

# Solid (dibenzo-18-crown-6)K<sub>60</sub>: significant enhanced air-stability and appearance of a strong <sup>13</sup>C NMR signal of C<sub>60</sub><sup>−</sup> below 200 K with an unexpected negative chemical shift

Jian Chen,<sup>a,b</sup> Fui-Fang Cai,<sup>a</sup> Qian-Fen Shao,<sup>c</sup> Zu-En Huang<sup>\*a</sup> and Shi-Ming Chen<sup>c</sup>

<sup>a</sup> Department of Chemistry, Fudan University, Shanghai 200433, PR China

<sup>b</sup> Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, PR China

<sup>c</sup> Research Center of Analysis and Measurement, Fudan University, Shanghai 200433, PR China

Two novel properties, which arise primarily from intermolecular interactions between two aryl rings of the crown ether and neighbouring C<sub>60</sub><sup>−</sup>, are found in solid (dibenzo-18-crown-6)K<sub>60</sub>, viz. significantly enhanced air-stability and appearance of a strong <sup>13</sup>C NMR signal of C<sub>60</sub><sup>−</sup> below 200 K with an unexpectedly negative chemical shift.

Recent interest in controlling the electronic properties of alkali-metal [60]fullerides (A<sub>n</sub>C<sub>60</sub>) via chemical approaches has been growing rapidly.<sup>1</sup> It was reported that coordination of NH<sub>3</sub> to an A<sup>+</sup> ion has a remarkable effect on the superconductivity of A<sub>3</sub>C<sub>60</sub>.<sup>1</sup> We recently discovered that solvating the K<sup>+</sup> ion by thf in K(thf)<sub>x</sub>C<sub>60</sub> solid (0 < x < 1) can dramatically change the electronic state of C<sub>60</sub><sup>−</sup>.<sup>2</sup> In this communication, we report the first example that both air-stability and solid-state physical properties of alkali-metal [60]fulleride salts can be altered dramatically and simultaneously by employing simple supramolecular chemistry.

(Dibenzo-18-crown-6)K<sub>60</sub> **1**<sup>†</sup> was prepared according to our previous method:<sup>3–6</sup> under argon, a combination of potassium (16 mg, 0.41 mmol), C<sub>60</sub> (>99.5%, 295 mg, 0.41 mmol), dibenzo-18-crown-6 (148 mg, 0.41 mmol) and 1-methylnaphthalene (0.5 ml) was stirred in 60 ml thf for ca. 2 h. After centrifugation, the black microcrystalline product was obtained by layering hexane over the dark red–purple solution. The solid was washed with benzene and hexane and dried *in vacuo* to produce **1** in 87% yield. Anal. Calc. for C<sub>80</sub>H<sub>24</sub>O<sub>6</sub>K **1**: C, 85.79; H, 2.14. Found: C, 85.01; H, 2.23%.

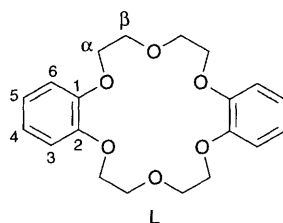
A broad EPR signal (g = 1.9997, ΔH = 40.0 G) is observed in solid **1** at 300 K. In addition, a minor, sharp signal (g = 2.0005, ΔH = 3.5 G) is superimposed on the broad signal and is estimated to be <5% of overall signal intensity. According to previous studies on Na<sup>+</sup>(crown) and K<sup>+</sup>(thf) salts of C<sub>60</sub><sup>−</sup>,<sup>2,7</sup> the broad and sharp signals in **1** can be assigned to the <sup>2</sup>E and <sup>2</sup>A states of C<sub>60</sub><sup>−</sup> respectively.

Compound **1** is identified unambiguously by <sup>13</sup>C NMR spectroscopy (Table 1, Figs. 1 and 2). A single peak at δ 188 at 295 K is characteristic of C<sub>60</sub><sup>−</sup> species<sup>2–4,6,8,9</sup> and no C<sub>60</sub> (δ 143) or C<sub>60</sub><sup>2−</sup> (δ 183,<sup>4</sup> 184<sup>10</sup>) signals were detected [Figs. 1(c), 2(a)], indicating that disproportionation reactions such as 2C<sub>60</sub><sup>−</sup> → C<sub>60</sub> + C<sub>60</sub><sup>2−</sup> did not occur. It is particularly intriguing that there are marked down-field shifts for C3/C6 (Δδ 37.5 ppm) and C4/C5 (Δδ 33.4 ppm) of the crown ether aryl rings in solid **1** compared with its solution (Table 1). On the basis of the usual conformation of A<sup>+</sup> (dibenzo-18-crown-6),<sup>11</sup> we propose that the extraordinary large down-field shifts in C3/C6 and C4/C5 originate from intermolecular van der Waals interactions between two aryl rings of crown ether and the neighbouring paramagnetic C<sub>60</sub><sup>−</sup>. Such intermolecular interactions, which might be similar in some aspects to those found in [(η<sup>2</sup>-C<sub>60</sub>)Ir(CO)Cl{PhCH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>PPh<sub>2</sub>}<sub>2</sub>] and [(3,4-dimethoxyphenyl)phenylmethano][60]fullerene,<sup>12,13</sup> are supposed to be the key structural factors responsible for the novel properties of solid **1** as described below. The relatively narrower linewidths of the <sup>13</sup>C NMR signals for C1/C2 [compared to C3/C6 and C4/C5, Fig. 1(a), (b)], combined with little change in shift (relative to solution), suggests that no substantial

**Table 1** Room-temperature <sup>13</sup>C NMR data of **1** and related compounds

Compound	Measurement conditions	Chemical shift (δ)					C <sub>60</sub> <sup>−</sup> linewidth (ppm)
		C1/C2	C3/C6	C4/C5	C <sub>α</sub>	C <sub>β</sub>	
L–KSCN <sup>a</sup>	CDCl <sub>3</sub> –(CD <sub>3</sub> ) <sub>2</sub> SO (1 : 1)	148.0	112.7	120.7	67.9	69.2	
L <sup>b</sup>	CPMAS	147.9	112.6	120.8	66.1	70.2	
<b>1</b> <sup>b</sup>	thf–[ <sup>2</sup> H <sub>8</sub> ]thf (4 : 1)	147.5	112.7	122.0	<sup>c</sup>	69.1	187.9 (2.1)
<b>1</b> <sup>b</sup>	solid-state, static	<sup>d</sup>	<sup>d</sup>	<sup>d</sup>	<sup>d</sup>	<sup>d</sup>	188.0 (17.9)
<b>1</b> <sup>b</sup>	MAS	147.8	150.2	155.4	<sup>d</sup>	<sup>d</sup>	188.0 (2.2)
<b>1</b> <sup>b</sup>	CPMAS	147.8	150.2	155.4	60.0	73.4	188.0 (2.2)

<sup>a</sup> Ref. 17. <sup>b</sup> This work. <sup>c</sup> Overlap with thf. <sup>d</sup> Difficult to detect due to chemical shift anisotropy.



van der Waals contacts exist between C1/C2 of the crown ether aryl rings and neighbouring  $C_{60}^-$  in solid **1**.

In sharp contrast to solid  $K(thf)C_{60}$ , which begins to decompose within a few minutes upon exposure to dry air, solid **1** is stable in dry air for at least 1 h as demonstrated by both EPR and  $^{13}C$  NMR measurements. The enhanced air-stability of solid **1** can be attributed mainly to intermolecular interactions between the two aryl rings of the crown ether and the neighbouring  $C_{60}^-$ , which blocks attachment of  $O_2$ . As expected from  $^{13}C$  NMR solution data (Table 1), which indicate that no such intermolecular contacts occur in solution, a THF solution of **1** is very air-sensitive. Our findings imply that

supramolecular chemistry can be introduced as a promising strategy to improve air-stability of alkali-metal [60]fulleride salts.

The variable-temperature  $^{13}C$  NMR spectra of solid **1** provide clear evidence for a phase transition at *ca.* 200 K. Unlike any known  $^{13}C$  NMR spectra of other  $C_{60}$ -based materials,<sup>2–6,8–10,14</sup> the low-temperature phase (<200 K) of solid **1** gives rise to a strong, broad  $^{13}C$  signal with an extremely unusual negative chemical shift. At 190 K, a chemical shift  $\delta$  of  $-182$  is observed (linewidth 123 ppm) (Fig. 2). Extensive  $^{13}C$  NMR investigations of solid **1** under various thermal cycling conditions<sup>15</sup> and careful blank tests have shown that this abnormal  $^{13}C$  resonance is an intrinsic property of  $C_{60}^-$  in solid **1** and not an artefact brought about by any possible impurities. Owing to intermolecular interactions between the two aryl rings of the crown ether and neighbouring  $C_{60}^-$ , the  $C_{60}^-$  molecules in solid **1** are more orientationally ordered and magnetically correlated than those in  $K(thf)C_{60}$  at low temperature, as demonstrated by variable-temperature (295–200 K)  $^{13}C$  NMR and EPR spectroscopy.<sup>15,16</sup> Although the exact details remain unclear at present, this unexpected phase transition might be associated with the magnetic ordering of spins on  $C_{60}^-$  molecules below 200 K. Further studies aimed at understanding the unusual origin of this puzzling phase transition are under way.

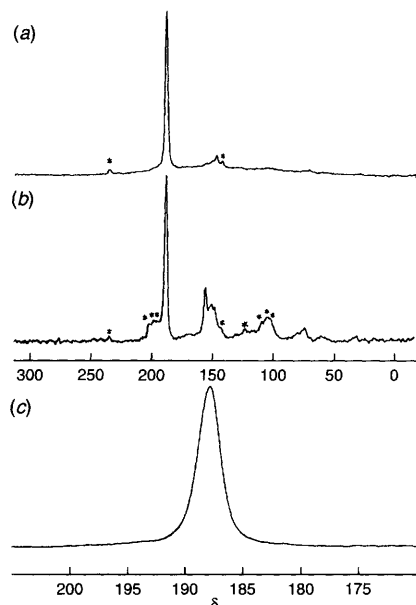
### Footnote

† Reed *et al.* have synthesized and characterized an analogous compound  $[Na(dibenzo-18-crown-6)(thf)_2]^+[C_{60}^-] \cdot thf$ .<sup>7</sup> They mentioned that the air stability of the sodium crown ether salt is lower than that of  $[Co(\eta-C_5H_5)_2][C_{60}^-]$ ; the thf solution of the latter is stable for several minutes upon exposure to air. However neither details of air-stability nor  $^{13}C$  NMR spectral measurements were reported for this sodium crown-ether salt, particularly in the solid state.

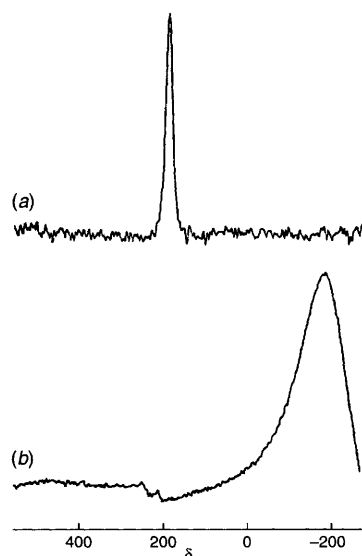
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**Fig. 1** 75 MHz NMR spectrum of **1** at 295 K at a spinning frequency of 3.5 kHz: (a)  $^{13}C$  MAS, (b)  $^{13}C$  CPMAS; \* indicates spinning sideband; (c) the expanded  $^{13}C$  MAS NMR region of  $C_{60}^-$  of **1** at 295 K



**Fig. 2** 75 MHz static variable-temperature  $^{13}C$  NMR spectra of **1** at (a) 295 and (b) 190 K