
Alain Pénicaud,∗†‡ T. Aarón Pérez-Benítez,† R. Gleason V.,† E. Muñoz P.,‡ and R. Escudero‡

Instituto de Química, Instituto de Física, and Instituto de Investigaciones en Materiales Universidad Nacional Autónoma de México Coyoacán, C.P. 04510, México D.F., México

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Despite the explosion of research on C60, mostly due to its novel chemical nature and the discovery of superconductivity and ferromagnetism in fullerene salts, there still exist only a few 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] (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]2[C60][I] but only of microcrystalline form. More recently, microcrystals of [Ru(bpy)3]2- [C60]- were synthesized by electrocrystallization, and Kobayashi et al. reported the synthesis of single crystals of PPN-C608 (PPN = [(C6H5)4P]2+), but to date, no report of the crystal structure has appeared.

To fully characterize the C60+ species, it is highly desirable to obtain single crystals. The first single-crystal X-ray structure of a salt of C60, that of Co(op)3C60, has recently been determined. 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.

C60 was either produced by the Kratschmer-Huffman technique and purified by column chromatography or bought from Aldrich.

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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. 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)2PI 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]- were harvested on the cathode. As expected for monoanionic salts of C60, no air sensitivity was observed.

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. The NMR 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. It shows absolutely no bands due to C602- (954 and 830 nm).

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 around 4 centers at (0,1/2,1/2). The C60+ anions are centered around 4/m centers at (0,0,1/2). The I3 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 I2/m failed. [(C6H5)4P]2[C60][I]- is a triclinic crystal salt with each anion surrounded by cations and vice versa. Specifically, there are no short contacts between C60- anions (shorter center to center distance 12.58 Å, Σdist = 10 Å) nor C60- and I- anions (shorter center-to-center distance = 8.90 Å, Σdist = 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 tetragonal distortion tetrahedra, one formed by C60- anions, the other by I- anions.

There are eight equivalent short contacts H···I (d = 2.82 Å, Σdist = 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

* Instituto de Química.
† Instituto de Física.
‡ Instituto de Investigaciones en Materiales.

1 On leave from Laboratoire de Physique des Solides (CNRS), Université de Paris-Sud, 91402 Orsay, France.
2 See "Bucky news service" available on Internet by sending mail to Buckyn @ iol.isrm.upsen.edu.
12 Crystal data for [(C6H5)4P]2[C60][I] indicate formula C62H40I4P2 (FW = 1443.3), crystal size 0.30 × 0.40 × 0.65 mm3, space group I4/m, a = 12.588(2) Å, c = 20.134(2) Å, V = 3190.5(7) Å3, Z = 2. Room temperature, Mo Kα radiation (λ = 0.7073 Å), R = 0.46, Rp = 0.48 for 145 parameters refined and 1006 reflections with F > 4σ(F); all non-H atoms refined with anisotropic parameters, H riding. Largest peak on the final Fourier difference map, 0.43 eÅ-3.
14 Anal. Found (Calcd for C60HI8I4P2): C, 87.78 (89.84); H, 2.71 (2.33); N, 0.20 (0.17).
to most previous reports on C$_{60}^-$-ESR (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 (2-6) × 10$^4$ Ω-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: [(C$_{6}H_5$)$_4$P$^{(1+x)/2+}$][C$_{60}^-$(I$^-$)], ($0 < x \ll 1$). 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 cations since there is no direct interaction between C$_{60}^-$ anions.

In conclusion, we have shown that the electrowcrystallization 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 [(C$_{6}H_5$)$_4$P][C$_{60}^-$(I$^-$)] 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.