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SINGLE CRYSTAL SYNTHESIS OF $[(C_6H_5)_4P]_2[C_{70}][I]$ BY ELECTROCRYSTALLIZATION AND EXPERIMENTAL DETERMINATION OF THE g-VALUE ANISOTROPY OF $C_{70}{\cdot}^-$ AND $C_{60}{\cdot}^-$ AT 4.2 K.

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We describe the synthesis by electrocrystallization and the crystal packing of $[(C_6H_5)_4P]_2[C_{70}][I]$. Magnetic susceptibility measurements show Curie-Weiss behaviour. ESR measurements on single crystals of $[(C_6H_5)_4P]_2[C_{70}][I]$ and $[(C_6H_5)_4P]_2[C_{60}][I]_x$ $(0 < x << 1)$ allowed us to determine the g tensor principal values at 4.2 K for both radicals $C_{60}{\cdot}^-$ ($g_x = g_y = 1.9970$, $g_z = 1.9998$, $g_{av} = 1.9979$) and $C_{70}{\cdot}^-$ ($g_x = g_y = 1.9996$, g_z (long axis) $= 2.0150$, $g_{av} = 2.0047$).

Keywords: A. fullerenes, B. chemical synthesis, E. electron paramagnetic resonance

The chemistry and physics of C_{70}, the next higher parent of Buckminsterfullerene C_{60} [1] have developed more slowly than that of C_{60}, mainly due to small available quantities. Progress in chromatographic separation as well as available commercial sources have now made C_{70} accessible to all laboratories. Despite close chemical nature, materials made out of C_{70} differ very much in their properties from their C_{60} analogs. Maximum conductivity of alkaline salts of C_{70} is 100 times smaller than their C_{60} analogs[2] without any superconducting transition reported. TDAE.C_{70} does not show any transition to a ferromagnetic state.[3] It is of great interest to be able to prepare single crystals of C_{70} salts in order to fully characterize them and to help understand the underlying reasons for the different physical phenomena in C_{60} and C_{70} salts. C_{70} as well as C_{60} has been shown to undergo successive one-electron reversible reduction up to C_{70}^{6-}.[4] Despite the great synthetic potential of the electrocrystallization technique for obtaining large size single crystals, only a few attempts have been made to apply it to C_{60} and C_{70}.[5-7] We recently reported[6] that it could be applied successfully to grow bulk single crystals of monoanionic $C_{60}{\cdot}^-$ salts. Single crystals of $[PPN^+]_2[C_{60}^{2-}]$ (PPN^+ = bis(triphenylphosphine)iminium) have also been obtained by slow cation exchange of a C_{60}^{2-} solution.[8] Using the electrocrystallization technique, we were able to grow single crystals of $[(C_6H_5)_4P^+]_2[C_{70}^-][I^-]$ and characterize them by X-ray diffraction, NIR spectroscopy and single crystal ESR.

Single crystals of $[(C_6H_5)_4P^+]_2[C_{70}^-][I^-]$ were obtained by electrocrystallization using the same conditions[6] as those used to prepare $[(C_6H_5)_4P]_2[C_{60}][I]_x$ $(0 < x << 1)$ (**1**) with the exception of a 1:1 mixture of toluene and CH_2Cl_2. Care was taken to stop the electrocrystallization after 50 % of the current necessary to reduce all C_{70} to C_{70}^-

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was used. No air sensitivity was observed as was the case for the parent salt (**1**). The NIR spectrum shows a band centered around 1380 nm of similar shape and position as previously reported for C_{70}^- in solution.[9]

Using an X-ray diffractometer, cell determination on a single crystal gave the following parameters (tetragonal system): a = 12.682(4) Å, c = 21.660(3) Å and V = 3484(1) Å^3. Those parameters closely compare with those of (**1**): a = 12.588(2) Å, c = 20.134(2) Å and V = 3190.5(7) Å^3. We, therefore, assumed the two salts to be isostructural, the longer c axis in $[(C_6H_5)_4P^+]_2[C_{70}^-][I^-]$ being due to the C_{70} long axis aligned with the tetragonal axis. Nevertheless, an attempt was made to solve the structure of the C_{70} salt in order to determine the iodide content, crucial in asserting the charge formulation of the compound, which showed to be partial in (**1**). Despite the low number of reflections that could be collected due to disorder, (the C_{70} long axis (5-fold axis) is colinear with a lattice 4-fold axis, resulting in a smeared-out electron density distribution and a low diffraction power) we could check that both salts are isostructural, entering a rigid model for the C_{70} molecule.[10] The structure of $[(C_6H_5)_4P^+]_2[C_{70}^-][I^-]$ and (**1**) can be conceptually described as a tetragonally distorted anti-CsCl structure with near cubes (8.968 x 8.968 x 10.830 Å^3) of $(C_6H_5)_4P^+$ ions alternately centered by a fulleride or iodide ion.[11] Closest center to center distance between C_{70}^- ions is 12.682 Å ($\Sigma_{vdW} \approx 10$ Å in the equatorial plane). No deficiency was found on the iodide site contrary to the C_{60} salt (**1**). The elemental analysis[12] is consistent with full occupation of the iodide site. However, the slightly low iodine content does not allow one to totally rule out the possibility of a small iodide deficiency.

ESR spectra were recorded on a Varian X-band (9.3 GHz) spectrometer equipped with an Oxford ESR900 helium cryostat on single crystals of $[(C_6H_5)_4P^+]_2[C_{70}^-][I^-]$ and $[(C_6H_5)_4P]_2[C_{60}][I]_x$ whose orientations had been previously determined on a precession camera. For $[(C_6H_5)_4P^+]_2[C_{70}^-][I^-]$, at room temperature, a single broad line ($\Delta H \approx 600$ Gauss) is observed while no accurate determination of the g factor is possible. Upon cooling, the linewidth decreases dramatically (Figure 1). Below 20 K, several lines emerge from the previously unique resonance signal, whose relative intensities are sample dependent. We, therefore, conclude to a sample breakage upon cooling (when attempting to cool down single crystals for better structure determination, we also observe irreversible loss of good mosaicity). However, starting with an oriented single crystal and cooling down slowly, we obtained at 4.2 K most of the signal intensity in a given line whose g extrema were found to be $g_z = 2.0150$ along c (C_{70} long axis) and $g_x = g_y = 1.9996$ in the (a,b) plane. Note that the degeneracy in the (a,b) plane is expected from the quadratic crystal symmetry. In fact, the other lines correspond to the same g values with a rotation of the principal axes. The trace of the g tensor leads to an equivalent isotropic value g = 2.0047. The linewidth was found almost independent of the crystal orientation ($\Delta H \approx 1.5$ Gauss at 4.2 K). The temperature dependence of the spin susceptibility (deduced by double integration of the resonance signal) is shown in Figure 2. A Curie-Weiss dependence is found at low temperature ($\theta \approx -5$ K) indicating the presence of antiferromagnetic interactions while $\chi^{-1}(T)$ saturates at higher temperature. For $[(C_6H_5)_4P]_2[C_{60}][I]_x$, we obtained at 4.2 K, the following values: $g_x = g_y = 1.9970$, $g_z = 1.9998$. Note that again, the (a,b) plane degeneracy is imposed by the crystal symmetry. The trace of the g tensor leads to an equivalent isotropic value g = 1.9979 [13] in complete agreement with the original value of Wudl et al. (1.9991 ± 0.0002 at 300 K).[5a]

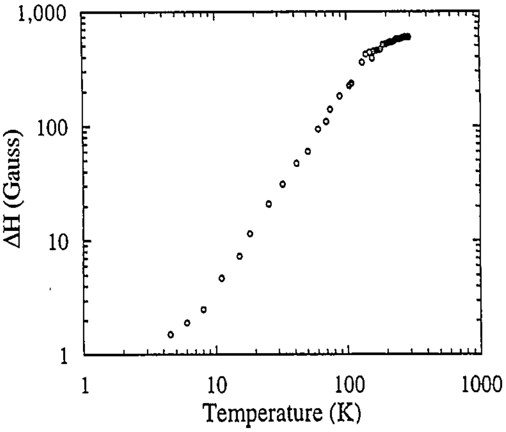

Fig. 1 Variation of the ESR signal linewidth with temperature.

Magnetic susceptibility measurements were performed on a SQUID susceptometer from room temperature down to 4 .2 K under various magnetic fields. Sample holder contribution as well as diamagnetic susceptibility[14] ($\chi_{dia} = -1070\ 10^{-6}$ emu.mole^{-1}) were substracted from the experimental data. At 1 kG, the susceptibility shows a strong deviation from the expected Curie or Curie Weiss law for isolated spins. This deviation progressively diminished at 10 and 30 kG. Consequently,

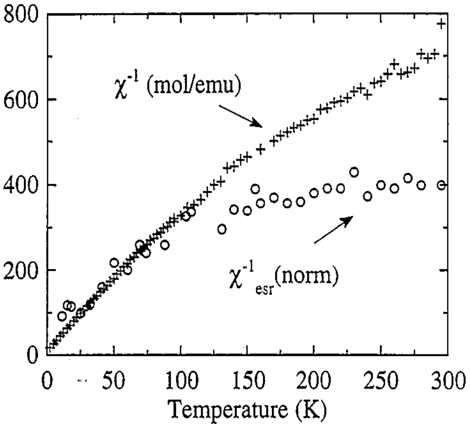

Fig. 2 Plot of the reciprocal spin magnetic susceptibility (χ^{-1}_{esr}(norm)) and the reciprocal bulk molar magnetic susceptibility (χ^{-1} (mol/emu), measured at 50 kGauss) versus temperature. The spin susceptibility curve was normalized to fit the low temperature part of the bulk (SQUID) susceptibility (see text).

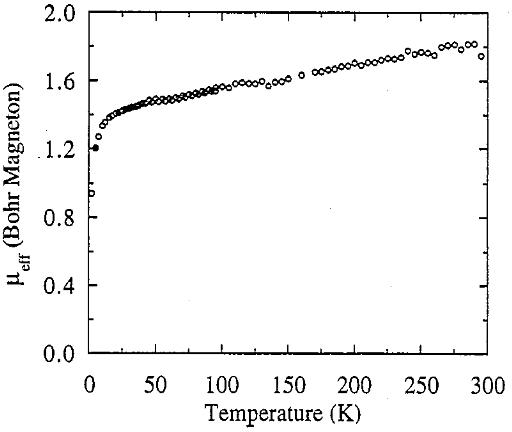

Fig. 3 Magnetic moment ($\mu_{eff} = 2.83\,(\chi.T)^{1/2}$) as a function of temperature at 50 kGauss.

we assumed it to be due to ferromagnetic impurities. At 50 kG, the susceptibility follows an almost normal behaviour. The variation of the inverse susceptibility with temperature (Figure 2) is remarkably similar to the one obtained from ESR but with a less marked saturation at high temperature. Note that the ESR curve has been normalized to fit the low temperature part of the SQUID curve. At higher temperatures the linewidth is very large ($\Delta H \approx 600$ Gauss) and impairs an accurate determination of the signal intensity. Both curves suggest a Curie-Weiss behaviour with a negative θ of a few kelvins, with the possibility of some added (activated) contribution at high temperature ($T > 150$ K). $\chi.T$ and μ_{eff} both tend to the expected value (μ_{eff} (spin only) = 1.73 μ_B, $\chi.T = 0.37$) for isolated spins 1/2 at room temperature (see Figure 3).

The structure resolution and the chemical analysis show full occupancy of the iodide site leading to the simple charged formulation, $[(C_6H_5)_4P^+]_2[C_{70}^-][I^-]$. Thus, the only magnetic species present are the $C_{70}^{\bullet-}$ radicals, well apart from each other. This contrasts with the situation in (**1**) where some doubts remain about the possibility of residual spin density on the phosphonium cations.[6]

Reed et al.[15] obtained expected values of $\mu_{eff} \approx 1.80\ \mu_B$ for diluted spins 1/2 in $[PPN^+][C_{60}^-][PhCN][THF]$ ($PPN = [(C_6H_5)_3P{=}]_2N^+$) and $[PPN^+]_3[C_{60}^{3-}]\cdot 2CH_3CN$. Anomalous effects have been observed in $[(C_6H_5)_4P]_3[C_{60}][Cl]_2$ and tentatively explained in term of a singlet-triplet activation.[16] However, in that case, some doubts remain about the exact stoichiometry (which impair the treatment of the magnetic data) as pointed out in the original article.[5a] Further studies on the solid state, particularly magnetic, properties of the *well-defined* (i.e. *structurally characterized*) title compound and (**1**) are underway in our laboratory.

In conclusion, we were able to grow single crystals of $[(C_6H_5)_4P^+]_2[C_{70}^-][I^-]$ and determine the principal values of the g tensor at 4.2 K for the radicals $C_{70}^{\bullet-}$ and $C_{60}^{\bullet-}$.

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10. $[(C_6H_5)_4P^+]_2[C_{70}^-][I^-]$: formula $C_{118}H_{40}IP_2$ (FW = 1646.5), crystal size 0.28 x 0.25 x 0.22 mm^3, space group P4/nnc, a = 12.682(4) Å, c = 21.660(3) Å, V = 3484(1) Å^3, Z = 2. Room temperature, Mo Kα radiation (λ = 0.71073 Å), 1910 independent reflections collected, 694 with $I > 3\sigma(I)$. The iodide and $(C_6H_5)_4P^+$ ions were found to occupy, respectively, the sites (0,0,0) and (0, 1/2, 1/4) and were refined anisotropically. A rigid model of the C_{70} molecule (obtained from a minimized CHEM3D model) with its center at (0,0,1/2) and its long axis colinear with the lattice 4-fold axis was included in the scale factor calculation. The resulting R value was 0.21. If the model was rotated by 45 ° along c (both orientations place one of the C_{70} 2-fold axis on a lattice 2-fold axis in the (a, b) plane), the R factor jumped to 0.48.
11. An elegant description of the crystal packing has been made for the isostructural salt $[(C_6H_5)_4P^+]_2[C_{60}^-][Cl^-]$: ref 7.
12. Elemental analysis: obs. (calcd for $C_{118}H_{40}IP_2$): C 85.28, 85.06 (86.08), H 2.41, 2.42 (2.45), P 3.69 (3.76), I 6.08, 5.87 (7.71).
13. The g value we previously reported (ref 5, g =2.001 ± 0.0015) was determined on a powdered sample at room temperature. The value at 120 K was 1.998.
14. The diamagnetic susceptibility of C_{70}, - 496 10^{-6} emu.mole^{-1} was calculated from the experimental gram susceptibility, - 0.59 ± 10^{-6}: R.S. Ruoff, D. Beach, J. Cuomo, T. McGuire, R.L. Whetten, F. Diederich, *J. Phys. Chem.* **1991**, 95, 3457-3459.
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