Preliminary communication

Fulleride compounds of the transition metals: NaCoC$_{60}$ · 3THF

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Abstract

The fullerene compound C$_{60}$, which exhibits a rather high electron affinity, undergoes an electron transfer reaction with the low-valent cobalt(−I) complex Na[Co(CO)$_4$] to form the black compound NaCoC$_{60}$ · 3THF. The new material is characterized by elemental analyses, by IR, Raman, ^{13}C MAS-NMR and EPR spectroscopy, and by magnetic susceptibility measurements. It appears to contain covalent C$_{60}$-transition metal interactions, and therefore constitutes a new type of bimetallic fulleride compound. © 1997 Elsevier Science S.A.

1. Introduction

One of the most fascinating developments in modern chemistry has been the discovery of new molecular allotropes of carbon such as C$_{60}$ and its higher homologues. [1] The electronic structure and chemistry of C$_{60}$, especially, have been much studied and, consistent with the presence of a triply degenerate LUMO, up to six electrons can be added electrochemically to form the series of anions [C$_{60}$]$^{n-}$ ($n = 1$–6; referred to collectively as fullerides) [6,7]. Similar reductions may be effected utilizing the alkali metals, and fulleride salts M$_n$C$_{60}$ (M = Li, Na, K, Rb; $n = 1$–3) have been isolated and characterized; [4,5] some of these compounds are semiconductors, others metals which, interestingly, also behave as high temperature superconductors ($T_c >$ 30 K [4,5]).

In contrast to the large number of known alkali metal and alkaline earth compounds, fullerides doped with bare transition metal atoms or ions are limited to as yet rather ill-defined compounds of stoichiometries M$_n$C$_{60}$ (M = Pd, Pt), prepared by reaction of C$_{60}$ with zero-valent metal complexes of dibenzylideneacetone [8–12], and Eu$_n$C$_{60}$, prepared by reaction of C$_{60}$ with solutions of europium metal in liquid ammonia [13]. However, it seems likely that incorporation of transition metals, with

variable numbers of d electrons, should result in the formation of very interesting, possibly quite novel materials, and we now describe a new route, utilizing low valent metal carbonyl complexes and of a probably general nature, to the synthesis of transition metal fullerides.

2. Methods and discussions

Since C$_{60}$ has a high electron affinity (2.6–2.8 eV [1–5]) while carbonylate anions of the types [M$_x$(CO)$_y$]$^{z-}$ (M = transition metal; x, y, z = integers) have sufficiently low ionization potentials that they are generally very good reducing agents [14–16], it was anticipated that reactions of C$_{60}$ with, for instance, Na[Co(CO)$_4$], would involve electron transfer and the concomitant formation of both a fulleride anion and the unstable, 17-electron species Co(CO)$_4$. The latter dimerizes to [Co(CO)$_4$]$_2$ with a second order rate constant of 4×10^8 M^{-1} sec^{-1} [17], and the overall reaction could be as in Eq. (1). Any orange dimer formed would be readily identified on the basis of its carbonyl stretching bands in the IR spectrum.
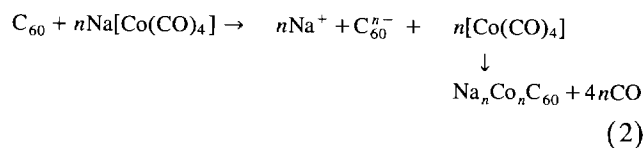
$$C_{60} + n\text{Na[Co(CO)}_4] \rightarrow \text{Na}_n\text{C}_{60} + n\text{Co(CO)}_4$$
$$\downarrow$$
$$0.5n[\text{Co(CO)}_4]_2 \qquad (1)$$
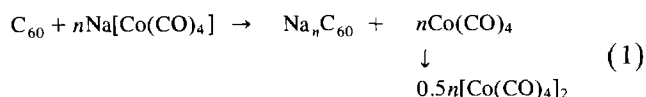
On the other hand, loss of CO and incorporation of the cobalt atoms into the fulleride lattice might also

occur, giving rise to a novel type of cobalt-containing fulleride as in Eq. (2):

$$C_{60} + nNa[Co(CO)_4] \rightarrow \quad nNa^+ + C_{60}^{n-} + \quad n[Co(CO)_4]$$
$$\downarrow$$
$$Na_nCo_nC_{60} + 4nCO$$

(2)

We have found that refluxing a suspension of C_{60} with a THF solution of $Na[Co(CO)_4]$ [18] results in the formation of a black precipitate and a dark solution which contains no $[Co(CO)_4]_2$ (IR). Apparent intermediates with ν_{CO} at 1992, 1966 and 1920 cm^{-1} were observed temporarily, but the final solution exhibited no carbonyl stretching bands. The solid was characterized by elemental and thermogravimetric analyses, which indicate that the molecular formula of the compound is $NaCoC_{60} \cdot 3THF$. [2]

The IR spectrum of $NaCoC_{60} \cdot 3THF$ (Nujol mull) exhibits bands at 1428, 1181, 575 and 526 cm^{-1}, slightly broadened but similar in frequency to bands in the spectra of C_{60} and many C_{60}-containing materials [5]. Weak bands at 2970, 2844, 1067, 905, and 851 cm^{-1} correspond to THF absorbances. The FT Raman spectrum of solid $NaCoC_{60} \cdot 3THF$ is completely reproducible from one sample to the next, and is shown in Fig. 1b, where it is compared with the Raman spectrum of C_{60} (Fig. 1a). Since the spectra were obtained under identical conditions, the observed changes attest to significant changes in the nature of the bonding on going from C_{60} to $NaCoC_{60} \cdot 3THF$.

The predicted 10 Raman active vibrational modes [5] of the C_{60} molecule have been observed both in solid state films and powders [5], and it has been further established that η^2-binding of C_{60} as an olefin in a coordination compound [19–21] results in activation of previously silent modes and splitting of degenerate modes as a result of external influences which lower the symmetry of the molecule. There is a striking resem-

blance between the Raman spectrum of $NaCoC_{60} \cdot 3THF$ and those reported by Chase and Fagan [21] for a series of complexes of nickel, palladium and platinum of the type $M(\eta^2-C_{60})L_2$ (L = tertiary phosphine), for which reduction of the microsymmetry of C_{60} from I_h to C_{2v} resulted in many lower frequency normal modes becoming Raman active.

Raman spectra of alkali metal fullerides [5] lack the rich detail present in Fig. 1b. In these materials, alkali metal ions are accommodated in the interstitial sites of a C_{60}^{n-} crystal lattice and there are no covalent interactions between metal ions and C_{60} molecules. Although the latter undergo a weak Jahn–Teller distortion upon reduction [5], the overall effects on the vibrational spectra are minimal. Interestingly, the doping process does result in frequency shifts which are dependent only on the charge on the fulleride ion [5]; the narrow, strong band of the $A_g(2)$ pentagonal pinch mode (1467 cm^{-1} in C_{60}) [1–5] has been shown to shift to lower frequency by $\sim$ 6–7 cm^{-1} per electron added to C_{60}, independent of the nature of the alkali metal ion. On this basis, the 8 cm^{-1} shift observed for $NaCoC_{60} \cdot 3THF$ represents approximately a one electron reduction of C_{60}, consistent with the formulation. In view of the effect that metal coordination has on the Raman spectrum of C_{60}, it seems that the cobalt atoms present in $NaCoC_{60} \cdot 3THF$ are not simply accommodated as dopant species in the C_{60} lattice, but are in fact covalently bonded to the C_{60}. A weak band, attributable to a CH stretching mode of coordinated THF, was also observed at 1977 cm^{-1}. However, THF is a weak scatterer and all other THF modes are obscured by the fulleride bands.
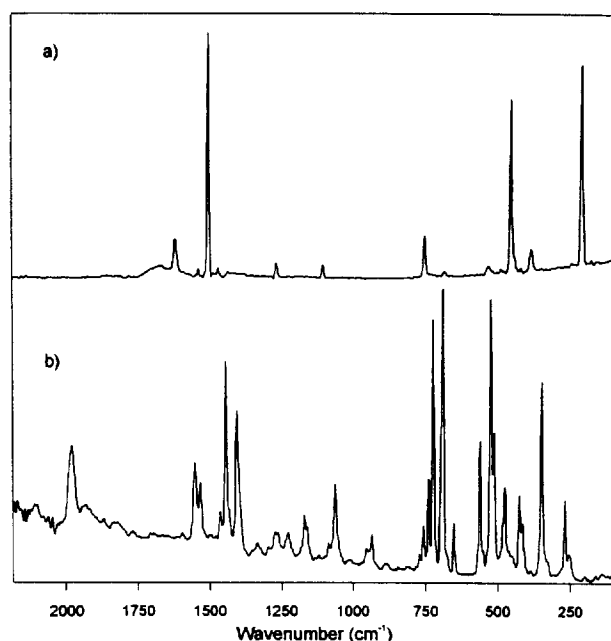
Fig. 1. Raman spectra of (a) C_{60} and (b) $NaCoC_{60} \cdot 3THF$.

Consistent with this interpretation of the Raman data, a ^{13}C MAS-NMR spectrum of $NaCoC_{60} \cdot 3THF$ exhibited, in addition to THF resonances, resonances at δ 162(w), 149(w), 145(s) and 137(w), quite different from the spectrum of C_{60} (δ 143). While observation of ^{13}C resonances may seem incompatible with the paramagnetism of the material (see below), in fact ^{13}C NMR spectra have been reported for several paramagnetic alkali metal fullerides.

Useful insight into the electronic structure of $NaCoC_{60} \cdot 3THF$ has been obtained from magnetic susceptibility data and EPR and near IR spectroscopic measurements. The solid material exhibits an EPR resonance at $g = 1.999$, the peak-to-peak width varying from 10 G (at 90 K) to 40 G (at 298 K), rather similar to the EPR spectrum of C_{60}^{-} although g values for the C_{60}^{2-} and C_{60}^{3-} ions are comparable [22,23]. The near IR spectrum in DMSO (the only solvent for the material found to date) exhibits a band at 1074 nm, in the region where C_{60}^{-} (but not C_{60} or C_{60}^{2-} absorb [5].

The magnetic susceptibility of the solid was measured over the temperature range 4–310 K, and a plot of magnetic moment vs. temperature is shown in Fig. 2. The room temperature magnetic moment per mole of $NaCoC_{60} \cdot 3THF$ is ~ 3 BM, corresponding to two unpaired electrons, and the data seem to imply the presence of two paramagnetic centres undergoing a very weak antiferromagnetic exchange. It is thus tempting to infer a degree of magnetic coupling between pairs of doublet ($S = 1/2$) species such as Co(0) atoms, C_{60}^{-} anions and/or CoC_{60} molecules.

We can only speculate as yet about the structure, as crystal growing experiments have to date yielded only poorly diffracting materials. A polymeric lattice structure containing units of the type $[-(\eta^3\text{-}C_{60})(\mu\text{-Co})(\eta^4\text{-}C_{60})-]_n$ (allylic and diene modes of coordination, respectively) would result in 16-electron cobalt complexes, but the magnetic and EPR spectroscopic properties of $NaCoC_{60} \cdot 3THF$, discussed above, would seem to require a weaker, much more novel type of metal–ligand interaction. A polymeric structure containing direct fullerene C–C bonds, as occurs with C_{60} itself ([5],

Chap. 11), may also be possible. As mentioned above, the sodium content of the material is somewhat low and, while the analyses may well be in error, the formulation $Na_{0.5}CoC_{60} \cdot 3THF$, with fullerene C–C bonds is possible and could contribute to the lowering of the symmetry which gives rise to the complex Raman spectrum. On the other hand, the solubility in DMSO and the observation of a fulleride spectrum in that solvent, as well as the formation of an oxidation product (see below), argue against this possibility. While little chemistry of $NaCoC_{60} \cdot 3THF$ has yet been studied, the material is somewhat air-sensitive and exposure to air results in both appearance of a resonance attributable to C_{60} at δ 143 in the ^{13}C MAS-NMR spectrum and in complete loss of the EPR signal. Extraction of some C_{60} with toluene then becomes possible, consistent with oxidation of the C_{60}^{-} ion, but detailed Raman spectra of the fully oxidized material cannot be obtained because of intense fluorescence in the frequency range 5900–9300 cm^{-1} (absolute, not Raman shifted frequencies). It is anticipated that air oxidation of $NaCoC_{60} \cdot 3THF$ would result in the formation of CoO, and we note that Co(II) ions in oxide lattices fluoresce in the near infrared [24]. Prior to the onset of strong fluorescence, shifting of the $A_g(2)$ pentagonal pinch mode from 1457 to 1467 cm^{-1} occurs, consistent with oxidation to C_{60}. Attempts to better characterize this system chemically and crystallographically continue. We are also investigating the reactions of C_{60} with other simple and complex carbonylate anions, finding, for instance, that while $Na_2[Fe(CO)_4]$ seems to form an analogous iron fulleride compound, $Na[Mn(CO)_5]$ and $Na[CpFe(CO)_2]$ take part in simple electron transfer processes to form the corresponding metal–metal bonded dimers $[Mn(CO)_5]_2$ and $[CpFe(CO)_2]_2$ and, presumably, NaC_{60} [M. Bengough, L. French, E. Jandciu, M.C. Baird, unpublished results].

Fig. 2. Variation of magnetic moment of $NaCoC_{60} \cdot 3THF$ with temperature.

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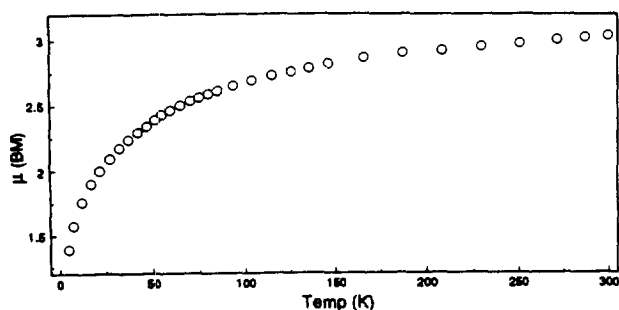[4] H. Ehrenreich, F. Spaepen (Eds.), Solid state physics, Fullerenes, Vol. 48, Academic Press, New York, 1994.

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