Characterization of the mixed fullerene radical-anion salt $[PPh_4^+]_2C_{60}^{\bullet-}Cl_{1-x}^-I_x^-$

W. Schütz,[a] J. Gmeiner,[a] A. Schilder,[a] B. Gotschy*[a] and V. Enkelmann[b]

[a] *Physikalisches Institut und Bayreuther Institut für Makromolekülforschung (BIMF), Universität Bayreuth, 95440 Bayreuth, Germany*

[b] *MPI für Polymerforschung, 55021 Mainz, Germany*

$[PPh_4^+]_2C_{60}^{\bullet-}Cl_{1-x}^-I_x^-$ is prepared by electrocrystallisation and the stoichiometry carefully investigated by elemental analysis.

Electrocrystallisation is an attractive method for the synthesis of bulk single crystals of fullerene radical-anion salts. These salts are excellent model systems for the study of the molecular and spin dynamics of fullerene monoradical anions in the solid state. This is due to the fact that many of the physical properties of C_{60} charge-transfer complexes or radical-anion salts are simply monomolecular properties of C_{60} anions. Three such salts are $[PPh_4^+]_2C_{60}^{\cdot-}Cl^-$ (**1**),[1,2] $[PPh_4^+]_2C_{70}^{\cdot-}I^-$ (**2**)[3] and $[PPh_4^+]_2C_{60}^{\cdot-}I_x$ (**3**).[4,5] **3** was claimed to be a non-stoichiometric system with $x \approx 0.3$.[4] To take account of the iodine deficiency either partial charges on the phenylene units or an incomplete charge transfer from the phenylene units to C_{60} was suggested. Both possibilities are not particularly plausible for two reasons. First, **1**, **2** and **3** are nearly isostructural with each other as revealed by X-ray analysis.[1–4,6] Secondly, our susceptibility measurements, which are compatible with measurements of Pénicaud *et al.*,[3,4] show Curie–Weiss behaviour with a Curie temperature of *ca.* -1 K and a Curie constant of 0.375 emu K mol^{-1}. This is the expectation value for spin-only magnetism of a spin $S = \frac{1}{2}$ system. Finally, iodine deficiencies were not seen by X-ray diffraction. To resolve the problem, bulk single crystals of **3** were prepared according to the procedure of ref. 3. C_{60} [Hoechst (gold grade)] and $[PPh_4]I$ (Aldrich, recrystallised several times from CH_2Cl_2) were dissolved in toluene–dichloromethane, and the mixture was poured into an H-cell containing platinum electrodes. Pénicaud *et al.* reported that $[PPh_4]I$ is part of the crystal structure and suggest, from X-ray and elemental analysis, a formulation $[PPh_4^+]_2C_{60}^{\cdot-}I_x^-$ ($0.15 < x < 0.35$). Elemental analyses obtained by us and Pénicaud are compared in Table 1.

Our values coincide well with the values published by Pénicaud *et al.* except for the presence of Cl, which was obviously not investigated previously. From these values we reformulate **3** as $[PPh_4^+]_2C_{60}^{\cdot-}Cl_{1-x}^-I_x^-$ ($x = 0.15$). The chlorine anions are in the centre of the unit cell. The X-ray analysis reveals that the unit cell is statistically occupied by Cl^- and I^-, whereby we find a probability of 90% for Cl^- and 10% for I^-. This is within the accuracy of the elemental analysis. These values are smaller than the values reported by Pénicaud *et al.*, but this certainly depends on the details and parameters of the crystal growth. Thus **3** is a mixed salt rather than a system with a deficiency of iodine.

Table 1 Elemental analyses for **3**

Atom	mol%	mass%	mass% (ref. 3)
C	72.08	89.56	87.78
H	25.99	2.71	2.71
P	1.37	4.38	4.42
I	0.09	1.12	1.32
Cl	0.48	1.76	

The source of the chlorine can only be from dichloromethane. Indeed the electrochemical instability and the decomposition of dichloromethane under electrolysis has been known for a long time.[7] The typical reaction path is given by eqns. (1) and (2).

$$CH_2Cl_2 + e^- \longrightarrow CH_2Cl\cdot + Cl^- \qquad (1)$$

$$CH_2Cl\cdot + e^- \longrightarrow CH_2^{\cdot} + Cl^- \qquad (2)$$

C_{60}^- and Cl^- are formed at the cathode and combine with PPh_4^+ to form the salt **3**.

The 50 kHz wide solid-state ^{1}H NMR spectrum of **3** is superimposed by a narrow line, which disappears at lower temperatures. This suggests that toluene is included in the solid samples. From the ratio of the wide and narrow lines we obtain 0.25 toluene molecules per formula unit, within the experimental uncertainty of the elemental analysis.

In conclusion, we can say that the concept of partial charges in **3** is invalid; $[PPh_4^+]_2C_{60}^{\cdot-}Cl_{1-x}^-I_x^-$ ($x = 0.15$) is a genuine salt and is isostructural and isomorphous with **1** and **2**. The original discrepancies between the proposed formula unit and static susceptibility have been resolved.

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