$(NH_3)_6Na_3C_{60}$: Room-temperature Synthesis of a Body-centred Cubic $C_{60}{}^{3-}$ Compound

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Reaction of face-centred cubic Na_3C_{60} with ammonia at room temperature affords body-centred cubic $(NH_3)_6Na_3C_{60}$ in which both octahedral and tetrahedral interstices in the fulleride array are occupied: despite the similarity in $C_{60}{}^{3-}$ packing to Cs_3C_{60}, no superconductivity is observed above 6 K.

The electronic properties of superconducting alkali-metal fullerides[1] may be controlled chemically *via* the influence of the counter ions on the packing, intermolecular separation, charge and orientational order of the $C_{60}{}^{n-}$ anions in the solid state. The superconducting transition temperature (T_c) of the face-centred cubic (fcc) A_3C_{60} (A = alkali metal) systems increases monotonically with the volume of the unit cell.[2] The highest T_c fulleride $Cs_3C_{60}{}^{3}$ (T_c = 40 K under 15 kbar of hydrostatic pressure), however, is body-centred cubic at high pressure (a = 11.52 Å).In this communication, we report the preparation of a body-centred cubic $C_{60}{}^{3-}$ array at room temperature by reaction of Na_3C_{60} with 0.06–0.3 bar of NH_3.

In Na_3C_{60},[4] the sodium ions occupy all the octahedral and tetrahedral sites in the fcc structure (the space-group symmetry is lowered to $Pa\bar{3}$ by orientational order of the anions),[5] but the compound is not superconducting, in contrast with other A_3C_{60} fullerides. We find the reactivity and crystal chemistry of Na_3C_{60} with NH_3 to be quite different to that of $C_{60}{}^{3-}$ fullerides containing the heavier alkali metals. Reaction of Na_2CsC_{60} and K_3C_{60} with 0.5 bar of NH_3 affords $(NH_3)_4Na_2CsC_{60}$[6] and $(NH_3)K_3C_{60}$[7] (both products have fcc-related fulleride packing) whereas Na_3C_{60} yields the amorphous black solid $(NH_3)_{12}Na_3C_{60}$ under these conditions; the loss of crystallinity is ascribed to the large volume change associated with the uptake of 12 equiv. of NH_3. We therefore explored reactivity with lower vapour pressures of NH_3 in an effort to find a more controlled reaction which would yield crystalline products. Reaction with 0.3 bar of NH_3 at room temp. results in the rapid uptake of NH_3 (complete in 20 min at room temperature) to yield $(NH_3)_6Na_3C_{60}$.† Powder X-ray diffraction shows a dramatic change in crystal structure from the starting material and the diffraction pattern is readily indexable as a bcc cell with a lattice parameter of 12.09 Å. Coordination of NH_3 to Na results in a change of volume per C_{60} from 711 to 885 Å^3. $(NH_3)_6Na_3C_{60}$ is stable indefinitely when sealed under He, but loses ammonia slowly in the dry-box and rapidly under dynamic vacuum at room temperature.

Structure refinement involved the use of both laboratory powder X-ray and time-of-flight neutron diffraction, due to the similar X-ray scattering power of the Na^+ and NH_3 moieties (both of which contain 10 electrons). The neutron refinement is complicated by orientational disorder of the ND_3 molecule, and full details will be given elsewhere.[8] Here we concentrate on the results of the X-ray Rietveld analysis in space group $Im\bar{3}$, which is sufficient to locate the Na and N atoms in the bcc fulleride array, and to refine a sensible $C_{60}{}^{3-}$ anion geometry without C–C bond length constraints. The transition from fcc to bcc packing changes the near-neighbour environment of the fulleride from twelve equidistant nearest neighbours at 10.02 Å to eight neighbours at 10.47 and six at 12.10 Å. This both produces more interstitial volume for the larger, complexed cation to occupy, and changes the size and number of interstitial sites. The bcc array contains six equivalent distorted tetrahedral sites at the 12(g) 1/2, x, 0 positions ($x \approx 1/4$), which are occupied in K_6C_{60}.[9] These sites have a hard-sphere radius of approximately 1.7 Å, and refinement of the powder neutron diffraction data clearly shows that they are occupied by ammonia (the scattering length difference allows clear distinction between sodium and nitrogen). In addition, there are smaller, distorted octahedral sites in the midpoint of each edge of the cell and in the middle of each face (Fig. 1). Difference-Fourier analysis of the X-ray data using the neutron-derived nitrogen position showed scattering density ascribed to sodium

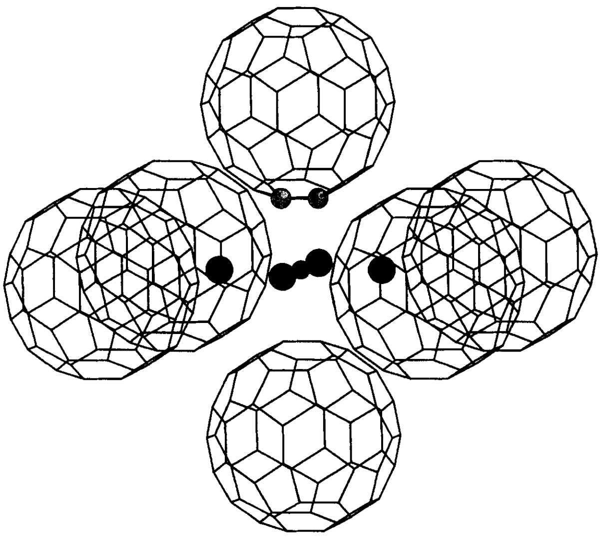

Fig. 1 Location of the interstitial sites in a body-centred cubic C_{60} array. The distorted octahedral sites [at (1/2, 1/2, 0) and equivalent positions] have two 'axial' C_{60} neighbours at $a/2$ and four 'equatorial' C_{60} neighbours at $a/2^{\frac{1}{2}}$ giving the smallest 'axial' radius of the site as 1 Å. A sodium cation (darkest shading) is shown at the centre of this site. The tetrahedral sites are occupied by ammonia molecules (whose nitrogen atoms are represented in the Figure with lighter shading). In the structure of $(NH_3)_6Na_3C_{60}$, the close contact between the C(1) carbons (indicated by enlargement and the lightest shading) of the 'axial' $C_{60}{}^{3-}$ anions and the centre of the octahedral site produces sodium displacement towards the 'equatorial' $C_{60}{}^{3-}$ anions, close to the <110> directions.

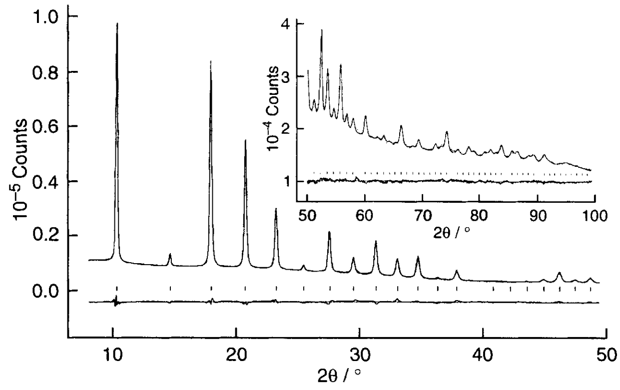

Fig. 2 Rietveld refinement of 8–50 and 50–100° (inset) powder X-ray datasets. The data are plotted as points, the fit is the solid line and the difference is given below. The ticks mark the positions of the Bragg reflections. For histogram 1, R_{wp} = 0.0261, R_e = 0.0112, R_F = 0.0411, $R_{F^{**}2}$ = 0.0786: for histogram 2, R_{wp} = 0.0105, R_e = 0.0076, R_F = 0.0342, $R_{F^{**}2}$ = 0.0389. χ^2 = 3.6. Space group $Im\bar{3}$: a = 12.097(1) Å; Na at 24(g) 0.3646(7), 0.3910(9), 0; N at 12(e) 0.5000, 0.2785(7), 0; C(1) at 24(g) 0.0570(3), 0, 0.2851(4); C(2) at 48(h) 0.1181(2), 0.0975(3), 0.2518(3); C(3) at 48(h) 0.0594(2), 0.1919(3), 0.2142(3). Hydrogens were placed at positions derived from refinement of powder neutron diffraction data.[8] Sodium positions were at a quarter occupancy.

in the vicinity of (0.4, 0.4, 0). This arises from displacement of the sodium cations away from the centre of the octahedral sites towards one of the more distant 'equatorial' C_{60} molecules in the plane. The sodium is displaced off the < 110 > planes onto the 24(g) (*x*, *y*, 0) positions. Fig. 2 shows the two histogram X-ray Rietveld refinement and Fig. 3 the resulting structure. The centre of the octahedral site is surrounded by four ammonia molecules at a distance of 3 Å and the cation displacement from the centre produces two Na···N distances of 2.13(1) and 2.18(1) Å and an N–Na–N angle of 177.6(5)° [the Li···N distance in the $Li(ND_3)_3$ complex in $Li_{0.23}(ND_3)_{0.63}TiS_2$ is 1.98 Å,[10] allowing an estimate of 2.2 Å for an Na···N distance in the $Na(NH_3)_2$ complex here]. The closest Na···C and N···C distances of 3.01 and 3.55 Å respectively are also chemically sensible.

The strong coordination of sodium by NH_3 produces a powerful chemical driving force for all the sodium cations in the structure to be coordinated by NH_3 molecules, and may be the cause of the contrast in reactivity and crystal chemistry with previously studied fullerides. The distortion of the C_{60} packing from fcc to bcc (which is easy to imagine in terms of the distortion of a body-centred tetragonal cell‡ and occurs rapidly at room temperature here) leaves a greater interstitial volume, allowing the NH_3 molecules to occupy the tetrahedral sites and all of the sodium cations to become equivalent by occupying the smaller octahedral sites, where they are coordinated by NH_3 to form almost linear $(NH_3)_2Na^+$ groups.

The absence of superconductivity in $(NH_3)_6Na_3C_{60}$ is particularly noteworthy: as in superconducting Cs_3C_{60}, the $C_{60}{}^{3-}$ anions form a bcc array, though the interfulleride separation is larger due to the size of the $Na(NH_3)_2{}^+$ complex cation. We may therefore conclude that the expanded lattice parameter of the novel ammoniated material reported here decreases the intermolecular t_{1u} wavefunction overlap sufficiently to convert the t_{1u} electrons from itinerant to Mott–Hubbard localised behaviour.

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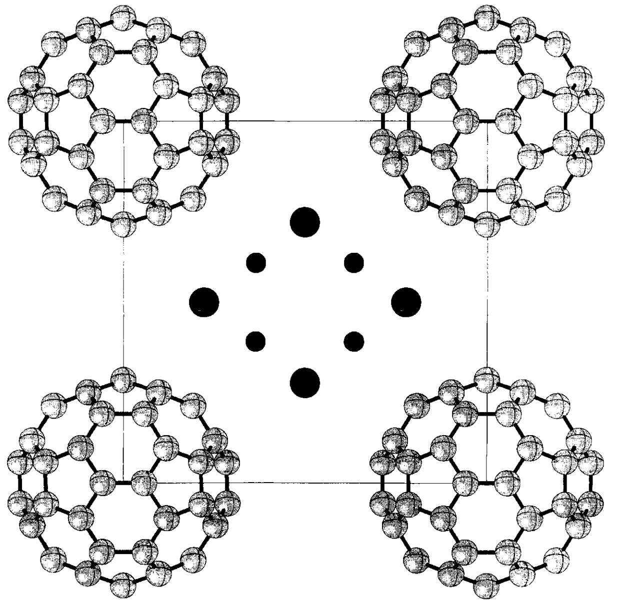

Fig. 3 Unit cell of $(NH_3)_6Na_3C_{60}$ viewed along [001]. Sodium and nitrogen are represented as in Fig. 1, and the carbon atoms are shown as light spheres. The sodium cations are positionally disordered over the 24(g) positions with a quarter occupancy and hence only one of the four sodium sites shown in the face of the unit cell is occupied in any given cell.

Footnotes

† All air-sensitive fullerides and starting materials were handled in a dry-box under helium. C_{60} was prepared by column chromatography of arc-generated soot[11] and purified by sublimation under dynamic vacuum. Na_3C_{60} was synthesised both by reaction of stoichiometric quantities of sodium and C_{60} in a stainless-steel tube sealed in an evacuated Pyrex tube, and by reaction of Na_5Hg_2 with C_{60}. Both sets of samples showed identical reactivity towards ammonia.

Ammonia (NH_3 and ND_3) was dried by condensation onto sodium metal and then exposed to Na_3C_{60} *via* a dual vacuum manifold. Reaction of 58 mg (0.074 mmol) Na_3C_{60} with 2.05 mmol NH_3 at 273 mbar in an all-glass apparatus produced a pressure drop (measured using an electronic pressure transducer) corresponding to a composition $(NH_3)_{6.2\,\pm\,0.2}Na_3C_{60}$. The Pyrex ampoule was then sealed under the NH_3 pressure and opened in the dry box. Weight gain measured indicated that the sample had taken up 6 equiv. NH_3. Magnetisation measurements at 20 Oe with a Cryogenic Consultants SCU500 SQUID magnetometer showed no evidence for superconductivity above 6 K. Powder X-ray diffraction measurements were performed on samples sealed in 0.7 mm capillaries under helium using a Siemens D5000 diffractometer with Cu-Kα_1 radiation from a Ge incident beam monochromator and a 6° linear position sensitive detector. Data for Rietveld analysis were collected in two histograms from 8 to 50° and 50 to 100° with counting times of 1000 and 4000 s per degree, respectively. Powder neutron diffraction measurements were carried out on the POLARIS diffractometer at the ISIS spallation neutron source, Rutherford Appleton Laboratory on a 0.5 g sample of $(ND_3)_6Na_3C_{60}$ in a vanadium can sealed with a PTFE washer. Rietveld refinement was carried out with the GSAS suite of programmes,[12] using a pseudo-Voigt peakshape function and a twelve-term power series expansion to model the background in the X-ray case, and a twenty-term cosine Fourier series with a double exponential decay convoluted with a pseudo-Voigt function to model the neutron time-of-flight background and peakshape.

‡ An fcc cell with lattice parameter a_{fcc} and volume V may also be described as a body-centred tetragonal (bct) cell with $a_{bct} = b_{bct} = a_{fcc}/2^{\frac{1}{2}}$,, $c_{bct} = a_{fcc}$ and volume $V/2$. The bct *a* and *b* directions are rotated 45° about c_{bct} with respect to the fcc *a* and *b* directions.

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