Crystallographic Characterisation of the Lattice Structure $C_{60}\cdot[Fe_4(CO)_4(\eta^5\text{-}C_5H_5)_4]$ as the 1/3 Benzene Solvate

Jonathan D. Crane and Peter B. Hitchcock
School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton, East Sussex BN1 9QJ, UK

Co-crystallisation of C_{60} and $[Fe_4(CO)_4(\eta^5\text{-}C_5H_5)_4]$ from benzene solution yields crystals of $C_{60}\cdot[Fe_4(CO)_4(\eta^5\text{-}C_5H_5)_4]\cdot 3C_6H_6$ containing the ordered lattice structure $C_{60}\cdot[Fe_4(CO)_4(\eta^5\text{-}C_5H_5)_4]$ in which the inter-C_{60} contacts are restricted to within parallel double-columnar stacks

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Interesting redox and photophysical properties render buckminsterfullerene (C_{60}) appealing as a building block for new materials, either as the neutral molecule or in its reduced forms.[1-4] In particular Group 1 and 2 metal salts of the reduced anions $C_{60}{}^{n-}$ (n = 3, 10 or 12) have been found to be superconductors with relatively high transition temperatures ($T_c \leqslant 33$ K).[5,6] In these compounds close inter-C_{60} contacts are maintained in three dimensions and the (super)conductivity is isotropic. Restriction of the inter-C_{60} contacts to one or two dimensions will yield anisotropic lattice structures and modify the electrical conduction and/or photoactive properties of these materials. Guest molecules may also be trapped in the interstitial cavities present in a C_{60}-based host lattice. These features can be built into C_{60} compounds through the exploitation of intermolecular forces; notably C_{60} acts as an electron acceptor and forms classical charge-transfer complexes with electron donors through π-stacking interactions. This strategy has been used to stabilise close-packed layers of C_{60} molecules in the ferrocene intercalate $C_{60}\cdot 2[Fe(cp)_2]$ (cp = $\eta^5\text{-}C_5H_5$) in which only one of the cp rings of $[Fe(cp)_2]$ is involved in a π-stacking interaction with C_{60}.[1] The first oxidation potential of the tetranuclear cluster $[Fe_4(CO)_4(cp)_4]$ is $\approx$0.08 V more negative than for $[Fe(cp)_2]$ (in CH_2Cl_2 solution),[7,8] and therefore occurs at $\approx +0.92$ V relative to C_{60}–$C_{60}{}^{-}$. The co-crystallisation of this complex with C_{60} was therefore investigated as it is more likely to bridge between C_{60} molecules as well as form stronger π-stacking interactions.

The fullerene C_{60} (*ca.* 15 mg) was dissolved in benzene at the reflux temperature to produce a saturated solution (5 cm^3) which was filtered hot into a saturated solution of $[Fe_4(CO)_4(cp)_4]$ (*ca.* 75 mg) in benzene (5 cm^3) at room temperature. Upon standing at room temperature for 2–3 d in a sealed flask, black needles of $C_{60}\cdot[Fe_4(CO)_4(cp)_4]\cdot 3C_6H_6$ (10 mg, $\approx$ 30%) were deposited and the structure was determined by single-crystal X-ray diffraction (Fig. 1).*

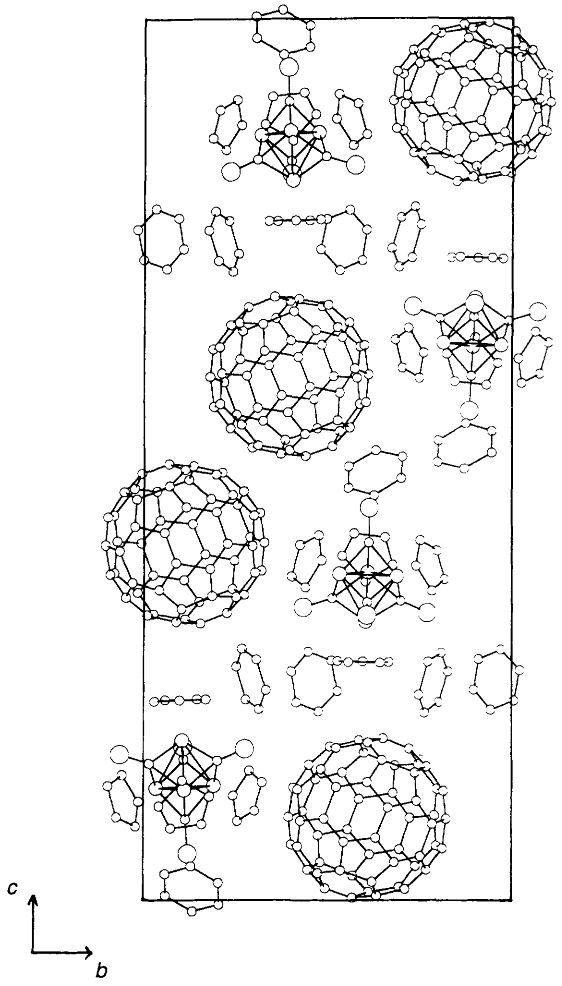

Fig. 1 Unit cell of $C_{60}\cdot[Fe_4(CO)_4(cp)_4]\cdot 3C_6H_6$ viewed perpendicular to the *bc* plane

At the temperature (173 K) of the structure determination the C_{60}, $[Fe_4(CO)_4(cp)_4]$ and C_6H_6 molecules are all ordered and possess no crystallographically imposed symmetry. The molecular structure of the C_{60} molecule is similar to that found in other single-crystal X-ray structure determinations; the

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* Crystal data: $C_{102}H_{38}Fe_4O_4$, M = 1550.8, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 9.944(2), b = 15.922(2), c = 38.368(10) Å, U = 6074.6 Å^3, Z = 4, D_c = 1.70 g cm^{-3}, $F(000)$ = 3144, monochromated Mo-Kα radiation, λ = 0.710 69 Å, μ = 10.0 cm^{-1}, T = 173 K. A crystal of size *ca.* 0.4 × 0.1 × 0.1 mm was used to collect intensities for 5976 unique reflections with $2 < \theta < 25°$ on an Enraf–Nonius CAD4 diffractometer. 4388 Reflections with $|F^2| > 2\sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/Lp$. The Fe atoms were located by heavy-atom methods using SHELXS 86[9] and the rest were located on difference maps. The Fe and C_{60} atoms were refined with anisotropic thermal parameters by full-matrix least-squares analysis using programs from the MOLEN[10] package. The other atoms were refined isotropically and hydrogen atoms were included at fixed calculated positions. Final parameters were: R = 0.065, R' = 0.080, S = 2.2, 761 variables, 4388 observed reflections, $(\Delta/\sigma)_{max}$ = 0.2, $(\Delta\rho)_{max,min}$ = +1.31, − 0.17 e Å^{-3}.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

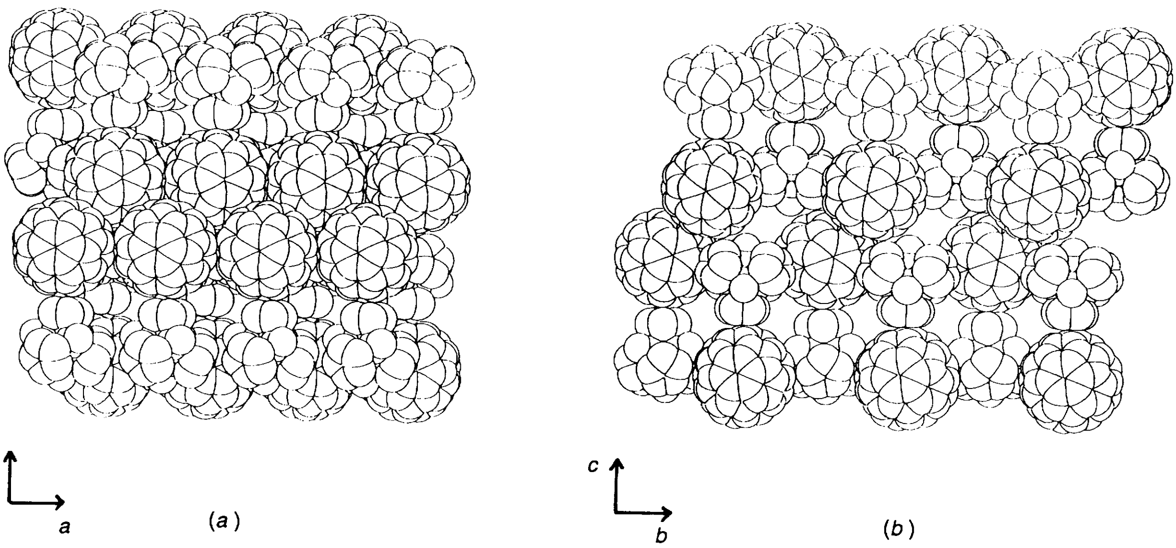

Fig. 2 Space-filling representations of the C_{60}•$[Fe_4(CO)_4(cp)_4]$ lattice structure with the C_6H_6 molecules omitted for clarity. (*a*) View perpendicular to the *ac* plane with the double-columnar stacks of C_{60} molecules parallel to the *a* axis; (*b*) view perpendicular to the *bc* plane showing the isolation of each stack from its neighbours by six co-parallel stacks of $[Fe_4(CO)_4(cp)_4]$ molecules

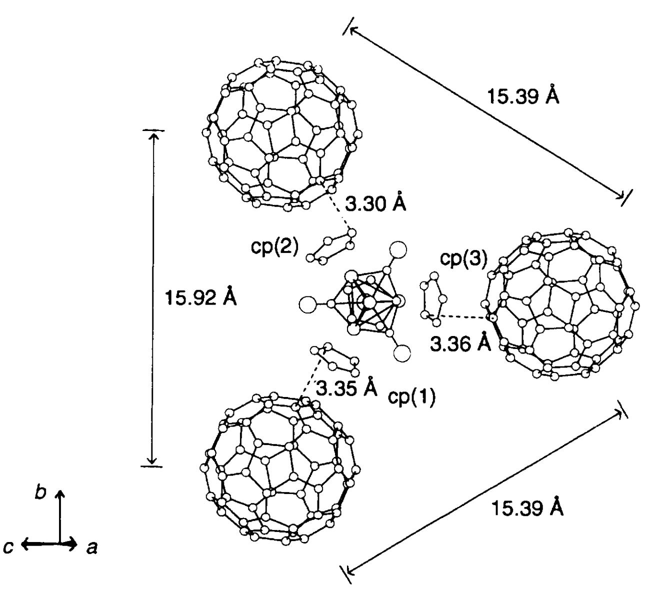

Fig. 3 The $[Fe_4(CO)_4(cp)_4]$ molecule bridges an isosceles triangle of C_{60} molecules (each from different stacks) through C_{60}–cp π-stacking interactions

average centre-to-carbon distance (C_{60} radius) is 3.52(2) Å, and bond length alternation is observed with average intra- and inter-pentagonal C–C distances of 1.46(5) and 1.36(5) Å respectively. The $[Fe_4(CO)_4(cp)_4]$ and C_6H_6 molecules exhibit no unusual structural features.

The structure can be described as a three-dimensional C_{60}•$[Fe_4(CO)_4(cp)_4]$ host lattice (Fig. 2) with guest benzene molecules occupying the interstitial cavities. The only inter-C_{60} contacts occur within the parallel double-columnar stacks aligned with the *a* axis.[2] The C_{60} centre-to-centre distances within these stacks are 9.94 (along *a* axis) and 9.91 Å, and these contacts are between parallel hexagonal rings slipped sideways relative to one another; a similar arrangement is found in the close-packed C_{60} layers in C_{60}•$2[Fe(cp)_2]$.[1] The shortest centre-to-centre inter-C_{60} distance between stacks is 14.38 Å, each stack being isolated from its neighbours by six co-parallel stacks of $[Fe_4(CO)_4(cp)_4]$ molecules, which also act as inter-C_{60} bridges through C_{60}–cp π-stacking interactions. Three of the four cp rings are involved in π stacking and the $[Fe_4(CO)_4(cp)_4]$ molecule lies in an isosceles triangle of C_{60} molecules (Fig. 3), which has two short centre-to-centre distances of 15.39 Å and one long distance of 15.92 Å (parallel to *b* axis). The closest $C(C_{60}) \cdots C(cp)$ contact distances for cp(1), cp(2) and cp(3) are 3.35(2), 3.30(2) and 3.36(2) Å respectively and all three π-stacking interactions are different and asymmetric; cp(2) is approximately parallel to a hexagonal face of the C_{60} molecule and cp(1) and cp(3) are approximately parallel to pentagonal faces, similar to the C_{60}–cp interaction found in C_{60}•$2[Fe(cp)_2]$.

The IR spectrum of C_{60}•$[Fe_4(CO)_4(cp)_4]$ (KBr disc) at room temperature displays a strong carbonyl band at ν(CO) = 1640 cm^{-1}, compared to 1626 cm^{-1} for pure $[Fe_4(CO)_4(cp)_4]$ (KBr disc). This small shift [$\Delta\nu(CO) = +14$ cm^{-1}] to higher wavenumber is consistent with a weak donor–acceptor interaction between the iron complex and the C_{60} molecule; electron withdrawal from the Fe_4 cluster weakens the metal-to-carbonyl back bonding and results in a small ν(CO) shift to higher energy. The four IR bands for the C_{60} molecule are not significantly perturbed either in position or intensity, and are found at 1428, 1182, 576 and 527 cm^{-1}.

Acknowledgements

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