C₆₀ is an electronegative molecule. One of the most intensely studied aspects of its chemistry is the preparation of compounds containing C₆₀⁻ fulleride anions. If the counter ions are electropositive metals from Groups I or II, they are small enough to occupy the interstitial sites in close-packed arrays of the fulleride. The resulting salts then have sufficient C₆₀⁻ C₆₀ overlap between the frontier π orbitals to allow delocalisation of the electrons, yielding metallic conductivity, and superconductivity in some compounds. The A₃C₆₀ fullerides have the highest superconducting transition temperatures (Tₛ) of any systems except the cuprates. Of particular relevance to the search for high-Tₘ molecular superconductors is the monotonic increase in Tₛ with volume per C₆₀⁻ anion in this series. The highest Tₛ observed to date is that of 40 K for Cs₃C₆₀, a metastable material produced by low-temperature synthesis.

In conventional solid-state synthesis, at the temperatures required to prevent C₆₀ decomposition (<650–800 °C), the volatility of most metallic elements is low and cation mobility in the C₆₀ lattice can be insufficient for reaction. The use of solution-chemistry routes to new fullerides can circumvent these problems, allowing access to a wide range of structural types and interesting physical properties, and opening up the possibility of extending the number of fullerides with molecular counter ions. On the other hand, cation solvation may prevent fulleride close packing. The known superconductors K₃C₆₀ and Rb₃C₆₀ have been synthesised from solution, as have several novel fulleride salts with organic counter cations such as [P(C₆H₅)₃]C₆₀, [P(CH₃)₄]C₆₀Cl[CF₃SO₂]⁺, [N{P{C₆H₅}₃}C₆₀Cl][PF₆]⁻ and [N{P{C₆H₅}₃}C₆₀Cl][PF₆]⁻ and the ternary fulleride Ba₂CuC₆₀.

The elemental closed-shell counter cations discussed in the preceding paragraph have spherical symmetry and a restricted size range. The electronic properties of the fulleride are controlled by the inter-C₆₀ separation and the relative orientations of the C₆₀ molecules. Molecular, as opposed to elemental, cations offer a wider distribution of sizes. In addition, the molecular shape can influence the fulleride packing and orientation. A first step in the use of non-elemental counter cation and shape to control the electronic properties of fulleride salts was the formation of complex counter cations by ligand coordination to the intercalated metals. Na₃CaC₆₀ affords (NH₄)₃Na₃CaC₆₀ containing the tetrahedral (NH₄)₃Na₃CaC₆₀ species on the octahedral site, body-centred tetragonal (NH₄)₃Na₃CaC₆₀ is prepared from K₂C₆₀ while face-centred cubic (fcc) Na₃C₆₀ yields body-centred cubic (bcc) (NH₄)₃Na₃C₆₀ with linear (NH₄)₃Na₃C₆₀ groups. Salts of large molecular counter cations do not show fulleride close packing: direct C₆₀⋯C₆₀ contact is lost as both cation and anion take part in the packing to form the solid. The double salts [P(CH₃)₄]C₆₀Cl have all crystal structures with large fulleride separations. TDAECa [where TDAE is tetrakis(dimethylamino)ethylene] has 10 Å C₆₀⋯C₆₀ contacts in one dimension and is a molecular ferromagnet with Tₑₘ = 16 K.

In this paper, we report the solution synthesis, reactivity, magnetic and electronic properties of [Ni(CH₃)₂]C₆₀.15thf. Tetraalkylammonium C₆₀ compounds have been studied at electrode surfaces but no bulk preparations or characterisation have been reported. The route adopted here is amenable to the preparation of molecular fullerides of higher charge, and the preparation and structure of the dianion salt [Ni(CH₃)₂]₂C₆₀⋅2CH₃CN is also reported.

Experimental

Materials

Pure C₆₀ powder was obtained by spark erosion, chromatography on alumina and sublimation under a dynamic vacuum of 10⁻² Torr at 500 °C.

NaC₆₀.5thf was prepared as described previously. N(CH₃)₄F was prepared by a modified literature method. N(CH₃)₄F was recrystallised from isopropyl alcohol [refluxed and distilled from CaH₂ (twice)] and the resulting alcoholate decomposed at 80 °C under dynamic vacuum (10⁻¹ Torr). Purity was checked by ¹H NMR spectroscopy and elemental analysis.

Solvents were distilled under dinitrogen from sodium potassium alloy (thf) and CaH₂ (CH₃CN). CD₃CN was distilled from CaH₂ (twice), degassed using freeze–thaw cycles, and stored under argon.

Synthesis

All samples were manipulated in a helium-filled MBraun Labmaster drybox, where a 25 W light bulb with a 1 cm hole would typically burn for 5 days. Reactions were performed under argon using standard Schlenk techniques with dual argon and vacuum manifolds.

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CH$_3$CN is slowed at lower temperatures and is negligible below -30°C. This allows the metathesis reaction with NaC$_{60}$·5thf to be carried out in CH$_3$CN at low temperature.

At -30°C a CH$_3$CN solution (20 ml) of N(CH$_3$)$_2$F (6.4 mg, 0.07 mmol) was added rapidly via a cannula to a CH$_3$CN solution (40 ml) of NaC$_{60}$·5thf (75.0 mg, 0.07 mmol). The volatiles were removed under reduced pressure at -30°C and the black residue extracted with thf (2 x 20 ml) at room temperature giving an intense cherry red solution and leaving a pale grey residue. The red thf solution was concentrated to ca. 2 ml and cooled to -80°C depositing black needle-like crystals in the supernatant. Filtration at -78°C and washing with pentane (2 x 5 ml) gave black fern-like microcrystals of [N(CH$_3$)$_2$]C$_{60}$·1.5thf in 80-90% yield. Filtration at -78°C and drying under reduced pressure or under a stream of Ar produced similar results.

The black microcrystalline solid is considerably less oxygen- and moisture-sensitive than NaC$_{60}$·5thf and can be handled in air for a few seconds without significant decomposition. It is soluble in CH$_3$CN and is extremely soluble in thf (>25 mg ml$^{-1}$), in contrast to NaC$_{60}$·5thf which has a considerably reduced solubility in thf and CH$_3$CN (<5 mg ml$^{-1}$).

Elemental analysis corresponded to the composition [N(CH$_3$)$_2$]C$_{60}$·1.5thf. found (calc.): C, 91.4 (93.1); H, 2.6 (2.7); N, 1.5 (1.6); Na, <0.1% (0). Integration of the $^1$H NMR (CD$_2$CN) resonances of thf, N(CH$_3$)$_2$" and an internal calibrant of ferrocene from several samples from separate preparations also gave a stoichiometry of [N(CH$_3$)$_2$]C$_{60}$ (1.5 ± 0.1)thf. NIR spectroscopy in CH$_3$CN showed a band at 1080 nm which is in accordance with the C$_{60}$ species in solution being a radical cation.

The alkali-metal fullerides NaC$_{60}$, K$_2$C$_{60}$ and K$_4$C$_{60}$ are all soluble in CH$_3$CN and can also be reacted with N(CH$_3$)$_2$F at -30°C and then extracted at room temperature with CH$_3$CN (this is necessary as none of these compounds are appreciably soluble in thf) to form [N(CH$_3$)$_2$]C$_{60}$·xCH$_3$CN, [N(CH$_3$)$_2$]C$_{60}$·xCH$_3$CN and [N(CH$_3$)$_2$]C$_{60}$·xCH$_3$CN, respectively.

**Powder X-ray diffraction**

Samples were contained in 0.5 mm diameter capillaries sealed under helium. Data was collected in transmission geometry on a Siemens D5000 instrument with a 6 degree linear position-sensitive detector and monochromatic Cu-K$_x$ radiation from a Ge(111) incident beam monochromator.

**Solid-state NMR spectroscopy**

Samples for $^{13}$C magic angle spinning (MAS) NMR spectroscopy (ca. 50 mg) were contained in a KEL-F insert within a 7 mm zirconia rotor and spun typically at ca. 3 kHz. Samples for static $^{13}$C NMR spectroscopy (ca. 50 mg) were flame-sealed in 5 mm internal diameter Pyrex tubes. $^{13}$C MAS NMR and static spectra were recorded at 50.32 MHz on a Bruker MSL200 spectrometer. Temperature control was achieved using a Bruker VT-1000 temperature control unit. Spectra were referenced externally to adamantane, relative to tetramethylsilane.

**Solution NMR spectroscopy**

Spectra were recorded on a Bruker AM-300 spectrometer at 300.13 MHz ($^1$H) referenced internally to the residual protosolvent resonance of CD$_2$CN relative to tetramethylsilane.

**Magnetic measurements**

Dc static susceptibility measurements were performed using a Cryogenic Consultants S600C SQUID magnetometer equipped with a Lakeshore temperature controller. Samples were contained in gelatin capsules with a sample mass of typically 50-80 mg. Correction for the diamagnetism of the container was achieved by measuring the moment of the empty gelatin capsule over a series of temperatures and external fields prior to filling the capsule with sample. Diamagnetic contributions from the core electrons of thf and N(CH$_3$)$_2$" were corrected for using Pascal's constants and those of C$_{60}$ using a correction of -2.58 x 10$^{-6}$ emu mol$^{-1}$.$^{2,27}$

**EPR spectroscopy**

Spectra were recorded on a Varian E-LINE Century series X-band spectrometer. Temperature control was achieved using an Oxford Instruments ITC 4 controller. Samples were contained in quartz tubes (Spectrosil) sealed with a Teflon stopcock. Spectra were referenced externally to a powdered sample of 2,2′-diphenyl-1-picyrlyldrazyl (dpph) radicals and the linewidth taken as peak to peak of the first derivative of the resonance.

**Conductivity**

The conductivity as a function of temperature from 120 to 300 K was measured using a two-probe dc technique on a section of a pellet (2 x 5 x 0.5 mm$^3$) pressed at room temperature (15 tons) and the four contacts made with silver paint. The sample was mounted on an eight-pin chip and onto a probe on a copper block. The probe was covered with a copper cover, sealed with indium wire and removed from the drybox and placed directly into the cryostat. Temperature control was achieved using an ITC 4 Oxford Instruments intelligent temperature-control unit. Two-probe resistances were measured before and after each experiment in the drybox and confirmed that the sample was not decomposing during the measurement. Measurements were performed on cooling and warming. No significant hysteresis was observed.

**Results**

**Powder X-ray diffraction**

The powder X-ray diffraction pattern of [N(CH$_3$)$_2$]C$_{60}$·1.5thf is shown in Fig. 1. The cell was determined to be hexagonal and refinement of observed reflections gave the cell dimensions as $a=10.131(4)$, $c=10.231(1)$ Å and $V=909.8$ Å$^3$. These cell parameters correspond to the anions being in van der Waals contact in all three dimensions; the structural motif suggested by the cell size is an AAA stacking of close-packed layers of c$_{60}$ molecules, as previously reported for (P$_2$)$_3$C$_{60}$.$^{28,29}$ and (I$_3$)$_2$C$_{60}$.$^{26}$ In this simple hexagonal structure, there are only two suitable positions [shown in Fig 2(a)] for species of the size of thf or N(CH$_3$)$_2$" in the unit cell: the two trigonal prismatic sites at ($±1/3$, $±2/3$, 1/2) [these sites are fully

![Fig. 1 Powder X-ray diffraction pattern of [N(CH$_3$)$_2$]C$_{60}$·1.5thf](image-url)
occupied in \((P_{3}1_{2}1C_{60})\), or the square sites in the \(ac\) or \(bc\) faces at \((1/2, 0, 1/2), (0, 1/2, 1/2)\) or \((1/2, 1/2, 1/2)\). Molecular mechanics computations, using the consistent-valence forcefield (CVFF) within the BIOSYM software,\(^{31,32}\) were employed to calculate and minimise the possible locations of the \((\text{N(CH}_{3})_{4})^{+}\) and thf molecules. All \(C_{60}\) molecules were assumed to be orientationally ordered in the \(P\overline{3}\) space group. Introduction of the tetramethylammonium cation into the simple hexagonal array clearly favours the trigonal-prismatic site over the square one. Diffraction patterns were calculated in which these sites are 50% occupied by the tetramethylammonium cation in a positionally disordered manner. However, this model clearly fails to reproduce the observed diffraction pattern [Fig. 3(a)] with the first two reflections calculated to be far too intense, suggesting the importance of modelling the scattering from the included solvent molecules which are required by the analytical and NMR data. Docking and energy-minimisation calculations in a simple hexagonal \(C_{60}\) array with half of the trigonal-prismatic sites occupied by the tetramethylammonium cations shows the thf molecules also prefer the trigonal-prismatic site over the square one. Two orientations of the thf, one with the molecular plane parallel and the other with this plane perpendicular to the layer stacking direction, are found to have very close total energies. The composition \([\text{N(CH}_{3})_{4}]_2C_{60}\cdot\text{thf}\) [Fig. 2(c)] has a diffraction pattern [Fig. 3(b)] which depends only slightly on the orientation of the thf (shown as parallel). It is, therefore, impossible to determine this orientation with the present data. Calculations were then performed to explore the inclusion of a second thf molecule into the structure. It was found that two molecules can occupy the trigonal site, but with a considerable total energy increase over the single occupied arrangement, as shown in Fig. 2(b). Minimisation shows that these two molecules are both aligned parallel to the stacking direction, with a substantial energy increase if they are ordered perpendicular. Occupation of the square site is much higher in energy and thus ignored in the subsequent discussion. The possibility of solvent molecules occluded on the surface of the crystals makes the 1.5 thf molecules per formula unit an upper limit. Therefore, it is proposed that the observed composition results from predominantly single occupation of the trigonal sites by thf, with the possibility of a random distribution of doubly occupied sites. The inclusion of 50% extra thf produces a calculated diffraction pattern which is still in reasonable agreement with the observed pattern, shown in Fig. 3(c).

\[\text{[N(CH}_{3})_{4}]_2C_{60}\cdot1.5\text{thf}\]

is also hexagonal and refinement of eight reflections gives cell parameters \(a = 10.226(2), c = 9.978(7)\) Å and \(V = 903.6\) Å\(^3\). The diffraction pattern can be approximately modelled by full occupancy of the trigonal prismatic sites by the tetramethyl ammonium cation [Fig. 2(d)]. The observed and calculated powder X-ray diffraction patterns of \([\text{N(CH}_{3})_{4}]_2C_{60}\) are shown in Fig. 4. Rietveld refinement using the program PROFIL\(^{33}\) with spherical shell scattering from the \(C_{60}\) and the \((\text{N(CH}_{3})_{4})^{+}\) cations gives \(R_1 = 18\%\), suggesting the model requires further modification for satisfactory agreement with the data.

\[13C\text{ solid-state NMR spectroscopy}\]

\(^{13}C\) NMR spectroscopy has been used extensively to probe the dynamics and relaxation mechanisms of alkali-metal fullerides and is an integral technique in the determination of the phase purity of a material containing \(C_{60}\). The room-temperature \(^{13}C([\text{H}])\) MAS NMR spectrum of \([\text{N(CH}_{3})_{4}]C_{60}\cdot1.5\text{thf}\) at 50.32 MHz shows only a single peak at \(\delta 185 (v_{1/2} < 100\ Hz)\) (Fig. 5) which is assigned to the \(C_{60}\) monoanion. No \(^{13}C\)
resonances could be observed from the thf or N(CH$_3$)$_4^+$ moieties (relaxation delays from 0.5 to 60 s were used). $^{13}$C{$_1^1$H} CP MAS NMR with contact times ranging from 0.5 to 50 ms did not show any resonances except the single peak at $\delta$ 185 ppm. This could be due to positional disorder of thf and N(CH$_3$)$_4^+$ plus orientational disorder of the fulleride resulting in the occupation of a large number of slightly differing sites and a very broad resonance, or broadening of the resonance by local moments on adjacent fulleride anions. Exposure of the solid to air resulted in decomposition over a period of minutes which was monitored by $^{13}$C{$_1^1$H} MAS NMR and showed new peaks at $\delta$ 143 and 55 assigned to C$_{60}$ powder and the N(CH$_3$)$_4^+$ cation, respectively. Peaks corresponding to thf were not observed. This is probably due to evaporation of thf from the decomposing sample. Decomposition is accompanied by a colour change from black to tan brown.

The room-temperature $^{13}$C{$_1^1$H} static NMR spectrum of [N(CH$_3$)$_4$]C$_{60}$·1.5thf at 50.32 MHz showed a single peak at $\delta$ 185 (v$_{c1^1}$=500 Hz) (Fig. 6). This indicates that the C$_{60}$ monoanions are undergoing isotropic reorientation which is fast (>10$^5$ s$^{-1}$) on the NMR timescale and thus averages out the chemical shift anisotropy. Cooling the sample below 200 K (Fig. 6) results in broadening and a large change in the chemical shift to lower field. The broadening is either due to restriction of the reorientation of the C$_{60}^{-}$ anions or to enhanced relaxation produced by local magnetic moments. The isotropic chemical shift (defined as the centre of gravity of the resonance) changes abruptly below 200 K, in agreement with the magnetisation and EPR measurements, but its temperature dependence cannot be fitted to a Curie-Weiss law at any temperature. The temperature independence of the shift at 230 K and above is consistent with metallic behaviour in this temperature range. The $^{13}$C MAS NMR spectra of the [N(CH$_3$)$_4$]C$_{60}$ fullerides produced by reaction of N(CH$_3$)$_4$F with the C$_{60}^-$ anions are shown in Fig. 7 (a)-(c). They show a common feature at $\delta$ 180, which we assign to [N(CH$_3$)$_4$]C$_{60}$.

Magnetic measurements

Dc magnetic susceptibility measurements of [N(CH$_3$)$_4$]C$_{60}$·1.5thf as a function of temperature at 1 T show non-Curie-Weiss behaviour over the entire temperature range and a large drop in the susceptibility at ca. 200 K (Fig. 8). The susceptibility as a function of temperature after zero-field cooling
and field (1 T) cooling did not show any hysteresis below or above the transition at 200 K. The magnetisation as a function of applied field at 6 K from 0 to 3 T was linear and did not show hysteresis or saturation.

Attempts to fit the magnetisation data over the whole temperature range were unsuccessful. In itinerant electron systems, sharp drops in magnetisation are observed in the Kondo insulators, which are systems of considerable current interest.\textsuperscript{34} FeSi, now considered an early prototype of this class of material, has a qualitatively similar temperature dependent susceptibility to [N(CH\textsubscript{3})\textsubscript{4}]C\textsubscript{60} at 6 K, but the narrow band equations used to fit its susceptibility fail quantitatively here.\textsuperscript{35}

As \textsuperscript{13}C NMR measurements indicate a significant change in the molecular dynamics in the region of the magnetic transition, and the \textsuperscript{13}C NMR total shift becomes temperature dependent below this transition, we then analysed the data above and below the transition separately.

A convenient starting point for understanding the data is to consider the effective magnetic moment per C\textsubscript{60} [\mu\textsubscript{eff}/\mu\textsubscript{B} = 2.82(\chi\textsubscript{eff}T)^{1/2}], which is shown in Fig. 8. A localised array of non-interacting S = 1/2 C\textsubscript{60} anions would have a temperature-independent value of 1.73 \mu\textsubscript{B}. Although the high-temperature limiting value is indeed 1.7 \mu\textsubscript{B}, there is no temperature region over which the Curie law is obeyed. At low temperature, below the 200 K transition, fits to \chi = C/T + A + f(T), where f(T) is a slowly varying function of temperature (discussed in more detail with respect to the high-temperature data) and C/T and A represent respectively Curie and temperature-independent contributions to the susceptibility, are successful [Fig. 9(a)]. In all the fits, regardless of the precise form of f(T), C = 0.035–0.04 emu mol\textsuperscript{-1} K, corresponding to a magnetic moment of 0.6 \mu\textsubscript{B} per C\textsubscript{60}, and A = (7–8) \times 10\textsuperscript{-4} emu mol\textsuperscript{-1}.

The data between 230 and 300 K cannot be fitted successfully with the function \chi = A + C/T; this functional form has incorrect curvature. The Curie–Weiss law yields a significantly poorer fit than found at low temperature, with unphysically large values of \theta (–450 K) and \mu\textsubscript{eff} (2.5 \mu\textsubscript{B} per C\textsubscript{60}). The second-order polynomial, \chi = a + bT + cT\textsuperscript{2}, provides a much better fit, with the size of the linear and second-order contributions being comparable to the constant term over this temperature range. This behaviour is appropriate for a metal with a small Fermi energy. Fits to the functional form appropriate to the paramagnon-enhanced correlated metal,\textsuperscript{36} \chi = \chi\textsubscript{Pauli} \left[1 – (T/AT\textsubscript{p})\textsuperscript{2}\right] also provide a considerable improvement over the Curie law fits. Including the low-T Curie tail as a

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fixed term makes little difference to the fit. The fit shown in Fig 9(b) is to \( \chi = \chi_0 [1 - (T/B)^2] + 0.04/T \) with \( \chi_0 = 16 \times 10^{-6} \) emu mol\(^{-1}\) and \( B = 661 \) K.

Electron spin susceptibility measurements were performed by double integration of the EPR signal between 130 and 290 K and showed a transition similar to that observed in the dc susceptibility data [Fig 10(a)]. The linewidth [Fig 10(b)] above 230 K shows an increase with increasing temperature, as has been noted previously in the literature. The \( g \) value remained constant within experimental error at 2.00 over the temperature range studied. A benzonitrile glass of \([\text{N}(\text{CH}_3)_2]\text{C}_60 \cdot 1\text{Sthf} \) did not show any signs of a transition and the linewidth increased with temperature with a constant \( g \) value of 1.999, consistent with other reports of frozen glass solutions of \( \text{C}_60^– \).

Conductivity

The room-temperature conductivity of a pressed pellet is 0.01 \( \Omega^{-1}\text{cm}^{-1} \), and the temperature dependence appears characteristic of a semiconductor with an activation energy of approximately 0.36 eV, a distinct transition is observable below 200 K, which may be associated with the transition seen in the magnetism. Significant grain-boundary effects are to be expected in such an unsintered pellet, but the key point for the purposes of the present paper is that the conductivity is significantly higher than in other \( \text{C}_60^– \) salts with isolated fulleride anions.

Some reactivity

Exposure of solid \([\text{N}(\text{CH}_3)_2]\text{C}_60 \cdot 1\text{Sthf} \) to air causes oxidation to \( \text{C}_60 \), observed by \(^{13}\text{C} \) MAS NMR spectroscopy. On exposure to air, a red thf solution of \([\text{N}(\text{CH}_3)_2]\text{C}_60 \cdot 1\text{Sthf} \) deposits a tan-brown solid \( \text{C}_60 \) within 30 s. However, a red CH$_3$CN solution becomes a very deep orange-brown on exposure to air. Removal of the volatiles under reduced pressure gives a dark brown-black reflective solid, which is insoluble in all common organic solvents including CH$_3$CN.

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N(CH3)2Cl. This is due to reduction of [Fe(η-C5H5)(CO)2Cl] by C60.

Suspension overnight of [N(CH3)2]3C60·1.5thf with stirring in a solution of 1.5 mol dm−3 n-butyllithium produced intercalation of lithium cations and presumably reduction of the [N(CH3)2]3C60·1.5thf host giving a black solid, 2. After filtration and washing with hexane, 1H Li MAS NMR spectroscopy showed a broad peak at δ 3 (ν1/2 = 3 kHz) and 13C MAS NMR studies revealed two peaks at δ 183 and 181 (ν1/2 ≈ 200 Hz for both). Compound 2 is currently under investigation.

Several attempts at intercalation of rubidium metal at temperatures from 100 to 300°C caused decomposition of [N(CH3)2]3C60·1.5thf as observed by 13C MAS NMR spectroscopy. No superconductivity was observed in these solids, which had broad MAS NMR resonances at δ 145 and 186; tentatively consistent with disproportionation of the monoanion salt into C60 and a more reduced fulleride on reaction with rubidium.

Solution 1H NMR spectroscopy shows that thf can be removed from [N(CH3)2]3C60·1.5thf under dynamic vacuum (10−3 Torr) at 80°C, but 13C MAS NMR spectroscopy of the desolvated material always showed a broad peak at δ 143 in addition to a peak at δ 183, indicating that removal of thf is associated with decomposition. Powder X-ray diffraction of the desolvated material showed broad Bragg peaks that precluded confident indexing. [N(CH3)2]3C60·1.5thf is prone to loss of crystallinity on prolonged standing in the drybox, which we associate with thf loss.

Discussion

We have isolated simple hexagonal arrays containing close-packed layers of C60 anions, with tetramethylammonium as the counter cation. Energy minimisation and powder X-ray diffraction suggest location of the TMA+ (tetramethylammonium) cations at the trigonal-prismatic sites, although the details of the structures proved inaccessible from the powder data. The lattice parameters show that close packing is still possible in the hexagonal packing. The second moiety [thf or N(CH3)2]+ is associated with the high powder conductivity compared with [PPN]C60 and [PC6H5]2C60Cl. The temperature-independent terms in the fit above 230 K are close to 2μBH, found for many fulleride metals [γ(K,C60) = 10×10−4 emu mol−1]. The tight-binding bandwidth, W=2μr, may be estimated as 0.4 eV, using z=8 and τ=0.025 eV from (K,C60).29 This is compared with estimates of the Hubbard U of 1–1.5 eV,09 suggesting that it is appropriate to use the paramagnon model for spin fluctuations produced by interelectron repulsion in narrow-band metals to analyse the data. Here, the density of states at the Fermi energy, EF, evaluated from the magnetic response, Nf(γ=2μBH,γ, where Nf is per spin, i.e. orbital states) is enhanced over that predicted from the bare density of states, Nf, as Nf=NN/(1−θN) where θ is the Stoner parameter. In addition, excitation of paramagnons due to the incipient local moment character (spin fluctuations) gives the susceptibility a temperature dependence in narrow band systems. A quantitative expression for this is γ=2μBH[1−3.2z2/24KNμ(T/θN)2], where K=1−θN [see the fit in Fig. 9(b)]. Here γ=10×10−4 emu mol−1 yields Nf=20 states eV−1 spin−1 C60. We then use a free-electron estimate of Nf of 8 states eV−1 C60 spin−1 to find a Stoner enhancement of the susceptibility of the order of 2.5 (similar to that found for [K,C60]4+) and an unenhanced Fermi temperature of 1865 K. The free-electron Fermi temperature with one electron per C60 in a triply degenerate band is 1800 K and so the magnitude and temperature dependence of the susceptibility are consistent with the correlated itinerant electron model.

Within this interpretation of the high temperature data, the transition at 230 K would be due to significant changes in the transfer integrals being associated with the change in molecular dynamics indicated by the variable-temperature NMR measurements. The transition would then be similar to the metal–metal transition seen in Na,C60-ythf (γ=0.36–0.42, y=1.5–2.9). However, in order to account for the substantial Curie tail at low temperature, either 10% S=1/2 impurities (extraneous or trapped at C60 sites in the otherwise metallic solid) must be present in the sample, or the electronic structure of the solid is such that each C60 carries a local moment of 0.6 μB in the metallic state. An alternative interpretation of the transition is therefore as a metal–insulator transition where the delocalised electrons become 0.6 μB local moments on the C60 anions and the constant term A derived from the analysis of the low-temperature data, is ascribed to van Vleck temperature-independent paramagnetism. This description of the low-temperature state is consistent with either localised or delocalised models for the high-temperature behaviour and would agree with the temperature dependence of the 13C shift below 30°C.
the transition. The small local moment can then be ascribed to use of the simple Cune model in a situation where assignment of electronic character as purely localised is oversimplified.

The small variation of the EPR linewidth with temperature at high temperature is also suggestive of metallic behaviour above the transition. Quantitative interpretation of the linewidth may require following Janossy et al. and results in a conduction electron scattering time of $\tau = 4 \times 10^{-14}$ s, four times smaller than that found for Rb$_2$C$_{60}$. The physically sensible values derived from analysis of the high-temperature phase EPR and $\gamma$ data with the assumption of a narrow-band metal increase our confidence in this assignment. Below 200 K, the temperature dependence of the linewidth is more marked, suggestive of either a longer, more temperature-dependent $\tau$ in the more highly conducting metallic phase, or a transition to a localised C$_{60}$ system.

$[N(CH_2)_{12}]_2C_{60}^+$ is an example of a C$_{60}$ monoanion salt in which the single $t_{1u}$ electron does not promote the formation of oligomeric or polymeric units, despite the close interfullerene contacts. The magnetic data show that strong interactions between the $t_{1u}$ electrons make the magnetic response considerably more complex than would be expected from a localised array of C$_{60}^+$ anions: a coherent interpretation within an itinerant electron model above the transition, but a decisive distinction between strongly coupled local spins and the fullerenes of complex aggregated catons in that the close-packed fullerene layers are stacked in a simple hexagonal AAA manner, this seems to require the presence of two large guest species (cation or solvent molecule), which occupy the two trigonal-prismatic sites in this array.

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