

Preparation and Characterisation of $C_{60}(\text{ferrocene})_2$

Jonathan D. Crane, Peter B. Hitchcock, Harold W. Kroto, Roger Taylor and David R. M. Walton

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

C_{60} cocrystallises with ferrocene to give black $C_{60}(\text{ferrocene})_2$, which contains discrete C_{60} and ferrocene molecules; the ferrocene does not reduce C_{60} , but the structure appears to be stabilised as a result of weak intermolecular charge-transfer interactions.

Buckminsterfullerene (C_{60}) is a molecular building block, which can be used to prepare new materials with interesting properties.¹⁻³ It behaves as a mild oxidising agent, displaying six reversible one-electron reductions in solution,⁴ and may be described as a partly delocalised electrophilic poly-alkene. As an electron acceptor, C_{60} can be expected to interact with electron-donors (D) to form either charge-transfer complexes, $C_{60}D_n$, or charge-separated systems, $[C_{60}^{n-}][D^+]_n$. The extent of charge separation has important bearing on the preparation of molecular conductors and soft ferromagnets.^{2,5}

Discrete C_{60} molecules have been successfully incorporated into novel ionic and molecular materials. For example, alkali metal 'salts', $C_{60}M_n$ ($n = 3, 4, 6$) have been prepared and ($n = 3$) display high temperature superconductivity.² C_{60} is an ideal guest for α -, β - or γ -cyclodextrin [especially the latter, with which it forms a water-soluble, encapsulated complex, $C_{60}(\gamma\text{-cyclodextrin})_2$].⁶ Analogous behaviour was not observed with the larger oblate spheroidal fullerene, C_{70} . C_{60} also cocrystallises with 1,4-hydroquinone to yield a solid, formulated as $C_{60}(1,4\text{-hydroquinone})_3$,⁷ which consists of a polymeric hydrogen-bonded lattice containing large cavities occupied by the C_{60} molecules. The stability of this compound is

undoubtedly enhanced by favourable charge-transfer interactions between the electron-rich hydroquinone molecules and electron-deficient C_{60} entities. Similar interactions appear to exist between C_{60} and the weakly donating ferrocene molecule $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]$ to give the crystalline complex $C_{60}(\text{ferrocene})_2$, described below.

Mixing saturated benzene solutions of C_{60} and ferrocene in a 2:1 vol. ratio gave a deep-red solution from which black plates crystallised upon standing (2-3 days). At this stage the orange supernatant solution contained only a trace of C_{60} and was removed by decantation. The small amount of free ferrocene, which also crystallises during this procedure, was removed by sublimation at 60-70 °C. Washing the crystals with organic solvents leads to a loss of surface lustre. The presence of ferrocene in the washings from freshly prepared crystals suggests occurrence of a leaching process which presumably leaves a layer of (insoluble) ferrocene-deficient C_{60} at the surface domain.

The crystals were stable out of solution and were shown by single-crystal X-ray diffraction to have the formulation $C_{60}(\text{ferrocene})_2$, the structure of which was determined at 143 and 296 K using the same crystal.† Except for standard minor differences in the unit cell dimensions and thermal parameters, the two structures were identical. Data given below refer to the low-temperature result.

$C_{60}(\text{ferrocene})_2$ consists of close-packed layers of C_{60} molecules, stacked directly one above the other, parallel to (001). This packing of the C_{60} molecules is different from the face-centred cubic (fcc) packing of pure C_{60} ,² but similar to that reported for the iodine intercalate $C_{60}(\text{I}_2)_2$.⁸ The holes between the layers contain ferrocene molecules according to the packing arrangement in the bc plane (Fig. 1). One C_5H_5

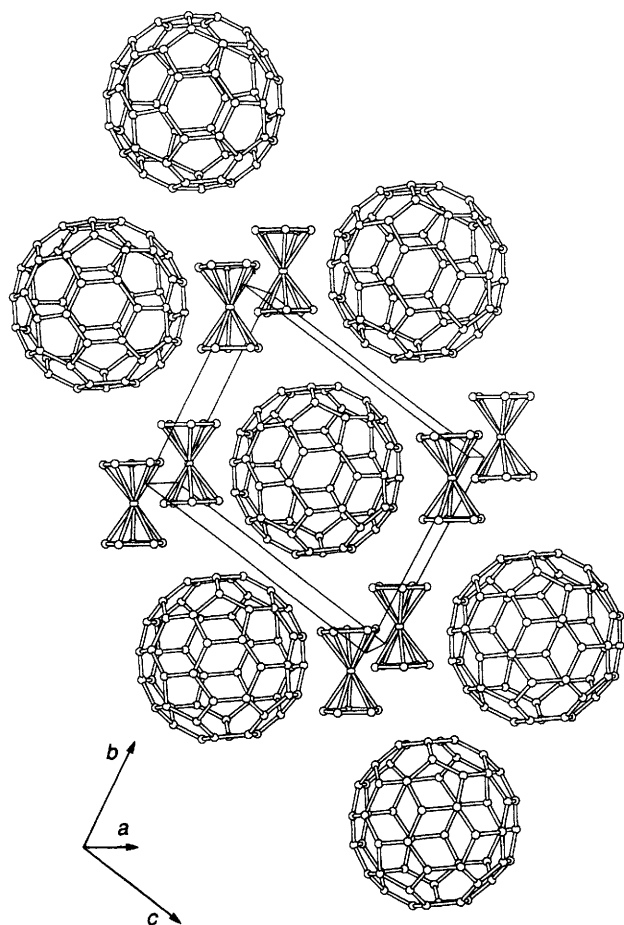


Fig. 1 Packing arrangement for $C_{60}(\text{ferrocene})_2$ in the bc plane

† Crystal data: $C_{80}H_{20}Fe_2$, $M = 1092.7$, triclinic, space group $P\bar{1}$ (No. 2). Low-temperature structure (143 K): $a = 9.899(3)$, $b = 10.366(4)$, $c = 11.342(3)$ Å, $\alpha = 95.55(3)$, $\beta = 90.96(3)$, $\gamma = 118.33(3)^\circ$, $U = 1017.1$ Å³, $Z = 1$, $D_c = 1.78$ g cm⁻³, $F(000) = 552$. Monochromated Mo-K α radiation, $\lambda = 0.71069$ Å, $\mu = 7.7$ cm⁻¹. A crystal of size ca. $0.4 \times 0.4 \times 0.1$ mm was used to collect intensities for 4872 unique reflections with $2 < \theta < 28^\circ$ on an Enraf-Nonius CAD4 diffractometer. 4229 reflections with $I > 2\sigma(I)$ were used in the refinement. The Fe and C atoms were located by direct methods using SHELXS-86 and refined with anisotropic thermal parameters by full-matrix least-squares analysis using programs from the MOLEN package. Hydrogen atoms were located on a difference map and refined with isotropic thermal parameters. Final parameters were: $R = 0.060$, $R' = 0.088$, $S = 2.9$, 410 variables, 4229 observed reflections, $(\Delta/\sigma)_{\text{max}} = 0.02$, $(\Delta\delta)_{\text{max,min}} = +0.75, 0.21$ e Å⁻³.

High-temperature structure (296 K): $a = 10.094(5)$, $b = 10.528(4)$, $c = 11.306(3)$ Å, $\alpha = 95.29(3)$, $\beta = 90.65(3)$, $\gamma = 118.47(4)^\circ$, $U = 1049.6$ Å³, $D_c = 1.73$ g cm⁻³. Monochromated Mo-K α radiation, $\lambda = 0.71069$ Å, $\mu = 7.5$ cm⁻¹. The same crystal was used to collect intensities for 5046 unique reflections with $2 < \theta < 28^\circ$. 4430 reflections with $I < 2\sigma(I)$ were used in the refinement. The Fe and C coordinates were taken from the low-temperature structure and refined as above. Final parameters were: $R = 0.052$, $R' = 0.076$, $S = 2.9$, 410 variables, 4430 observed reflections, $(\Delta/\sigma)_{\text{max}} = 0.03$, $(\Delta\rho)_{\text{max,min}} = +0.69, -0.14$ e Å⁻³.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

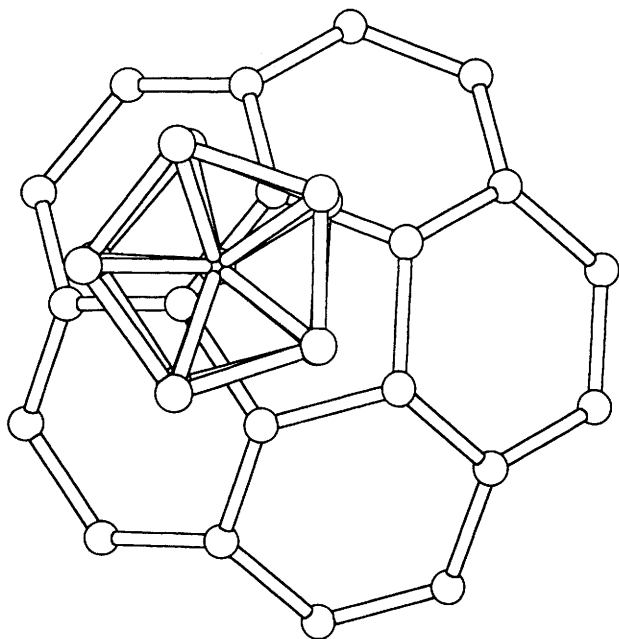


Fig. 2 One C_5H_5 ring of the ferrocene is parallel to a pentagonal face of the C_{60} at an inter-plane distance of 3.3 Å. The eclipsed ferrocene is also slipped sideways by 0.8 Å.

ring, Cp(1), of a ferrocene molecule is situated in a plane parallel to a pentagonal face of C_{60} with an inter-plane distance of 3.3 Å (Fig. 2). This value is typical for the π -interactions between aromatic molecules and may be compared with the inter-plane distance in graphite, *viz.* 3.35 ± 0.05 Å, and the stacking distance of 3.14(10) Å in the analogous charge-transfer complex (tetracyanoethene) (ferrocene).⁹ The two C_5 rings are in approximately the same orientation, but slipped sideways by 0.8 Å (Fig. 2). The other C_5H_5 ring, Cp(2), is not associated with C_{60} . Adjacent ferrocene molecules are staggered relative to one another in such a way that the Cp(1) ring slots between the two Cp rings of its neighbour (Fig. 1). As the C_{60} molecule lies on a crystallographic inversion centre, the overall structure may be described as an interlaced arrangement of parallel ferrocene- C_{60} -ferrocene sandwiches. The orientation of the C_{60} and ferrocene molecules for the side-on interactions is shown in Fig. 3. The arrangement of the ferrocene molecules creates concave van der Waals surfaces into which the convex surface of the C_{60} fits.

The nearest neighbour distances between the centres of the C_{60} molecules are the unit-cell axis lengths 9.899, 10.366 and 11.342 Å together with 10.396 Å along the *ab* diagonal. The geometries of all four contacts are similar and may be described as between two parallel hexagonal faces which are shifted sideways relative to one another. Within C_{60} the distance of the carbon atoms from the centre of the molecule varies between 3.525(3) and 3.550(3) Å, with an average of 3.537(7) Å. The difference in length between the two types of C-C bond is clearly seen. The 30 inter-pentagonal 'double' C-C bonds range between 1.380(6) and 1.395(6) Å with an average of 1.387(6) Å and the 60 intra-pentagonal 'single' C-C bonds range between 1.438(5) and 1.461(6) Å with an average of 1.450(6) Å. There is no apparent simple correlation between the variation in C-C bond lengths and the proximity of neighbouring C_{60} or ferrocene molecules.

In the ferrocene molecule the two Cp rings are in an eclipsed geometry and their planes are very nearly parallel, with a Cp-Fe-Cp angle of 177.8°. The average Fe-C distance is 2.047(5) Å and the perpendicular Fe-Cp distance is 1.650(4) Å. These distances are in full agreement with the

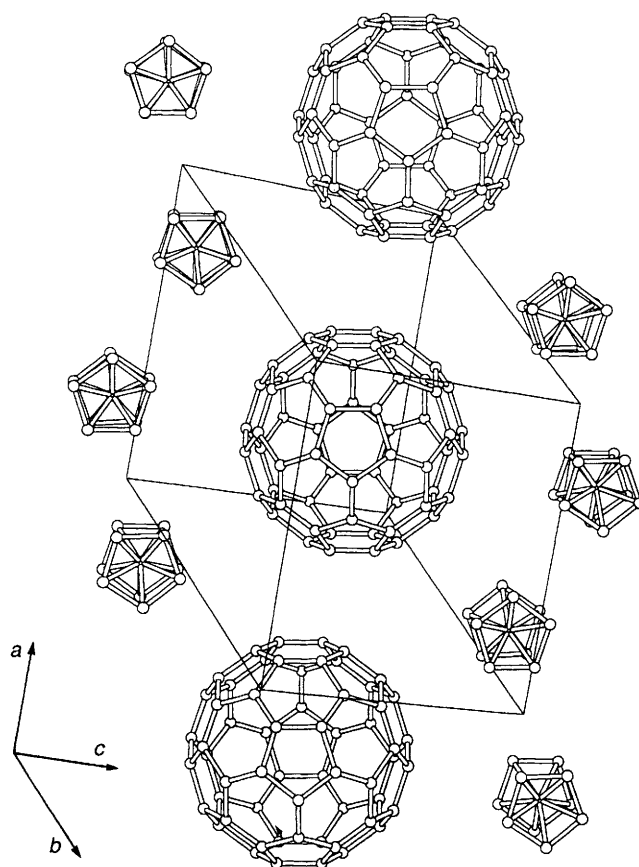


Fig. 3 Packing arrangement showing the side-on interactions between the ferrocenes and the C_{60} molecules

expected presence of neutral ferrocene in a molecular complex, rather than of an oxidised ferricinium cation in a salt.

We thank BP, ICI and the Royal Society for financial support of this work.

Received, 9th September 1992; Com. 2/104839F

References

- H. W. Kroto, A. W. Allaf and S. P. Balm, *Chem. Rev.*, 1991, **91**, 1213.
- Special issue on Buckminsterfullerenes, *Acc. Chem. Res.*, 1992, **25**, Issue No. 3.
- H. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 293.
- Q. Xie, E. Pérez-Cordero and L. Echegoyen, *J. Am. Chem. Soc.*, 1992, **114**, 3978; Y. Ohsawa and T. Saji, *J. Chem. Soc., Chem. Commun.*, 1992, 781.
- J. S. Miller, A. J. Epstein and W. M. Reiff, *Chem. Rev.*, 1988, **88**, 201.
- T. Andersson, K. Nilsson, M. Sundahl, G. Westman and O. Wennerström, *J. Chem. Soc., Chem. Commun.*, 1992, 604; W. Kutner, P. Boulas and K. M. Kadish, *J. Electrochem. Soc.*, 1992, **139**, 243C (Abstr. of the Society Meeting, St Louis, 17-22 May 1992, 659FUL).
- O. Ermer, *Helv. Chim. Acta*, 1991, **74**, 1339.
- Q. Zhu, D. E. Cox, J. E. Fischer, K. Kniaz, A. R. McGhie and O. Zhou, *Nature*, 1992, **355**, 712.
- E. Adman, M. Rosenblum, S. Sullivan and T. N. Margulis, *J. Am. Chem. Soc.*, 1967, **89**, 4540.