Solid (dibenzo-18-crown-6)KC_{60}: significant enhanced air-stability and appearance of a strong ^{13}C NMR signal of C_{60}^- below 200 K with an unexpected negative chemical shift

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

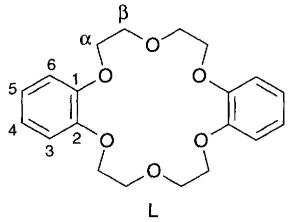
Recent interest in controlling the electronic properties of alkali-metal [60]fullerides (A_nC_{60}) *via* chemical approaches has been growing rapidly.[1] It was reported that coordination of NH_3 to an A^+ ion has a remarkable effect on the superconductivity of A_3C_{60}.[1] We recently discovered that solvating the K^+ ion by thf in $K(thf)_xC_{60}$ solid ($0 < x < 1$) can dramatically change the electronic state of C_{60}^-.[2] 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)KC_{60} **1**† was prepared according to our previous method:[3–6] under argon, a combination of potassium (16 mg, 0.41 mmol), C_{60} (>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 $C_{80}H_{24}O_6K$ **1**: C, 85.79; H, 2.14. Found: C, 85.01; H, 2.23%.

A broad EPR signal ($g = 1.9997$, $\Delta H = 40.0$ G) is observed in solid **1** at 300 K. In addition, a minor, sharp signal ($g = 2.0005$, $\Delta H = 3.5$ G) is superimposed on the broad signal and is estimated to be <5% of overall signal intensity. According to previous studies on Na^+(crown) and K^+(thf) salts of C_{60}^-,[2,7] the broad and sharp signals in **1** can be assigned to the ^2E and ^2A states of C_{60}^- respectively.

Compound **1** is identified unambiguously by ^{13}C NMR spectroscopy (Table 1, Figs. 1 and 2). A single peak at δ 188 at 295 K is characteristic of C_{60}^- species[2–4,6,8,9] and no C_{60} (δ 143) or C_{60}^{2-} (δ 183,[4] 184[10]) signals were detected [Figs. 1(*c*), 2(*a*)], indicating that disproportionation reactions such as $2C_{60}^- \rightarrow C_{60} + C_{60}^{2-}$ 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^+ (dibenzo-18-crown-6),[11] 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_{60}^-. Such intermolecular interactions, which might be similar in some aspects to those found in $[(\eta^2\text{-}C_{60})Ir(CO)Cl\{PhCH_2OC_6H_4CH_2PPh_2\}_2]$ and [(3,4-dimethoxyphenyl)phenylmethano][60]fullerene,[12,13] 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 ^{13}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 ^{13}C NMR data of **1** and related compounds



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Compound	Measurement conditions	Chemical shift (δ)					C_{60}^- linewidth (ppm)
		C1/C2	C3/C6	C4/C5	C_α	C_β	
L–KSCN[a]	$CDCl_3$–$(CD_3)_2SO$ (1 : 1)	148.0	112.7	120.7	67.9	69.2	
L[b]	CPMAS	147.9	112.6	120.8	66.1	70.2	
1[b]	thf–[$^2H_8$]thf (4 : 1)	147.5	112.7	122.0	[c]	69.1	187.9 (2.1)
1[b]	solid-state, static	[d]	[d]	[d]	[d]	[d]	188.0 (17.9)
1[b]	MAS	147.8	150.2	155.4	[d]	[d]	188.0 (2.2)
1[b]	CPMAS	147.8	150.2	155.4	60.0	73.4	188.0 (2.2)

[a] Ref. 17. [b] This work. [c] Overlap with thf. [d] 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.

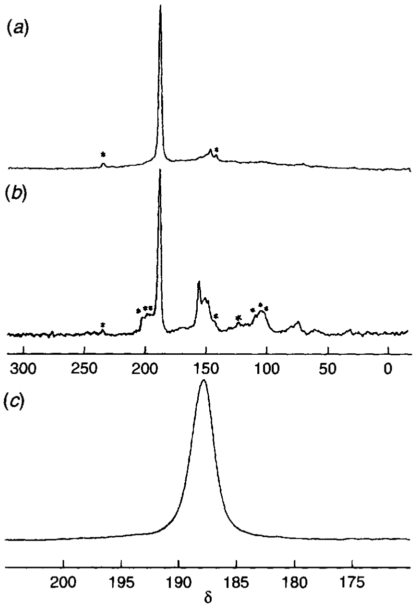

Fig. 1 75 MHz NMR spectrum of **1** at 295 K at a spinning frequency of 3.5 kHz: (*a*) ^{13}C MAS, (*b*) ^{13}C CPMAS; * indicates spinning sideband; (*c*) the expanded ^{13}C MAS NMR region of C_{60}^- of **1** at 295 K

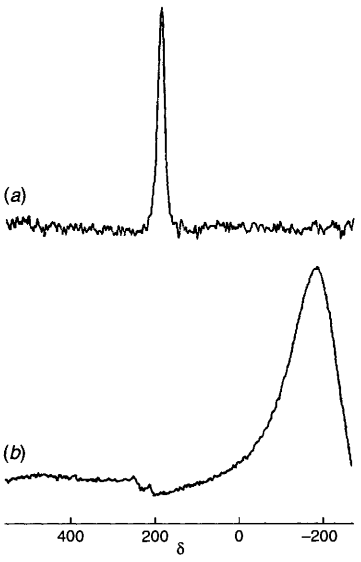

Fig. 2 75 MHz static variable-temperature ^{13}C NMR spectra of **1** at (*a*) 295 and (*b*) 190 K

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,[2–6,8–10,14] 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 δ of −182 is observed (linewidth 123 ppm) (Fig. 2). Extensive ^{13}C NMR investigations of solid **1** under various thermal cycling conditions[15] 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.[15,16] 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}^-]·thf.[7] They mentioned that the air stability of the sodium crown ether salt is lower than that of [Co(η-$C_5H_5)_2$][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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