

A Stable Fullerene Charge-transfer Complex in the Solid State: HMTTEF-C₆₀

T. Pradeep,^{a†} K. K. Singh,^b A. P. B. Sinha^c and D. E. Morris^b

^a Lawrence Berkeley Laboratory, Berkeley, CA 94720, USA

^b Morris Research Inc., 1918 University Avenue, Berkeley, CA 94704, USA

^c Department of Material Science, University of California, Berkeley, CA 94720, USA

The first stable complex of C₆₀ with an organic electron donor has been synthesised; the complex, having C₆₀ and HMTTEF (hexamethylenetetrafulvalene) in a 1 : 1 ratio, is black, insulating, weakly magnetic, insoluble in most solvents and stable in air.

Conductivity¹ and superconductivity² in alkali-doped C₆₀ has spurred intense activity and the existence of a conducting charge-transfer complex of C₆₀ has been considered plausible. A number of organic donor-C₆₀ complexes have been studied in solution,³ essentially by absorption and fluorescence spectroscopy in order to understand the nature of the charge-transfer interaction. However, the only compound obtained in the solid state thus far is the soft ferromagnet, TDAE-C₆₀, which is unstable in air;⁴ (TDAE = tetrakisdimethylaminoethylene). Here we report the synthesis and characterisation of a new charge-transfer complex of C₆₀ with hexamethylenetetrafulvalene (HMTTEF), one of the most powerful organic donors and a constituent of many organic conductors. This is the first report of a solid-state complex of C₆₀ which is stable in air. Elemental analysis shows that the compound is a 1 : 1 complex of C₆₀ with HMTTEF. The compound is insulating and weakly magnetic.

The compound was prepared by the reaction of HMTTEF with C₆₀ in toluene in an atmosphere of argon. The solution was heated to boiling with continuous magnetic stirring. After one hour of reaction, a black precipitate was obtained and the solution turned colourless. The product was washed with toluene and dried *in vacuo*. Care was taken to avoid exposure to atmosphere during synthesis. However, the product does not seem to be sensitive to atmosphere as the powder diffractogram was essentially unchanged after two days of exposure to the laboratory atmosphere. Synthesis was then repeated in ambient atmosphere and the product was found to be the same. The X-ray powder diffractogram of the product does not contain any lines due to the reactants, indicating that a new compound has been formed. Carbon and hydrogen analysis (C, 62.2% H, 0.9%) indicates a molecular formula of C₇₂H₁₂Te₄ for the compound (assuming the same tel-

lurium : hydrogen ratio as in the reactant). This corresponds to a 1 : 1 addition complex between C₆₀ and HMTTEF.

X-Ray diffraction analysis of the sample was carried out on a Scintag PAD-V diffractometer using Cu-Kα radiation and an intrinsic Ge solid state detector with 200 eV energy resolution. The X-ray diffraction patterns of C₆₀, HMTTEF and the new compound are shown in Fig. 1. The diffractogram of the complex [Fig. 1(b)] is markedly different from those of the starting materials. None of the lines of the starting materials appears in the product. By fitting the positions of 30 diffraction peaks using the TREOR program,⁵ a trial unit cell has been obtained, with parameters: monoclinic, $a = 21.072 \pm 0.0165$, $b = 14.165 \pm 0.013$ and $c = 12.349 \pm 0.006$ Å with $\beta = 99.919 \pm 0.07^\circ$, $V = 3631.2$ Å³ and $Z = 4$. Further structural analysis is in progress.

The FTIR spectrum of the compound shown in Fig. 2 is essentially a superposition of the spectra of C₆₀ and HMTTEF. The spectrum shows small frequency shifts (4 cm⁻¹ or less), as is expected of an intermolecular complex with small charge transfer.

Although the original objective was to obtain an organic conductor, the material was found to be insulating with a room temperature two probe resistance of >20 MΩ. The absence of conductivity may be a consequence of the weak coupling between adjacent C₆₀ units separated by HMTTEF and/or insufficient charge-transfer.

HMTTEF-C₆₀ exhibits only weak magnetism. The magnetic susceptibility was investigated using a Quantum Design SQUID magnetometer over the temperature range 5–200 K. The susceptibility was found to be of the order of 10⁻⁶ emu g⁻¹ (conversion factor for SI units is, $4\pi \times 10^{-3}$ m³ kg⁻¹).

In conclusion, a new charge-transfer complex of C₆₀ with HMTTEF has been synthesised, which is weakly magnetic and

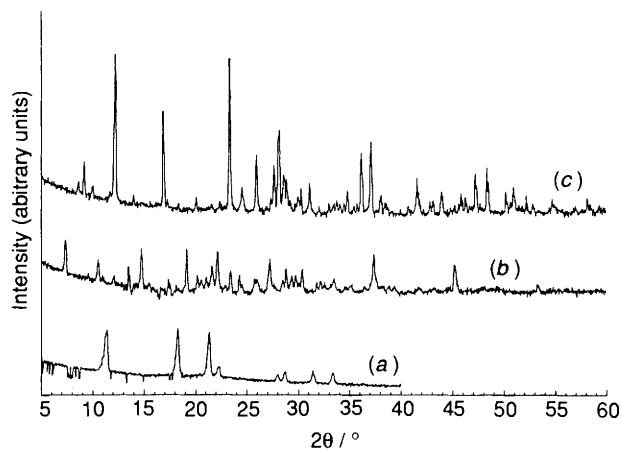


Fig. 1 X-Ray diffraction patterns of (a) C₆₀, (b) C₆₀-HMTTEF and (c) HMTTEF. See the appearance of new diffraction peaks at 2θ values of 7.57 and 19.10° in the complex (b). From the absence of any of the peaks seen in (a) or (c), we conclude that (b) is a single-phase sample.

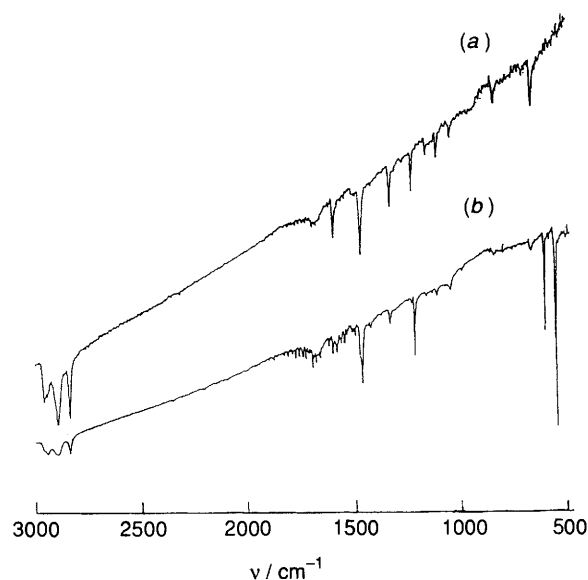


Fig. 2 The FTIR spectra of (a) HMTTEF and (b) C₆₀-HMTTEF. The spectrum of the complex is nearly a superposition of the spectra of the components, but with small frequency shifts (<4 cm⁻¹), see text.

† On leave from CSIR Centre of Excellence in Chemistry, Indian Institute of Science, Bangalore 560 012, India.

insulating. The extent of charge transfer is small. It may be possible to modify the electrical transport properties of this material by doping it with other electron donors.

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