

# Na<sub>2+x</sub>Hg<sub>y</sub>C<sub>60</sub>: post-transition metal intercalation chemistry of a C<sub>60</sub> host

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**The first examples of post-transition metal intercalation into a fullerene host are mercury-loaded derivatives of Na<sub>2</sub>C<sub>60</sub>.**

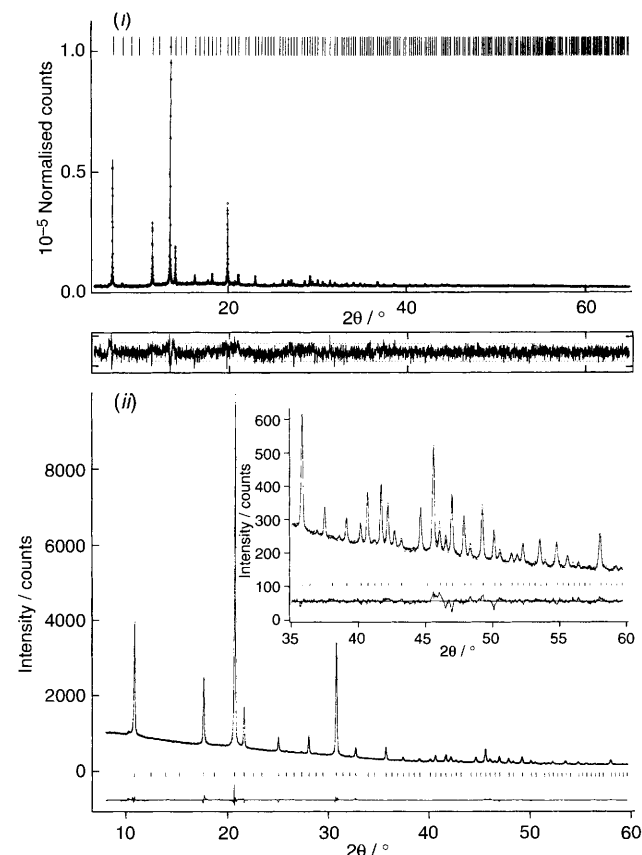
The intercalation chemistry of the face-centred cubic (fcc) C<sub>60</sub> host has given rise to metal fullerenes with interesting electronic properties.<sup>1</sup> Na<sub>2</sub>C<sub>60</sub>,<sup>2</sup> in which the guest cations are predominantly ordered on the tetrahedral sites in this array, is attractive for further intercalation due to the large, nearly vacant octahedral site. We have prepared several Na<sub>2+x</sub>Hg<sub>y</sub>C<sub>60</sub> phases ( $x = 0.0, 0.1; 0.08 < y < 0.24$ ) which are the first structurally characterised examples of the insertion of a post-transition metal into a fullerene host. Mercury occupies the octahedral site in accord with control of the reaction by the host structure.

Reaction of Na<sub>2</sub>C<sub>60</sub> with excess mercury vapour at a pressure of 4 atm in an isothermal evacuated Pyrex tube at 450 °C results in a dramatic change in the powder X-ray pattern of the host material. The intensity of the {111} reflection of Na<sub>2</sub>C<sub>60</sub> decreases sharply and the {311} reflection becomes dominant. Simulation of the X-ray pattern with the LAZY-PULVERIX program<sup>3</sup> shows that this arises from a large increase in the electron density on the octahedral site. Analysis of the powder pattern by a preliminary Rietveld refinement of the concentration of mercury (located at the centre of the octahedral site) indicated a composition Na<sub>2</sub>Hg<sub>0.13(2)</sub>C<sub>60</sub>, demonstrating that mercury intercalation into the Na<sub>2</sub>C<sub>60</sub> host is possible: the large effect on the diffraction pattern is shown quantitatively by the reduction in  $\chi^2$  from over 80 to below 4.0 on incorporation of the intercalated mercury into the refinement.

The new ternary phases are accessible directly by reaction of the alloy Na<sub>5</sub>Hg<sub>2</sub> with C<sub>60</sub> as well as by mercury intercalation into the Na<sub>2</sub>C<sub>60</sub> host described above. The reactions are carried out at temperatures of up to 450 °C† (above the liquidus of the Na–Hg phase diagram for all Na/Hg ratios) under mercury pressures of between 0.05 and 5 atm. In contrast, reaction of sodium, C<sub>60</sub> and a stoichiometric quantity of mercury (0.2–0.3 mol equiv. per C<sub>60</sub>) affords pure Na<sub>2</sub>C<sub>60</sub>. Reaction of Na<sub>2</sub>C<sub>60</sub> with mercury in a temperature gradient (Na<sub>2</sub>C<sub>60</sub> at 250 °C, Hg at 225 °C) or under isothermal conditions (at 250 and 450 °C) yields samples with  $y = 0.10(1), 0.13(1)$  and  $0.13(1)$  respectively. The largest concentration of intercalated mercury in Na<sub>2+x</sub>Hg<sub>y</sub>C<sub>60</sub> is afforded by direct formation of the ternary phase through reaction of C<sub>60</sub> with Na<sub>5</sub>Hg<sub>2</sub> at a final reaction temperature of 400 °C: for  $x = 0.1$ , this yields  $y = 0.24(1)$  [450 °C gives  $y = 0.17(1)$ ]. Samples with lower mercury concentrations can be prepared by thermal deintercalation of mercury from Na<sub>2+x</sub>Hg<sub>y</sub>C<sub>60</sub>, e.g.  $x = 0.0, y = 0.19$  in a gradient from 250 to 23 °C affords  $y = 0.08(1)$ .

Rietveld analysis (Fig. 1) of powder X-ray diffraction data‡ confirms the picture of intercalation of mercury into the Na<sub>2+x</sub>C<sub>60</sub> host. The C<sub>60</sub><sup>2-</sup> anions remain orientationally ordered in space group  $Pa\bar{3}$  and adequate fitting of the high-angle reflections required the introduction of a second orientation of the C<sub>60</sub> anion corresponding to rotation of 40° about the <111> directions away from the global minimum (which occurs at a similar setting angle to that found for Na<sub>2</sub>C<sub>60</sub>).<sup>4</sup> Mercury was located and refined at the centre of the octahedral site, while the sodium cations remained predominantly located on the tetrahedral site (Fig. 2). Refinement of a small

concentration of sodium on the 8c  $x,x,x$  position ( $x \approx 0.41$ ), displaced from the centre of the octahedral site, both improves the quality of the fit and significantly reduces the mercury

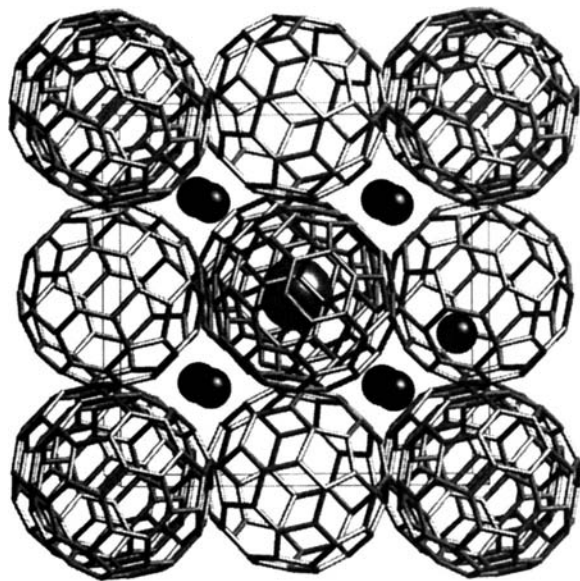


**Fig. 1** Rietveld refinements in space group  $Pa\bar{3}$  of (i) Na<sub>2</sub>Hg<sub>0.168(1)</sub>C<sub>60</sub> refined from synchrotron data using the SR15LS code.  $\chi^2 = 1.66$ ,  $R_{wp} = 0.0256$ ,  $R_1 = 0.104$  for 628 reflections.  $f(C_{60}$  major orientation) = 0.78(1),  $f(Hg)$  = 0.165(1),  $U(Hg)$  = 0.098(3) Å<sup>2</sup>,  $U(C)$  = 0.0351(1) Å<sup>2</sup>,  $U(Na)$  = 0.043(1) Å<sup>2</sup>,  $a = 14.1913(1)$  Å. (ii) Na<sub>2.1</sub>Hg<sub>0.24(1)</sub>C<sub>60</sub> refined from laboratory powder X-ray diffraction data using GSAS.  $\chi^2 = 2.94$ ,  $R_{wp} = 0.0226$ ,  $R_{F+2} = 0.0619$  for 152 reflections.  $f(Hg)$  = 0.24(1),  $U(Hg)$  = 0.10(2) Å<sup>2</sup>,  $U(C)$  = 0.04(1) Å<sup>2</sup>,  $U(Na)$  = 0.05(2) Å<sup>2</sup>,  $f(Na, \text{tetrahedral})$  = 0.92(4),  $f(Na, \text{octahedral})$  = 0.13(4),  $x(Na, \text{octahedral})$  = 0.42(2),  $f(C_{60}$  major orientation) = 0.78(9),  $a = 14.194(1)$  Å. The inset is the high-angle region of the fit. The observed data are shown as points, the calculated model is a solid line: in (i) the difference divided by the esd of each point is shown below, with dotted lines representing a level of  $\pm 3\sigma$ , while in (ii) the lower plot is the simple difference curve. Ticks indicate the positions of the Bragg reflections. Mercury was refined on the 4b 1/2, 1/2, 1/2 position. Significant thermal motion is typically associated with the octahedral site species in fullerenes (in Rb<sub>3</sub>C<sub>60</sub>,  $U_{oct} = 0.14$  Å<sup>2</sup> at 298 K,<sup>10</sup> while in K<sub>3</sub>C<sub>60</sub>,  $U_{oct} = 0.22$  Å<sup>2</sup> at 298 K<sup>10</sup> and 0.08 Å<sup>2</sup> at 5 K.<sup>11</sup> Two orientations of the C<sub>60</sub> molecule were used, at the setting angles described in the text, with 6:6 and 6:5 bond lengths of 1.40 and 1.45 Å; positional parameters of the carbon atoms were not refined. Two sodium positions (8c  $x,x,x$ ) were incorporated; the tetrahedral sodium  $x$  coordinate did not refine to be significantly different from the ideal value of 0.25 and was fixed at this value. In (i), all the sodium occupies the tetrahedral site.

thermal displacement parameter: the total sodium concentration was constrained to correspond to the reaction composition. The quoted values (and errors) for the mercury concentration throughout the paper are derived from Rietveld refinements of this quantity. All the mercury-loaded samples have lattice parameters ( $a$ ) very close to the 14.19 Å of the Na<sub>2</sub>C<sub>60</sub> host.

Most models of the electronic structure of alkali-metal fullerides assume complete valence electron transfer from the alkali metal to the fullerene for anion charges of <6. The first ionisation energy of mercury is 1007 kJ mol<sup>-1</sup>, compared to 495 kJ mol<sup>-1</sup> for sodium. The <sup>13</sup>C MAS NMR spectrum of Na<sub>2.1</sub>Hg<sub>0.17</sub>C<sub>60</sub> indicates a single phase with a chemical shift  $\delta$  171.8, very close to that of Na<sub>2</sub>C<sub>60</sub>.<sup>5</sup> The <sup>13</sup>C  $T_1$  temperature dependence is also similar to that of Na<sub>2</sub>C<sub>60</sub>, indicating nonmetallic behaviour and consistent with the absence of superconductivity in this phase. The octahedral site is large enough to accommodate zero-valent mercury with a radius of 1.51 Å. Intercalation of the Cs<sup>+</sup> cation ( $r = 1.70$  Å) into the octahedral site of Na<sub>2</sub>C<sub>60</sub> produces a marked contraction<sup>2</sup> in  $a$  to 14.132 Å, in contrast to the insertion of a similarly sized neutral species here. The structural and NMR data thus indicate that there is little charge transfer between mercury and C<sub>60</sub>, consistent with the high ionisation energy and large radius of mercury. The unchanged reactivity of Na<sub>2+x</sub>Hg<sub>y</sub>C<sub>60</sub> with ammonia provides chemical evidence for the uncharged nature of the mercury species: the expected weak interaction between neutral mercury and NH<sub>3</sub> results in expulsion of mercury from the ternary phase on exposure to NH<sub>3</sub> and formation of the same products afforded by Na<sub>2</sub>C<sub>60</sub>, containing sodium–ammonia complexes. Intercalation of neutral mercury has previously been observed in Hg<sub>x</sub>TiS<sub>2</sub>.<sup>6</sup>

The Na<sub>2+x</sub>Hg<sub>y</sub>C<sub>60</sub> series is thus an interesting example of intercalation compounds in which one guest (Na) transfers charge whereas the other (Hg) does not. This opens up the possibility of the use of Hg as a neutral ‘spacer’ in complex



**Fig. 2** The disordered structure of Na<sub>2.1</sub>Hg<sub>0.24(1)</sub>C<sub>60</sub>. The mercury loading found corresponds to approximately one mercury (large, black) per fcc unit cell, *i.e.* 25% occupancy of the octahedral site. The distances between this mercury and the octahedral sodium (small, black) indicate that both species do not occupy the same octahedral site. The remaining sodiums (small, black) occupy the tetrahedral sites. Only the major C<sub>60</sub> orientation is shown here (carbon atoms in black). The closest Hg–C contacts to this orientation are to the two carbon atoms at the junction of a six-membered ring and a five-membered ring on each of the C<sub>60</sub> molecules constituting the octahedral site ( $6 \times 3.71$  Å,  $6 \times 3.79$  Å).

fullerides, controlling the separation without affecting the fulleride charge.

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## Footnotes

† Two routes lead to the formation of ternary sodium–mercury–C<sub>60</sub> intercalates. (i) Na<sub>2</sub>C<sub>60</sub> (50 mg, 0.065 mmol) was sealed together with 100 mg Hg (0.499 mmol; Aldrich, triple distilled, 99.99%) in a Pyrex tube which was wrapped in aluminium foil and placed in a furnace at the temperatures described in the text for two weeks. (ii) Na<sub>4.8</sub>Hg<sub>2</sub> [123.9 mg, 0.2422 mmol, prepared by melting Na (Aldrich, 99.95%) with Hg in a sealed tube at 100 °C, sodium content verified by titration] was ground together with C<sub>60</sub> (419 mg, 0.5814 mmol prepared by spark erosion, purified by chromatography<sup>7</sup> and sublimation at 550 °C) and heated in a sealed ( $1 \times 10^{-5}$  Torr) 8 cm<sup>3</sup> Pyrex tube at 200 °C (4 days), 250 °C (1 day), 300 °C (1 day) and 350 °C (3 days). The tube was then opened in a helium-filled dry box, and the sample reground and resealed together with the recovered mercury. The sample was then reheated to 400 or 450 °C for 7 days. The required mercury pressure for formation of the ternary intercalate was produced either from the Na<sub>5</sub>Hg<sub>2</sub> alloy after reaction of all the sodium in (i) or from the added mercury in (ii).

Thermal deintercalation of mercury was performed for 2 days in an accurately measured temperature gradient in sealed Pyrex tubes. Complete deintercalation of mercury requires two distillations in a 400 °C temperature gradient and affords crystalline Na<sub>2</sub>C<sub>60</sub>. Under all synthetic conditions, excess Hg is retained adsorbed onto the sample and is lost more readily on distillation.

‡ Powder X-ray diffraction measurements were carried out on all samples sealed under helium in 0.7 mm capillaries with Cu-K $\alpha_1$  radiation on a Siemens D5000 diffractometer with a position sensitive detector in 0.02° steps with a counting time of 100 s per step. Synchrotron powder X-ray data were collected on station 9.1 at the Synchrotron Radiation Source, Daresbury Laboratory ( $\lambda = 0.99867$  Å) over an angular range of 5–55° in 0.01° steps with a counting time of 12 s per step at high angle, decreasing with angle to 2 s per step in the range 5–22°. Rietveld refinement in space group  $P6_3$  was carried out on data collected for all the samples discussed in the paper, using both the GSAS package<sup>8</sup> and the SR15LS code from the CCCL suite of Rietveld analysis software.<sup>9</sup> All the isotropic thermal displacement parameters of the carbon atoms were constrained to be the same, as were those of the octahedral and tetrahedral sodium atoms. <sup>13</sup>C Magic angle spinning (MAS) solid-state NMR measurements (see graphical abstract) were carried out using a Bruker MSL 200 spectrometer with the samples in Kel-F inserts in 7 mm zirconia rotors and spun at a rate of 3.5 kHz. Chemical shifts are reported with respect to an adamantane external standard.

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