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New Metallic C_{60} Compound: $Na_xC_{60}(THF)_y$

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Despite the great interest aroused by the first discovery of the superconductivity of K_3C_{60},[1] the recent development of conducting C_{60} materials seems to be somewhat stagnant. The obstacle for progress may be the extreme air sensitivity of the C_{60} radical salts, which prevents unambiguous characterization of these systems. To facilitate further progress, well-defined new conducting C_{60} materials are highly desirable. To our knowledge, except for the solution-phase syntheses of M_3C_{60} (M = K, Rb) by the Argonne group[2,3] and the preliminary proposal of the Rice University group,[4] all the metallic (or superconducting) C_{60} compounds hitherto reported were prepared by doping the alkali-metal atoms in a dry process. A novel synthetic route to alkali-metal–C_{60} compounds in liquid ammonia media was developed very recently.[5]

We have tried to grow single crystals of conducting C_{60} compounds in organic solvents in the homogeneous phase. From the viewpoint of electron transport phenomena, solid-state $C_{60}^{\bullet-}$ radical anions stabilized by appropriate cations have drawn attention. Wudl reported the electrochemical formation of $[(C_6H_5)_4P]_3(C_{60})Cl_2$[6] as a microcrystalline powder. Recently the X-ray crystal structure of the analogue $[(C_6H_5)_4P]_2(C_{60})[I]_x$[7] was reported. Transition-metal derivatives of $C_{60}^{\bullet-}$, e.g., $Cr(TPP)^+C_{60}^{\bullet-}$ [8] and $[Ru(bpy)_3]^+C_{60}^{\bullet-}$,[9] were also reported; the latter was found to be semiconducting. Bard reported electrochemical formation of $C_{60}^{\bullet-}$ films stabilized by *n*-butylammonium cation,[10] and Chabre demonstrated intercalation of lithium into solid C_{60}.[11] After we succeeded in obtaining $PPN^+C_{60}^{\bullet-}$ [12] (PPN^+ = bis(triphenylphosphoranylidene)ammonium cation, $N[P(C_6H_5)_3]_2^+$) we tried to get C_{60} compounds doped with alkali metals in the solution phase. We found that large rod-shaped crystals (ca. 4.0 mm × 0.5 mm × 0.5 mm) of a novel Na salt of C_{60} could be grown on a platinum electrode by an electrocrystallization method. All solvents were of HPLC grade and were distilled under nitrogen prior to use. Under an inert atmosphere in a H cell with a Pt electrode, a THF solution (5 mL) of $NaB(C_6H_5)_4$ (40 mg) as supporting electrolyte was added dropwise to a chlorobenzene solution (15 mL) of pure C_{60} (7 mg), and then the solution was electrolyzed at constant current (0.2 μA) for ca. 1 week. Black, shiny single crystals $Na_xC_{60}(THF)_y$ were harvested on the cathode.

Since the crystals were very unstable in the atmosphere, we examined X-ray photographs of the single crystals sealed in glass capillaries. Oscillation and Weissenberg photographs revealed that the Na and K salts are isostructural to each other and have hexagonal unit cells. The lattice constants determined by a four-circle diffractometer are as follows: Na salt, a = 15.331(4) Å, c = 9.965(4) Å, V = 2028(1) Å^3; K salt, a = 15.386(4) Å, c = 9.993(6) Å, V = 2049(1) Å^3. At first sight, the X-ray powder patterns of the Na and K salts seemed to fairly resemble those of the well-known superconducting salts of M_3C_{60} (M = K, Rb, ...) with fcc lattices.[13] Therefore, despite the determination of hexagonal unit cells by the four-circle diffractometer and the observation of hexagonal symmetry by the Weissenberg photographs, the possibility of cubic unit cells was carefully reexamined. On the basis of the 2θ values of 10 strong Bragg reflections obtained by the four-circle diffractometer, we tried to redetermine the lattice constants by using the program for indexing the X-ray powder patterns. A solution was not obtained if the cubic unit cell was assumed for the compound. However, all the reflection spots could be indexed by adopting the hexagonal unit cell. The obtained lattice constants of Na and K salts were almost the same as those determined by the X-ray four-circle diffractometer. Thus, the possibility of cubic unit cells was ruled out and the crystals of Na and K salts obtained in the present study were concluded to be new alkali-metal complexes of C_{60}.

The elemental analyses were repeated three times, which indicated invariably the existence of H atoms: C (87.58, 92.45, 91.60), H (2.58, 2.77, 1.53), N (0, 0, 0). In order to clarify the origin of H, the solid-state ^{1}H and ^{13}C NMR spectra of the Na salt were examined. The ^{1}H NMR spectra showed that the signals of ^{1}H originated from THF molecules, and the ^{13}C spectra revealed the existence of three different types of C atoms: one peak (δ = 158.0 ppm) comes from C atoms of C_{60}, and the other two peaks (δ = 81.7 ppm and 41.0 ppm) are those of C atoms of THF. A singlet ^{23}Na NMR signal (δ = −6.9 ppm) was also observed. Consequently, the chemical species constructing the crystal are Na, C_{60}, and THF. The ICP analyses showed the Na content to be 1.01%. The density of the crystals was measured by the floating method, where a mixed solution of tetrachloroethane

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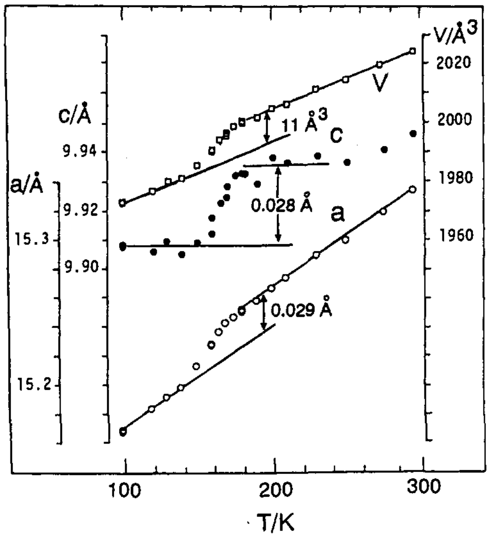

Figure 1. Temperature dependence of the lattice constants of Na_xC_{60}-$(THF)_y$.

and dibromoethane was used. The obtained densities are 1.83 ± 0.05 g/cm^3 (Na salt) and 1.91 ± 0.04 g/cm^3 (K salt). Using these densities and the unit cell volumes determined by X-ray experiments, the total weights of the molecules involved in the unit cells were calculated as 2235 g/mol (Na salt) and 2363 g/mol (K salt). The weight percent of H of Na salt (2.7–1.5%) indicates that the number of hydrogen atoms in the unit cell is 60–34. That is, the number of THF molecules is 7–4. The Na content (1.01%) shows the number of Na atom to be about 1 (=22.6/23). Since the molecular weight of $Na(THF)_n$ (n = 4–7) is 527–311, the unit cell must contain more than two C_{60} molecules. The number of C_{60} molecules in the unit cell was determined to be 2.37–2.67. Thus, we have to conclude that the composition of the Na salt should be described at present as $Na_{0.39\pm0.03}C_{60}$-$(THF)_{2.2\pm0.7}$. The large variation of the elemental analyses, in particular, the H content (the number of THF molecules), may be due partly to the air- and/or moisture-sensitive nature of the compounds.

The lattice constants a and c were determined in the temperature range 100–300 K by the four-circle diffractometer. The phase transition was clearly observed around 170 K, shown in Figure 1. The lattice dimensions were shortened by about 0.029 Å ($\|_a$) and 0.028 Å ($\|_c$). The cell volume was reduced by 11 Å^3. The thermal expansion coefficients, $\alpha(\|_a)$, $\alpha(\|_c)$, and β (V), above and below the transition temperature are almost the same: $\alpha(\|_a) = 4.6 \times 10^{-5}$/deg, $\alpha(\|_c) < 1.4 \times 10^{-5}$/deg, $\beta = 9.9 \times 10^{-5}$/deg. The oscillation photographs taken at 100 K showed the diffuse streaks along the direction perpendicular to the c axis, indicating that the positional disorder remains at low temperature.

The ESR spectrum demonstrated a C_{60} anion radical signal, which resembles that of the PPN^+ salt of $C_{60}^{\bullet-}$.[12] ESR signals composed of a broad signal and a narrower "spike" are also similar to other $Na(crown)^+$ and $CoCp_2^+$ salts of C_{60} radical anion.[14] The temperature dependence of the ESR spectra of Na_xC_{60}-$(THF)_y$ gave a clear indication of the phase transition around 170 K.[15] The phase transition associated with the anomaly of magnetic susceptibility was also observed in SQUID measurements.

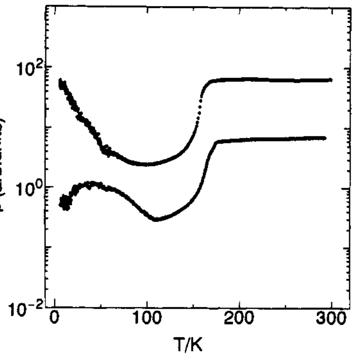

Figure 2. Typical resistivity behavior of two different samples of Na_xC_{60}-$(THF)_y$ measured along the c axis.

The lattice spacing c of 9.93 Å at room temperature indicating the direct C_{60}–C_{60} interactions and the partial oxidation state of C_{60} suggests the metallic nature of the system. The dc electrical resistivity of $Na_xC_{60}(THF)_y$ was measured by the conventional four-probe method. Four gold wires were bonded to the crystals with gold paint in a "bag" of nitrogen atmosphere. The temperature dependence of the resistivity was strongly influenced by the deterioration of the crystals. The room-temperature conductivity is about 50 S cm^{-1}. As shown in Figure 2, the resistivity decreased gradually down to 180 K, below which it decreased quite rapidly. This indicates that the transition observed by X-ray diffraction and ESR experiments as well as SQUID measurements is a metal–metal transition. The conductivity around 100 K is greater than 1000 S cm^{-1}, indicating that Na_xC_{60}-$(THF)_y$ is essentially an excellent molecular conductor. The resistivity below 100 K was strongly sample-dependent, for which structural disorder and the deterioration of the crystals was responsible. Most of the crystals exhibited a gradual resistivity increase at low temperature, but they did not lose the high conductivity even at 4.2 K. Few crystals showed a resistivity decrease at low temperature. Thus the measurements were repeatedly done on many crystals, but it was difficult to determine the intrinsic resistivity behavior at low temperature not only because of the sample dependence but also because of the noisy behavior below 70 K. More careful treatment of the crystals will be needed.

In conclusion, $Na_xC_{60}(THF)_y$ is the first metallic single-crystal C_{60} compound grown by an electrocrystallization process. The large single crystals obtained in this study will enable precise determination of the physical properties of this new metallic C_{60} compound.

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