Ba_2CsC_{60}: a ternary metal fulleride with a novel anion orientational order

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The new ternary fulleride Ba_2CsC_{60} is prepared by reduction of C_{60} by the metals in liquid ammonia followed by crystallisation at high temperature and adopts a novel orientational (dis)ordering of the anions in space group $Fm\bar{3}$.

In reduced C_{60} systems, the anion charge can be varied by altering the occupancy of the t_{1u} LUMO and t_{1g} 'LUMO + 1' frontier orbitals. The alkali-metal counter ions in the superconducting A_3C_{60} systems control the electronic properties *via* their direct influence on the interfulleride separation and orientational order at a fixed $C_{60}{}^{3-}$ charge,[1,2] but the synthesis of ternary fullerides, involving the intercalation of cations from other regions of the Periodic Table, has been little investigated. Recent work on the Ba–Rb–C_{60} system has allowed the observation of non-superconducting Ba_2RbC_{60} in a multiphase sample.[3] Here we present the synthesis and full structural characterisation of Ba_2CsC_{60}, a phase-pure ternary alkali-metal–alkaline-earth fulleride. Detailed structural analysis shows that the ternary nature of the compound has a profound influence on the crystal chemistry and, although the fulleride translational symmetry is fcc, a new type of orientational arrangement of the fulleride anions is stabilised.

The synthesis of alkaline-earth fullerides in general requires more forcing conditions[4] than the preparation of their alkali-metal counterparts due to the reduced volatility of the metals themselves and the lower solid-phase mobility of the alkaline-earth cations in the fulleride host. In the preparation of Ba_2CsC_{60}, we overcame this problem by using a liquid ammonia solution of stoichiometric quantities of Ba and Cs at −78 °C to reduce the fullerene—this technique has already been applied to the synthesis of K_3C_{60}.[5] Deammoniation under high vacuum and subsequent annealing (3 × 8 h, 600 °C, with intermediate grinding) in sealed tantalum tubes afforded a black crystalline powder with a 14.19 Å fcc unit cell. Rietveld refinement of laboratory powder X-ray diffraction data† revealed full occupancy of the octahedral and tetrahedral sites in the fcc fulleride array by Ba and Cs cations. Cation ordering can be studied using ^{133}Cs MAS NMR. The ^{133}Cs spectra shown in Fig. 1 are consistent with predominant Cs occupation of the octahedral site (δ −220, 91%) with a much smaller fraction on the tetrahedral site (δ −62.9).

The orientational order of the $C_{60}{}^{5-}$ anions is of greater direct relevance to the electronic properties. The highest point symmetry which is consistent with the presence of one orientation of a C_{60} molecule in a crystalline solid is $m\bar{3}$, and a C_{60} molecule with this symmetry may be placed in one of two so-called 'standard' orientations[6] with respect to the cubic symmetry operations (Fig. 3, later). Two of these orientations, related by 90° rotations about [001], are possible, as the interhexagon (6 : 6) bond perpendicular to the molecular twofold axis may be directed along [100] or [010]. The structure adopted by K_3C_{60} involves 50% occupancy of *both* orientations in a *disordered* manner in the $Fm\bar{3}m$ space group.[7] There are two possible ordered structures which have yet to be observed experimentally; full occupancy of either one orientation gives rise to the $Fm\bar{3}$ space group, while $P4_2/mnm$ corresponds to an *ordered* array of equal populations of both orientations.

The X-ray Rietveld is insensitive to anion orientation—no superstructure reflections indicative of $Pa\bar{3}$ symmetry were observed, but the distinction between ordered $Fm\bar{3}$ and disordered $Fm\bar{3}m$ could not be made. The orientations of the $C_{60}{}^{5-}$ anions can be revealed by powder neutron diffraction, as carbon has the largest scattering length of the constituent atoms. Rietveld analysis of room temperature time-of-flight powder neutron diffraction data shows that the new ternary fulleride adopts the $Fm\bar{3}$ structure with one orientation of the anion predominating (χ^2 = 19 *vs.* χ^2 = 26 in $Fm\bar{3}m$). However, the

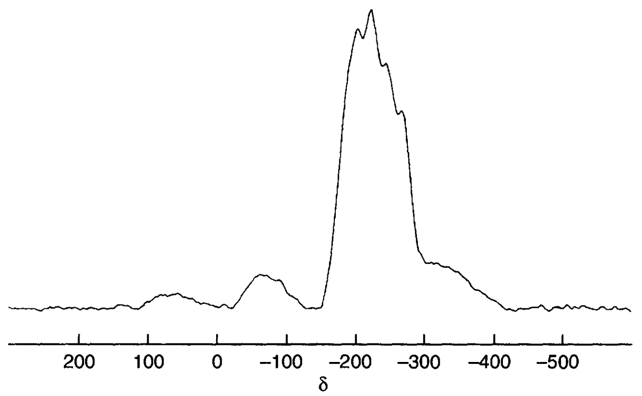

Fig. 1 ^{133}Cs MAS NMR spectrum of Ba_2CsC_{60}. The resonances at δ −220 and −63 are assigned to Cs cations on octahedral and tetrahedral sites respectively. This assignment is made on the basis of the ^{133}Cs spectra observed for fcc $CsRb_2C_{60}$ and Cs_2RbC_{60} where confirmatory X-ray evidence for the cation distribution is available and the octahedral resonance is both to high field of and broader than that from the tetrahedral Cs cation, with a similar shape to that observed here.[10] The small fraction at δ 57.0 (3.2%) is provisionally assigned to a second type of tetrahedral site; two tetrahedral cation resonances are observed in Rb_3C_{60}.[11]

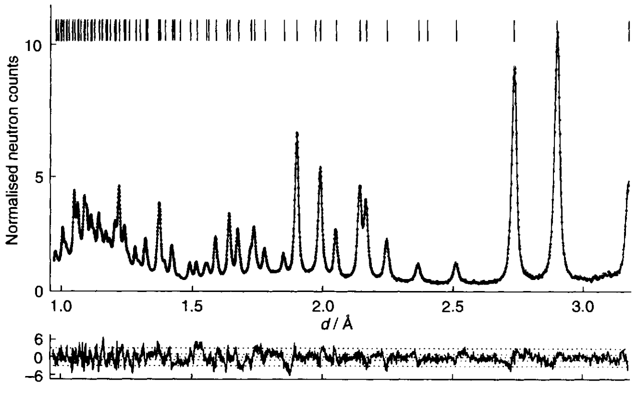

Fig. 2 Rietveld refinement of the time-of-flight neutron powder diffraction pattern of Ba_2CsC_{60}. Ticks mark the positions of the Bragg reflections, the observed data are shown as points, the calculated fit is a solid line and the difference divided by the estimated standard deviation of each point is shown at the bottom. The weak dashed lines on the difference plot represent a level of ±3σ. χ^2 = 3.6, R_{wp} = 1.42%, R_E = 0.75% (calculated using the observed data), R_{wp} = 3.50%, R_E = 1.86% (observed − background), R_I = 0.94% for 157 reflections. Space group $Fm\bar{3}$, a = 14.18950(5) Å.

refinement in $Fm\bar{3}$ was still unsatisfactory—introduction of anisotropic thermal displacement parameters on the carbon atoms produced a very marked improvement in the quality of the fit (χ^2 = 8.8), but inspection of the displacement ellipsoids showed that they were unphysical, suggesting that the improvement in the refinement was due to compensation for an incorrect description of the scattering density from the C_{60} molecules. Difference Fourier maps in the $Fm\bar{3}$ refinement showed several maxima on the surface of a sphere at 3.5 Å from the origin, suggesting that other orientations of the anion were present. Disorder in the C_{60} orientation was then studied in a series of refinements in which the setting angle, ϕ, of a second orientation of the C_{60} molecule about the $\bar{3}$ [111] axis was changed from 0^0 (one of the 'standard' orientations) in 10° steps. The goodness of fit with angle showed a sharp minimum at ϕ = 80°, which corresponds almost exactly to the second 'standard' orientation rotated by 90° about [100] from the first. The second orientation was then introduced into the structural model, and refinement of the fractions of the two orientations with isotropic temperature factors caused χ^2 to fall to 4.7. Refinement of the positions and anisotropic thermal displacement parameters for the carbon atoms (constrained such that the two orientations of the anion have the same shape) plus isotropic thermal displacement parameters for the metal sites produced the final refinement shown in Fig. 2 (χ^2 = 3.6, the best possible profile fit to the data is indicated by the LeBail integrated intensity extraction, which converges to χ^2 = 2.9). The partially disordered structure is shown in Fig. 3.

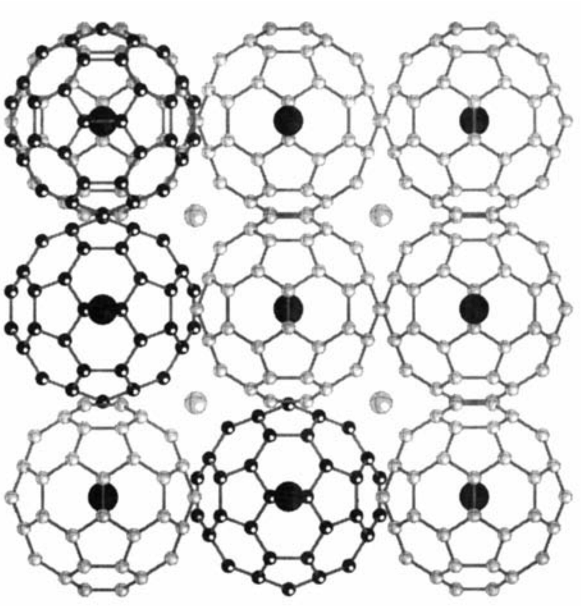

Fig. 3 The average structure of Ba_2CsC_{60} viewed along the [001] direction of the fcc unit cell. The two 'standard' orientations are present with fractions of 83% (carbon atoms shown as white) and 17% (black). The Ba cations on the tetrahedral sites (large, white) and the Cs cations (large, black) on the octahedral sites are also shown.

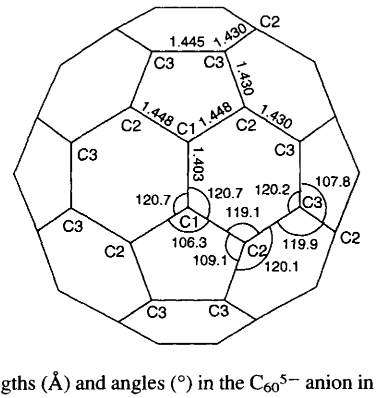

Fig. 4 Bond lengths (Å) and angles (°) in the $C_{60}{}^{5-}$ anion in Ba_2CsC_{60}. The bonds at the junctions of two hexagons and a hexagon and a pentagon are referred to as 6 : 6 and 6 : 5 bonds respectively in the text. Typical e.s.d.s are 0.002 Å on the bond lengths and 0.2° on the bond angles.

The bond lengths and angles refined for the $C_{60}{}^{5-}$ anion are chemically sensible (the angles lie within 1.7° of the ideal values) and provide an interesting contrast with those previously refined for $C_{60}{}^{3-}$ and $C_{60}{}^{6-}$ anions (Fig. 4). The loss of distinction between 6:6 and 6:5 bonds [which have mean lengths of 1.422(11) and 1.440(8) Å respectively here] is more pronounced than found for the $C_{60}{}^{3-}$ anion in K_3C_{60} [1.400(4) and 1.452(13) Å] but less than that found for the closed shell $C_{60}{}^{6-}$ species in K_6C_{60} [1.445(3) and 1.432(10) Å].[8]

The observation of the new $Fm\bar{3}$ symmetry with one predominant orientation of the anion shows that increasing the compositional complexity of the solid can influence the range of structures that are accessible in metal fulleride chemistry. The interplay between the new orientational arrangement of near neighbours and the 5− charge on the anion render Ba_2CsC_{60} non-superconducting. Further synthetic studies in ternary fullerides hold the promise of tuning both charge and orientational parameters for enhanced physical properties.

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Footnote

† X-Ray Rietveld refinement was performed with the GSAS suite of programs on data collected using a Siemens D5000 diffractometer with Cu-$K\alpha_1$ radiation and a 6° linear position sensitive detector. Powder neutron diffraction measurements were carried out on the POLARIS diffractometer at the ISIS spallation neutral source, Rutherford Appleton Laboratory, on a 0.5 g sample of Ba_2CsC_{60} in a 4 mm diameter indium-sealed vanadium can at room temp. for 24 h. Rietveld refinement was carried out on data from the high resolution ($\Delta d/d = 5 \times 10^{-3}$) 145° detector bank, using the TF14LS code.[9]

MAS NMR measurements were performed on a Bruker 200MSL spectrometer with a spinning speed of 3.5 kHz. ^{133}Cs chemical shifts are reported with respect to a 0.5 mol dm^{-3} CsCl aqueous solution.

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