F > 4σF; all non-H atoms refined with anisotropic parameters, H riding. Largest peak on the final Fourier difference map, 0.43 eÅ⁻³.

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

(14) Anal. Found (Calcd for C₁₀₈H₄₀I_{0.35}P₂): C, 87.78 (89.84); H, 2.71 (2.79); P, 4.42 (4.29); I, 1.32 (3.08).

(15) Heath, G. A.; McGrady, J. E.; Martin, R. L. *J. Chem. Soc., Chem. Commun.* 1992, 1272–1274. Lawson, Del R.; Feldheim, D. L.; Foss, C. A.; Dorhout, P. K.; Elliott, C. M.; Martin, C. R.; Parkinson, B. A. *J. Electrochem. Soc.* 1992, 139, L68–L71.

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(1) See "Bucky news service" available on Internet by sending mail to Bucky@sol1.lsrn.upenn.edu.

(2) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* 1985, 318, 162.

(3) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* 1990, 347, 354.

(4) Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* 1991, 350, 600.

(5) Allemand, P. M.; Khemani, K.; Koch, A.; Wudl, F.; Holzer, K.; Donovan, S.; Grüner, G.; Thompson, J. D. *Science* 1991, 253, 301.

(6) Allemand, P. M.; Srdanov, G.; Koch, A.; Khemani, K. C.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* 1991, 113, 2780–2781.

(7) Foss, C. A., Jr.; Feldheim, D. L.; Lawson, Del R.; Dorhout, P. K.; Elliott, C. M.; Martin, C. R.; Parkinson, B. A. *J. Electrochem. Soc.* 1993, 140, L84–L86.

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

(9) Balch, A. L.; Lee, J. W.; Noll, B. C.; Olmstead, M. M. *J. Chem. Soc., Chem. Commun.*, submitted for publication.

(10) For examples of the reverse concept with organic donors, see: Pénicaud, A.; Boubekeur, K.; Batail, P.; Canadell, E.; Auban-Senzier, P.; Jérôme, D. *J. Am. Chem. Soc.* 1993, 115, 4101–4112 and refs 5–8 therein.

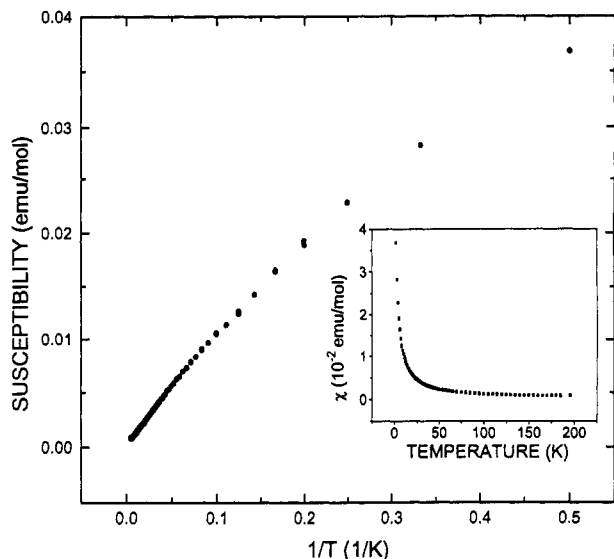


Figure 2. SQUID magnetic susceptibility as a function of reciprocal temperature. Inset: SQUID magnetic susceptibility versus temperature.

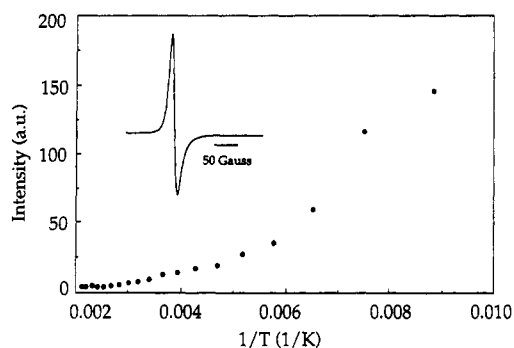


Figure 3. Relative ESR signal intensity as a function of reciprocal temperature. Inset: microcrystalline powder ESR spectrum at 113 K.

three short H...C distances ($d_{\text{H2-C13}} = 2.71 \text{ \AA}$, $d_{\text{H2-C7}} = 2.94 \text{ \AA}$, $d_{\text{H2-C8}} = 3.05 \text{ \AA}$).

SQUID magnetic susceptibility was measured from room temperature down to 4.2 K under a magnetic field of 10 kG. Sample holder contribution as well as diamagnetic susceptibility were subtracted from the experimental data. The data *do not* follow a Curie–Weiss law (Figure 2), despite isolated C_{60}^- radicals in the crystallographic structure.

ESR spectra were recorded on microcrystalline powder from 113 to 473 K. g values were calibrated using pitch ($\text{C}(\text{KCl})$, $g = 2.0028$) as a standard. The inset of Figure 3 shows the spectrum at 113 K. The g value and peak-to-peak linewidth at room temperature are respectively 2.001 ± 0.0015 and 50 G. We make the following observations: (i) no extra spike is observed, contrary

to most previous reports on C_{60}^- ESR;¹⁶ (ii) the linewidth increases linearly from 14 G at 113 K to reach a plateau of 50 G around 300 K; (iii) the spectrum is highly asymmetrical and remains so over the whole temperature range; (iv) the asymmetry is more pronounced at high temperatures; (v) the relative intensity of the signal (obtained by double integration of the first derivative absorption signal) does not follow a Curie–Weiss law (Figure 3).

Single-crystal four-points AC resistivity measurements using the Van der Pauw configuration show a room temperature resistivity of the order of $(2\text{--}6) \times 10^4 \text{ \Omega}\cdot\text{cm}$.

Both the X-ray structure ($x = 0.35$) and the elemental analysis ($x = 0.15$) point out a deficiency of iodide. The NIR spectrum shows that no extra charge can be attributed to C_{60} (no C_{60}^{2-} bands). This latter fact is further supported by the air stability (the X-ray structure was solved on an unprotected crystal that had been exposed to air for a month). This led us to the following charged formulation: $[(\text{C}_6\text{H}_5)_4\text{P}^{(1+x)/2+}]_2[\text{C}_{60}^-][\text{I}]_x$ ($0 < x \ll 1$). Indeed, preliminary treatment of the magnetic data indicate that they can be fitted with a model of two magnetic centers with an antiferromagnetic exchange integral of the order of -1 to -4 cm^{-1} (-1.4 to -6 K). Furthermore, resistivity data suggest an activated conduction mechanism which is possible only through partial electronic density on the tetraphenylphosphonium cations¹⁷ since there is no direct interaction between C_{60}^- anions.

In conclusion, we have shown that the electrocrystallization technique can be successfully employed to grow large, high-quality single crystals of C_{60} salts suitable for X-rays as well as physical studies. The crystal structure of $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{C}_{60}][\text{I}]_x$ shows fully isolated C_{60}^- anions in a very symmetrical environment. Further physical studies (CP-MAS NMR, ENDOR, He temperature, and single-crystal ESR) are underway to fully understand the properties and composition of this intriguing new material.

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Supplementary Material Available: Atomic numbering scheme, tables of positional and thermal parameters, bond lengths and angles, disorder model for the C_{60} molecule (Figure S1) (5 pages); tables of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

(16) Reference 13 and references therein.

(17) The same conclusion has been reached by an independent group when studying the magnetic properties of $[(\text{C}_6\text{H}_5)_4\text{P}]_3[\text{C}_{60}][\text{Cl}]_2$: Becker, U.; Denninger, G.; Dyakonov, V.; Gotschy, B.; Klos, H.; Rösler, G.; Hirsch, A.; Winter, H. *Europhys. Lett.* **1993**, *21*, 267–271.