

# A new combination of donor and acceptor: bis( $\eta^6$ -benzene)chromium and hexafluorobenzene form a charge-transfer stacked crystal

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Bis( $\eta^6$ -benzene)chromium reacts with hexafluorobenzene to yield a red charge-transfer complex  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2 \cdot \text{C}_6\text{F}_6]$  which contains stacks of alternating donor and acceptor molecules with close inter- and intrastack contacts; in addition to the charge-transfer complex, formation of  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$  is demonstrated by EPR and IR spectroscopy.

Non-covalent interactions have a major role in determining structures of molecular assemblies. The formation of stacks of donors alternating with acceptors can lead to special electronic and magnetic properties as in  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2][\text{TCNE}]$  or  $[\text{Fe}(\eta^6\text{-C}_6\text{Me}_3\text{H}_3)_2][\text{C}_6(\text{CN})_6]$ .<sup>1,2</sup> Stacking of aromatic rings ( $\pi$ -stacks) represents another motif, this time driven by quadrupolar interactions, e.g. in co-crystals of benzene and hexafluorobenzene.<sup>3</sup> Complex analogues of  $\text{C}_6\text{H}_6 \cdot \text{C}_6\text{F}_6$  are attracting interest for their optoelectronic properties.<sup>4,5</sup> Bis( $\eta^6$ -benzene)chromium **1** has potential for both these types of interaction: it has featured as a donor in  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2][\text{S}_2\text{O}_6 \cdot 2\text{SO}_2]$  and has been employed for crystal engineering.<sup>6,7</sup> Donor-acceptor (DA) complexes are also formed by **1** in  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2][\text{TCNE}]$  and  $[\text{Cr}(\eta^6\text{-C}_6\text{Me}_3\text{H}_3)_2][\text{TCNQ}]$  but they are arranged in stacks of the type  $\dots\text{A}_2\text{DD}\dots$  or in chains.<sup>8</sup>

Several authors have proposed that an electron-transfer process precedes C–F bond activation of perfluoroalkanes and perfluoroarenes by transition metal complexes,<sup>9–11</sup> although experimental support for redox initiation is sparse. If this proposal is to be reconciled with the redox potentials, there must be either preassociation of the fluorocarbon and transition metal complex, or the products must be stabilised by rapid irreversible dissociation (e.g.  $\text{C}_6\text{F}_6^-$  to  $\text{C}_6\text{F}_5 + \text{F}^-$ ), or more likely both.<sup>12</sup> Crabtree *et al.* recently reported that  $[\text{Fe}(\eta^5\text{-C}_5\text{R}_5)_2]$  (R = H or Me) associates with perfluoronaphthalene or perfluorophenanthrene in the solid state to form an irregular DA stack.<sup>13</sup> However, there was no optical evidence for a charge-transfer (CT) interaction. We report that **1** reacts with hexafluorobenzene to form a red CT complex in solution which crystallises as a donor-acceptor stack, and additionally that **1** undergoes one-electron oxidation by  $\text{C}_6\text{F}_6$  to a limited extent.

When a large excess of dry hexafluorobenzene is condensed onto a freshly sublimed sample of **1** and thawed under argon, a claret-coloured solution is obtained from which crystals grow over several weeks at room temperature. The crystals have two habits, red-pink blocks and thin yellow plates, both of which are stable only in the mother liquor. An X-ray crystal structure of a red-pink crystal mounted in its mother liquor in a capillary at room temperature revealed it to be  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2 \cdot \text{C}_6\text{F}_6]$ .<sup>†</sup> The structure contains face-to-face stacks of  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$  moieties alternating with  $\text{C}_6\text{F}_6$  units at regular intervals of ca. 3.5 Å, a value similar to that in  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2][\text{TCNE}]$ .<sup>2</sup> The stacks lie approximately parallel to the body diagonal of the triclinic unit cell (Fig. 1) such that the benzene rings of the  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$  units eclipse the  $\text{C}_6\text{F}_6$  rings in the same stack. The angle between the ring normals of the  $\text{C}_6\text{F}_6$  and  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$  units is 5.9°. Each  $\text{C}_6\text{F}_6$  lies approximately in line with one of the

$\text{C}_6\text{H}_6$  rings in a neighbouring stack. The minimum C...C distance between  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{F}_6$  lies within a stack, while the minimum Cr...F distance lies between stacks (Fig. 2, Table 1). The regularly spaced DA stacks contrast with those of  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2 \cdot \text{C}_{14}\text{F}_{10}]$ <sup>13</sup> and **[1]**<sup>†</sup> $[\text{TCNE}]$ .<sup>8</sup>

We have also attempted to solve the structure of the thin yellow plates at  $-100^\circ\text{C}$ . Although the crystal did not diffract well, we found that the structure was little changed from that of the red-pink blocks. A compression along *b* and *c* led to a contraction of 1.9% in the minimum intrastack C...C distance and 3.7% in the minimum interstack Cr...F distance.

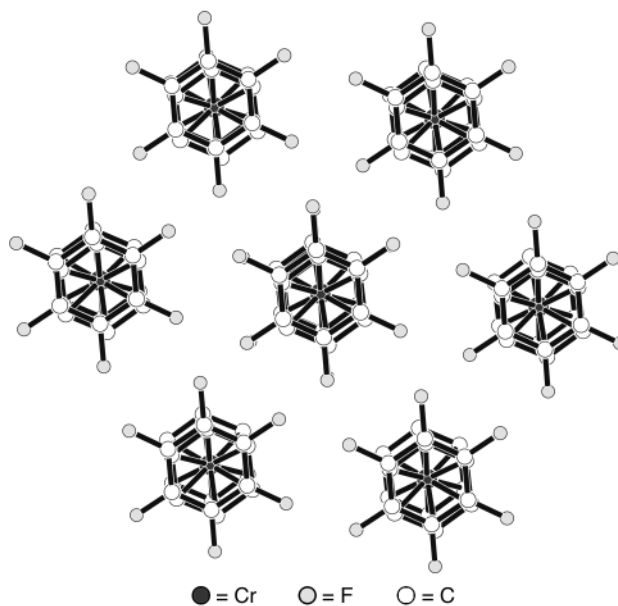


Fig. 1 Packing diagram for  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2 \cdot \text{C}_6\text{F}_6]$ , viewed down the body diagonal of the triclinic cell (hydrogen atoms omitted).

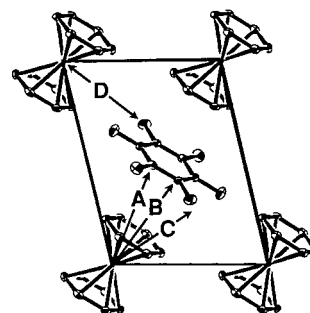


Fig. 2 ORTEP diagram (ref. 15) showing the key intra- and inter-stack spacings within the crystal structure of  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2 \cdot \text{C}_6\text{F}_6]$ , viewed down the *c* axis. The hydrogen atoms are omitted for clarity. The average C–C and Cr–C bond lengths within a  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$  unit are 1.397 and 2.134 Å. For the  $\text{C}_6\text{F}_6$  molecule, the C–C and C–F bond lengths average 1.365 and 1.341 Å.

**Table 1** Minimum contact distances in the structure of  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2\cdot\text{C}_6\text{F}_6]$ 

Label <sup>a</sup>	Type of contact	Contact atoms	Distance/Å
A	Intrastack $\text{C}_6\text{H}_6\cdots\text{C}_6\text{F}_6$	$r(\text{C}\cdots\text{C})$	3.480(4)
B	Intrastack $\text{Cr}\cdots\text{C}_6\text{F}_6$	$r(\text{Cr}\cdots\text{C})$	5.074(3)
C	Intrastack $\text{Cr}\cdots\text{C}_6\text{F}_6$	$r(\text{Cr}\cdots\text{F})$	5.312(3)
D	Interstack $\text{Cr}\cdots\text{C}_6\text{F}_6$	$r(\text{Cr}\cdots\text{F})$	4.490(2)

<sup>a</sup> labels A, B, C, D refer to Fig. 2.

When the reaction of **1** with  $\text{C}_6\text{F}_6$  was carried out with higher concentrations of **1**, a fine yellow precipitate separated from the claret solution. A UV–VIS absorption spectrum of the solution, measured after filtering off the precipitate, showed an absorption at 503 nm and a shoulder at 390 nm.<sup>16†</sup> On freezing in liquid nitrogen, the claret solution turned to a yellow glass, but the claret colour returned on melting. The corresponding absorption maxima lie to longer wavelength (542, 414 nm) on reaction of  $[\text{Cr}(\eta^6\text{-1,4-C}_6\text{H}_4\text{Me}_2)_2]$  with  $\text{C}_6\text{F}_6$  and to shorter wavelength (424 nm)§ on reaction of **1** with  $\text{C}_6\text{F}_5\text{H}$ . These absorption bands are assigned to charge-transfer transitions of the complexes  $[\text{Cr}(\eta^6\text{-arene})_2\cdot\text{C}_6\text{F}_{6-n}\text{H}_n]$  ( $n = 0, 1$ ) which must be present in solution. Redox potentials suggest that the ground state of the complex will be close to the  $\text{A}\cdot\text{D}$  description and the excited state close to  $\text{A}^+\cdot\text{D}^-$ .¶

The solutions from reaction of **1** with  $\text{C}_6\text{F}_6$  (whether dilute or more concentrated) gave a broad EPR signal at  $g = 1.987$  consistent with formation of  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+ \mathbf{1}^+$ .<sup>6</sup> Solid-state EPR spectra of the yellow precipitate from reaction of **1** with  $\text{C}_6\text{F}_6$  also revealed the presence of  $\mathbf{1}^+$  ( $g_{\parallel} = 2.002$ ,  $g_{\perp} = 1.983$ ), while IR spectra showed characteristic bands of both **1** and  $\mathbf{1}^+$ .<sup>17</sup> The presence of fluoride as a corresponding anion was revealed by its reaction with  $\text{Me}_3\text{SiOTf}$  yielding  $\text{Me}_3\text{SiF}$ .|| In order to ascertain the proportion of **1** which is oxidised, we investigated the effect of addition of  $\text{C}_6\text{F}_6$  to toluene solutions of **1**. A control sample of **1** in toluene showed only traces of  $\mathbf{1}^+$ . On addition of 2 and 5 equiv. of  $\text{C}_6\text{F}_6$ , well-resolved resonances ( $A_{\text{H}} = 3.4$  G) for  $\mathbf{1}^+$  were observed with intensities ca. 20 fold and 48 fold greater than the control, respectively. Comparison with the resonance of a standard solution of TEMPO ( $10^{-4}$  mol  $\text{dm}^{-3}$  in toluene) provided lower-limiting estimates that the solutions of **1** were 0.5 and 3.3% oxidised, respectively.\*\* The extent of oxidation is appreciably higher than expected to arise from impurities in the hexafluorobenzene. The formation of  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+\text{F}^-$  is reminiscent of the reaction of cobaltocene with perfluoroalkanes.<sup>10</sup>

These experiments lead to the following conclusions. (i) A donor–acceptor complex is formed between  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$  **1** and  $\text{C}_6\text{F}_6$  with a long-wavelength absorption in solution, assigned to a CT transition between **1** and  $\text{C}_6\text{F}_6$ . (ii) The complex crystallises as  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2\cdot\text{C}_6\text{F}_6]$  with a ...DADA... stacked structure with close intra- and inter-stack contacts. The claret colour is observed in the larger crystals. The structure is probably stabilised by charge-transfer and  $\pi$ – $\pi$  interactions. (iii) In addition to  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2\cdot\text{C}_6\text{F}_6]$ , salts including  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+\text{F}^-$  are formed in low conversion although half-wave potentials suggest that **1** is incapable of reducing  $\text{C}_6\text{F}_6$ .¶ (iv) The formation of the donor–acceptor complex and the oxidation of **1** provide support for related mechanisms for reactions of metal–hydride complexes with fluoroarenes.<sup>11, 12</sup>

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## Notes and references

† Crystal data for  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2\cdot\text{C}_6\text{F}_6]$ :  $\text{C}_{18}\text{H}_{12}\text{CrF}_6$ ,  $M = 394.28$ , red–pink blocks, triclinic, space group  $P1$ ,  $a = 7.3254(8)$ ,  $b = 9.2627(9)$ ,  $c = 6.6102(8)$  Å,  $\alpha = 100.026(9)$ ,  $\beta = 112.327(8)$ ,  $\gamma = 97.532(9)^\circ$ ,  $V = 398.87(8)$  Å<sup>3</sup>,  $Z = 1$ ,  $T = 293(2)$  K,  $\mu(\text{Mo–K}\alpha) = 0.778$  mm<sup>−1</sup>,  $F(000) = 198$ , 1477 reflections measured, 1401 unique ( $R_{\text{int}} = 0.040$ ), 116 parameters. The crystal was mounted in a capillary in its mother liquor. The structure was solved by direct methods (SHELX) (ref. 14) and refined by full-matrix least-squares on  $F^2$ . Goodness of fit on  $F^2$  1.083, final  $R1 [I > 2\sigma(I)]$   $R1 = 0.0392$ ,  $wR2 = 0.1027$ . CCDC 182/1238. See <http://www.rsc.org/suppdata/cc/1999/1027/> for crystallographic files in .cif format.

‡  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$  is yellow–green with a weak band at 640 nm and an intense band at 320 nm. The corresponding cation exhibits weak bands in the near-IR region and a more intense band at 340 nm (ref. 16). The CT band of  $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2\cdot\text{SO}_2$  is observed at 540 nm (ref. 6).

§ The short-wavelength shoulder will overlap the bands of  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$  in  $\text{C}_6\text{F}_5\text{H}$ .

¶ The half-wave potentials of  $\text{C}_6\text{F}_6/\text{C}_6\text{F}_6^-$  and  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+ / [\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$  are  $-2.55$  and  $-0.68$  V respectively vs. SCE. (ref. 18).

|| Characterisation of the anion in the yellow precipitate was complicated by paramagnetic  $\mathbf{1}^+$ . The precipitate was dissolved in  $\text{CD}_2\text{Cl}_2$ ,  $\text{Me}_3\text{SiOTf}$  added and the volatiles condensed into an NMR tube.  $\text{Me}_3\text{SiF}$  was identified by the eight central lines of the decet at  $\delta = 157.96$  ( $J_{\text{HF}} 7.6$  Hz) in the <sup>19</sup>F NMR spectrum (ref. 19). A control experiment with  $\text{C}_6\text{F}_6$ ,  $\text{CD}_2\text{Cl}_2$  and  $\text{Me}_3\text{SiOTf}$  generated only traces of  $\text{Me}_3\text{SiF}$ .

\*\* Complex **1** was freshly sublimed before use. Solutions in toluene ( $0.047$  mol  $\text{dm}^{-3}$ ) were made up in an argon-filled glove-box;  $\text{C}_6\text{F}_6$  (99.9%), previously dried over molecular sieves and degassed by freeze–pump–thaw methods, was added in the box with a microsyringe. Typical impurities are  $\text{C}_6\text{F}_5\text{Cl}$  and  $\text{C}_6\text{F}_5\text{Cl}_2$ . Since the addition of  $\text{C}_6\text{F}_6$  causes slight precipitation, the values of the percentage oxidation are lower limits.

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