

Synthesis and Characterisation of NaC₆₀·5thf

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The sodium salt of the monoanion [C₆₀]⁻, namely {Na⁺[C₆₀]⁻(thf)₅} is prepared and the ¹³C and ²³Na solid state NMR, EPR and UV spectra are reported; variable-temperature magnetic susceptibility measurements show a sharp reduction in the magnetic moment below 200 K.

Since the discovery of superconductivity for K₃C₆₀¹ the alkali metal fullerides have attracted considerable interest. These are known for M_x[C₆₀]^{x-}, where $x = 2, 3, 4$ or 6 when $M = \text{Na, K, Rb}$ and Cs ,² and $x = 1$ when $M = \text{Rb}$ or Cs .³ Alkali metal salts of the monoanion [C₆₀]⁻ are unknown *via* a solution chemistry route. There have been reports of the anion [C₆₀]⁻ formed by electrochemical reduction,⁴ by electrocrystallisation [PPh₄⁺C₆₀⁻(Ph₄PCl)] and N(PPh₃)₂⁺[C₆₀⁻]^{5,6} and the charge transfer compounds {Cr(tp)⁺[C₆₀]⁻(thf)₃}, where ttp = tetraphenylporphyrin and {[Fe(η⁵-C₅H₅)(η⁶-C₆Me₆)]⁺_nC₆₀ⁿ⁻} have been characterised.^{7,8} Here, we report a simple selective synthesis of the sodium salt of the C₆₀ monoanion {Na⁺[C₆₀]⁻(thf)₅} in excellent yield.

In a typical preparation, C₆₀† (150 mg, 0.21 mmol) in toluene (125 ml) was treated with Na[Mn(η-C₅Me₅)₂] (72 mg, 0.21 mmol) in thf (10 ml). A dark precipitate separated leaving a yellow supernatant solution of [Mn(η-C₅Me₅)₂]. The precipitate was washed with toluene (3 × 40 ml) and then extracted into thf (1 × 100 ml, 2 × 30 ml) giving an intense cherry-red solution. Removal of the solvent under reduced pressure at room temp. gave a dark-purple microcrystalline solid **1** in ca. 80% yield.

Na[Mn(η-C₅Me₅)₂] was chosen as the reducing agent since the anion [Mn(η-C₅Me₅)₂]⁻ has its first oxidation couple at -2.17 V (-1/0)⁹ and also a solution in thf may be added to toluene without precipitation. Microanalyses of **1** correspond closely to the solvated salt {Na[C₆₀](thf)₅}. ‡ **1** is extremely sensitive to oxygen and water, is soluble in thf, RCN (R=Me or Ph), Me₂SO EtOH and is slightly soluble in CH₂Cl₂.

Heating **1** progressively to 200 °C at 10⁻⁵ Torr causes a loss of thf as indicated by a corresponding steady increase in %C. The solvent could not be removed completely and above 200 °C **1** decomposed. We note that solution routes to other alkali metal anions of C₆₀ have invariably resulted in solvated systems and the solvent is retained even after heating under a vacuum.²

The UV spectrum of **1** in thf gave absorption bands at 262 and 339 nm which is in accord with that previously reported for the anion [C₆₀]⁻ formed in solution by electrochemical reduction.¹⁰

A study of the electrochemistry of **1** by a rotating disc experiment and scanning from 0 to -2 V showed that the bulk solution species of **1** was a monoanion (Fig. 1). The 50 MHz ¹³C wideline NMR powder spectrum of **1** (Fig. 2a) shows a narrow single resonance (δ 188, ν_{1/2} = 2 kHz), indicative of a very small chemical shift anisotropy, and a broad band in the region δ 40–90. On cooling, a significant down field shift and broadening was observed for the former (at 100 K, δ 235, ν_{1/2} = 7 kHz) and a smaller shift up field for the latter.

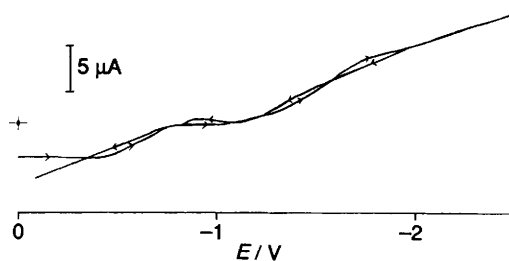


Fig. 1 Rotating disc electrochemistry of **1** in thf, 0.1 mol dm⁻³ Bu₄NPF₆, disc speed 900 rpm, scan rate 20 mV/s vs Ag/Ag⁺

recycle delays to avoid saturation of the ¹³C signal, the broad band integrates approximately in the ratio 1 : 3 with respect to the singlet at δ 188. We provisionally assign the single peak to the C₆₀⁻ anion and the broad band to the thf. The 100 MHz ¹³C MAS NMR spectrum of **1** shows a much reduced line width for the single resonance at δ 188 (ν_{1/2} < 200 Hz). All NMR measurements are consistent with rapidly rotating C₆₀⁻ anions.

The 53 MHz ²³Na wideline NMR powder spectrum of **1** shows a broad singlet (δ 0 ν_{1/2} = 12 kHz) which is essentially unchanged upon cooling to 100 K. The 105 MHz ²³Na MAS NMR spectrum (Fig. 2b), shows two major resonances at 9 and -23, in the ratio of approximately 1 : 1. The resonance at δ -23 appears to have a larger quadrupolar splitting, indicating a more anisotropic site. This suggests that the sodium ions in **1** have two or more different environments. Na⁺ coordinated by oxygen ligands has previously been reported¹¹ to resonate in the range δ -3 to -32 suggesting that the resonance at δ -23 may result from Na⁺ ions attached to thf molecules.

The variable temperature EPR spectrum of a frozen sample of **1** in PhCN was very similar to that previously reported for solutions in PhCN containing the anion [C₆₀]⁻.⁴ Thus, the linewidth of signal centred at $g = 1.999$ varies from 16 G (at 130 K) to 40 G (at 280 K) and there was a very sharp signal (<2 G) becoming evident at the higher temperatures possibly owing to decomposition.

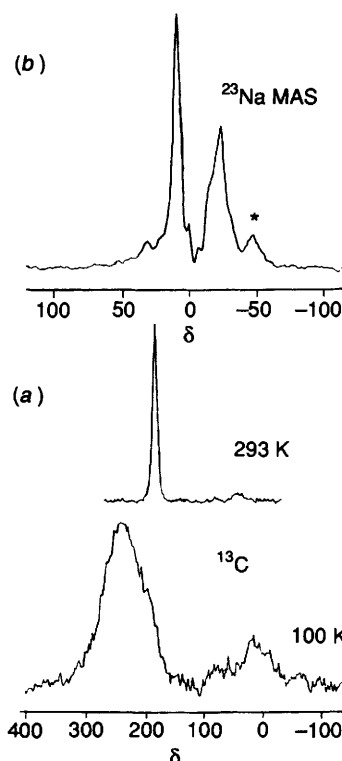


Fig. 2 (a) 50 MHz wideline variable temperature ¹³C NMR spectra of **1**, and (b) 105 MHz ²³Na MAS NMR spectra of **1**; the peak marked with an asterisk at δ -47 is a spinning sideband. Spectra were zero filled to 4096 points, and 100 Hz of Lorentzian line broadening was applied.

The EPR spectrum of a solid sample of **1** gave a signal with $g = 1.999$ and the linewidth varied from 8 G (at 120 K) to 35 G (at 290 K) but no sharp temperature independent signal was observed. Warming the solid sample from 150 to 180 K caused the intensity of the signal to increase markedly but further warming to room temp. caused only a small increase in intensity. This observation has a parallel in the magnetic susceptibility data determined at 0.5 T from 6–290 K (Figs. 3 and 4). The data shows that above 200 K **1** follows Curie–Weiss behaviour for a $s = 1/2$ spin system with $\mu = 1.70 \mu_B$ and a Weiss constant $\theta = -58$ K which indicates the presence of strong antiferromagnetic interactions. The data are consistent with the electron being predominantly localised

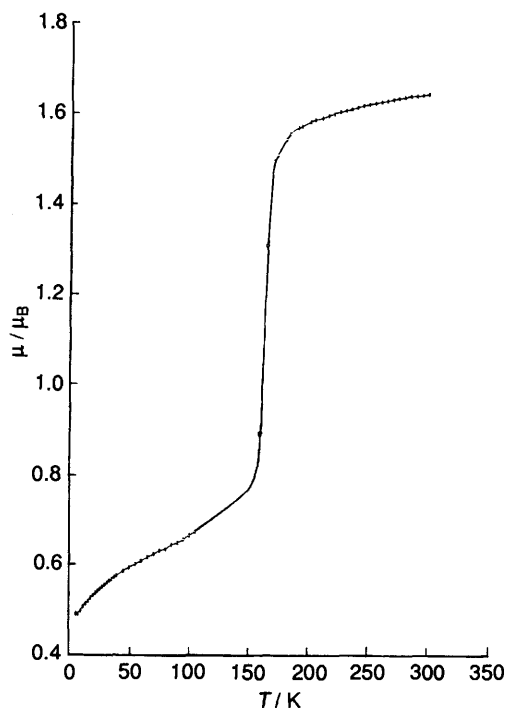


Fig. 3 Temperature dependence of the magnetic moment of **1** determined from magnetic measurements at 0.5 T. The diamagnetic constant used $\chi_d = -300 \times 10^{-6} \text{ emu cgs g}^{-1}$.

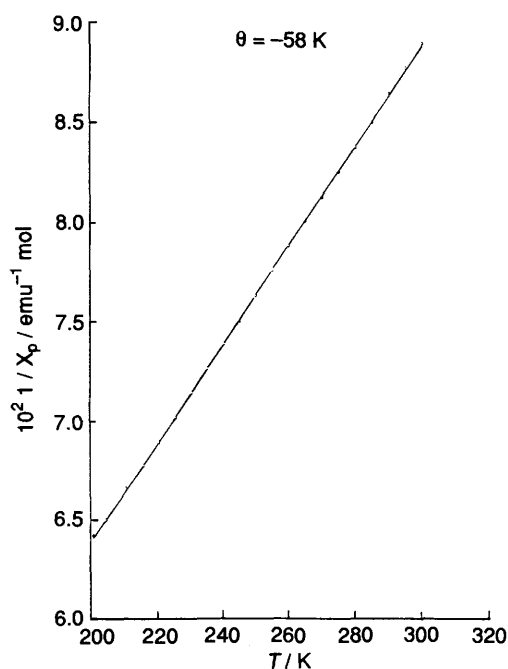


Fig. 4 Plot of the temperature dependence of χ^{-1} (χ = molar susceptibility) >200 K

on the C_{60} above 200 K. However, on cooling below *ca.* 200 K the corrected magnetic moment is temperature dependent decreasing to $\mu = \text{ca. } 0.8 \mu_B$ which is a half of the value found above 200 K. The cause of this effect is not known but we note there are temperature variable effects in the EPR and ^{13}C NMR spectra. It may be that spin pairing occurs giving a unit such as $\{[C_{60}]_3\}^{3-}$ or that half the C_{60} radical anions form dimers. We have previously reported evidence for the anion $\{(C_{60})_2\}^-$.¹²

The powder X-ray diffraction spectrum of $\text{NaC}_{60} \cdot 5\text{thf}$ yielded patterns with lower angle reflections than previously reported for alkali metal C_{60} salts² indicating a larger or lower symmetry unit cell. The weakness of the high angle data and the broadness of many reflections has so far precluded a satisfactory indexing. Annealing a sample of **1** at 150 °C for 7 days reduced the width of the X-ray reflections but monitoring the sample using ^{13}C NMR spectroscopy shows a new peak had appeared which may be due to a second phase.

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Footnotes

† C_{60} was prepared *via* carbon arc vapourisation and subsequent purification on an alumina column.

‡ Solid state ^{13}C NMR was performed at 50 and 100 MHz (secondary ext. ref. adamantane). ^{23}Na NMR (53 and 105 MHz) are referenced to aqueous 1 mol dm^{-3} NaCl, and are not corrected for quadrupole interactions. Rotating disc electrochemistry in thf, 10^{-3} mol dm^{-3} $\text{NaC}_{60} \cdot 5\text{thf}$, 0.1 mol dm^{-3} Bu_4NPF_6 , 900 rpm, 20 mV S^{-1} vs. Ag/Ag^+ EPR g values were determined vs. solid DPPH. SQUID data was analysed using a diamagnetic constant $\chi_d = -300 \times 10^{-6} \text{ emu cgs g}^{-1}$.

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