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The effect of counter-ions on the supramolecular arrangement of (benzonitrile)[1,2-bis(diphenylphosphino)ethane](η^5-cyclopentadienyl)iron(II) cations

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The title compound, [1,2-bis(diphenylphosphino)ethane](η^5-cyclopentadienyl)(4-nitrobenzonitrile)iron(II) iodide, [Fe(η^5-C_5H_5)($C_7H_4N_2O_2$)($C_{26}H_4P_2$)]I, crystallizes in the non-centrosymmetric space group *Cc*, which is a promising result for obtaining quadratic non-linear optical properties. However, the packing shows that the iodide counter-ion promotes the cancellation of almost all the dipoles, resulting in a supramolecular motif of cationic chains aligned in opposite directions making an angle of 35.2°. The use of PF_6^- as counter-ion induces the crystallization of the complex in a centrosymmetric space group. These results show that the introduction of different counter-ions, of different size and geometry, allows specific and directional intermolecular interactions that can determine the formation of a particular type of crystal packing.

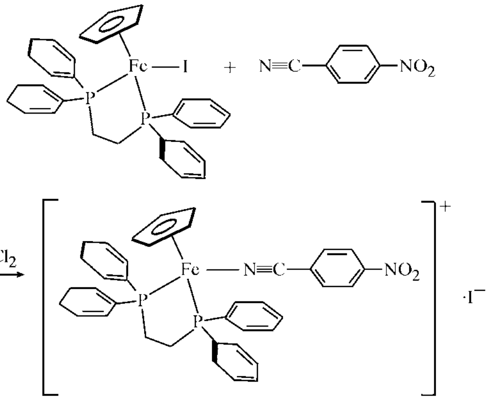
Comment

Molecular crystals, based on organic molecules or transition metal coordination complexes which assemble in the solid state as a consequence of non-covalent interactions, have been the subject of important research during the last decade (Aakeroy & Beatty, 2001). The interest in these materials stems from the potential to manipulate their solid-state properties by systematic variations of their molecular features and crystal-packing motifs.

The design of organometallic materials for second-order non-linear optical (NLO) applications is based on two steps, namely the maximization of the molecular non-linearity by the modification of the structural features of the molecule, and optimization of the crystal packing of the molecules in the solid state. Although the relation between macroscopic non-linearity and crystal structure is not yet completely understood and experimentalists still do not have complete control over the spatial arrangement of the molecules, the mechanisms leading to large microscopic effects are well understood and a large number of NLO molecules have been synthesized and investigated (Goovaerts *et al.*, 2001). Therefore, after an appropriate selection of molecules with high β (the molecular hyperpolarizability associated with second-harmonic generation phenomena), much improvement is possible if solid-state materials can be obtained with the desired arrangement to display enhanced macroscopic properties.

Among the different strategies developed to overcome this major obstacle, the creation of Coulombic interactions by varying the counter-ions is one approach (Marder *et al.*, 1991; Dias, Garcia, Rodrigues *et al.*, 1994). This effect can provide the driving force to overcome the centrosymmetry originating from dipolar interaction in organic and organometallic compounds. Some additional factors may also contribute to a better response in the solid state, these being mainly related to an adequate alignment of the chromophore in the bulk material, leading to optimal phase matching (Garcia, Rodrigues, Dias *et al.*, 2001).

From our previous work on organometallic compounds containing *p*-substituted benzonitriles coordinated to several iron(II) and ruthenium(II) derivatives (Dias, Garcia, Mendes *et al.*, 1994; Garcia, Robalo *et al.*, 2001; Wenseleers *et al.*, 1998; Garcia *et al.*, 2003), we have identified the metallic fragment [Fe(η^5-cyclopentadienyl)(dppe)]$^+$ [dppe is 1,2-bis(diphenylphosphino)ethane] as a good electron-donor group towards the coordinated nitrile and, in particular, the cationic complex [(η^5-C_5H_5)(dppe)Fe(*p*-$NCC_6H_4NO_2$)]$^+$, due to its good stability in solution and the solid state, seemed to be a good candidate for future studies. In order to improve the understanding of the role of counter-ion variation in the bulk material response, we have synthesized and characterized the new title complex, [FeCp(*p*-$NCC_6H_4NO_2$)(dppe)]I, (where Cp is η^5-C_5H_5), (I), and present its structural characterization here.



(I)

Complex (I) was obtained by the displacement of iodide by the nitrile ligand in the precursor compound [FeCpI(dppe)] (see scheme) with a slight excess of 4-nitrobenzonitrile in dichloromethane at room temperature. The dark-red cationic

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complex which formed was naturally stabilized by the iodide counter-ion. After work-up and recrystallization from dichloromethane–diethyl ether, the complex was obtained as dark-red crystals, fairly stable towards oxidation in air and moisture in the solid state. The formulation is supported by analytical data, and by IR and ^1H, ^{13}C and ^{31}P NMR spectra.

Complex (I) shows the characteristic $\nu(C\equiv N)$ stretching band at 2215 cm^{-1}, and two bands at 1513 and 1335 cm^{-1} for the asymmetric and symmetric stretching of the NO_2 group, respectively. The $\nu(C\equiv N)$ band shows a negative shift of 25 cm^{-1}. This result is consistent with our earlier studies (Diaz *et al.*, 1993; Garcia, Robalo *et al.*, 2001) of similar complexes, where the negative shift for the $\nu(C\equiv N)$ stretching vibration upon coordination was related to a decrease in the CN bond order, caused by the π back-bonding between the *d* orbitals of the metal and the π^* orbitals of the CN group.

Analysis of the NMR data shows that the coordination of *p*-nitrobenzonitrile leads to a significant shielding of the aromatic *ortho*-H atoms compared with the corresponding uncoordinated nitrile ligand (7.90 p.p.m. in $CDCl_3$). These data corroborate the metal–nitrile interaction based on the metal→nitrile π back-donation contribution. Comparing these results with the data obtained previously (Garcia, Robalo *et al.*, 2001) for the complex $[FeCp(dppe)(p\text{-}NCC_6H_4NO_2)]PF_6$ (6.75 p.p.m. for the *ortho* H-atoms in $CDCl_3$), we observe a difference of approximately 0.3 p.p.m. between the values found for these compounds with two different counter-ions, consistent with our earlier studies for similar ruthenium(II) complexes (Dias, Garcia, Rodrigues *et al.*, 1994).

The UV–vis absorption spectrum of complex (I), recorded in chloroform solution, exhibits an intense broad absorption band at 256 nm (ε = 3920 M^{-1} cm^{-1}) and a lower energy band at 464 nm (ε = 860 M^{-1} cm^{-1}), this band being attributable to a d–π^* metal-to-ligand charge-transfer (MLCT) transition from the Fe centre to the nitrile ligand. Comparison of this value with the corresponding data for the complex $[FeCp(dppe)(p\text{-}NCC_6H_4NO_2)]PF_6$ (461 nm; ε = 460 M^{-1} cm^{-1} for the MLCT band) shows a more intense lower energy MLCT for the iodide complex. Since such low-energy MLCT bands are typically associated with large molecular quadratic NLO responses (Garcia, Robalo *et al.*, 2001; Garcia *et al.*, 2002), the title compound seems to be a promising candidate for NLO properties. Furthermore, these results suggest that the Coulombic interactions derived from counter-ion variation may have an additional effect on the electronic interaction and contribute to a more effective polarization in the chromophore. This intramolecular effect should be more intense in the solid state.

The molecular structure of (I) is shown in Fig. 1. The cation has the typical pseudo-octahedral three-legged piano stool geometry around the Fe, on the assumption that the Cp group takes up three coordination sites. This geometry is supported by the angles around the metal centre, which are all close to 90° (Table 1), as well as by the remaining angles P1—Fe1—*Cp* [126.0 (12)°], P2—Fe1—*Cp* [131.9 (9)°] and N1—Fe1—*Cp* [121.6 (6)°] (*Cp* is the centroid of the cyclopentalienyl ring), which are all larger, as expected. This geometrical feature is comparable with those found in the family of compounds reported by our group (Garcia, Robalo *et al.*, 2001; Garcia *et al.*, 2003).

The Fe—N bond length in (I) [1.875 (13) Å] is similar to the corresponding distance found in $[FeCp(dppe)(p\text{-}NCC_6$-

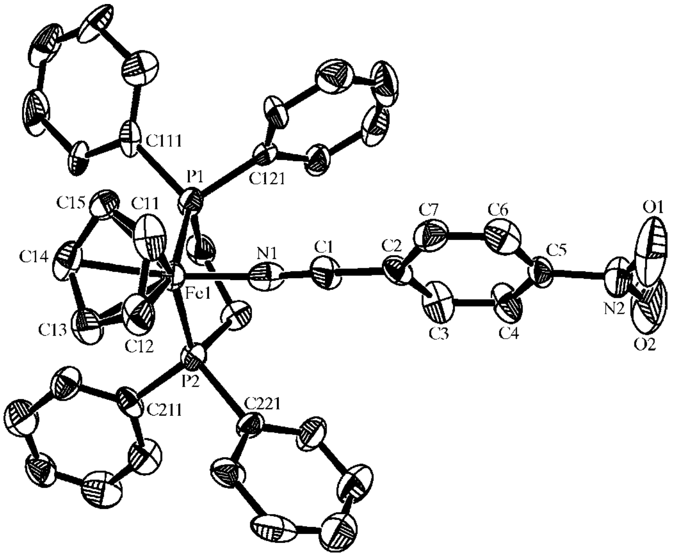

Figure 1
A view of the cation of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

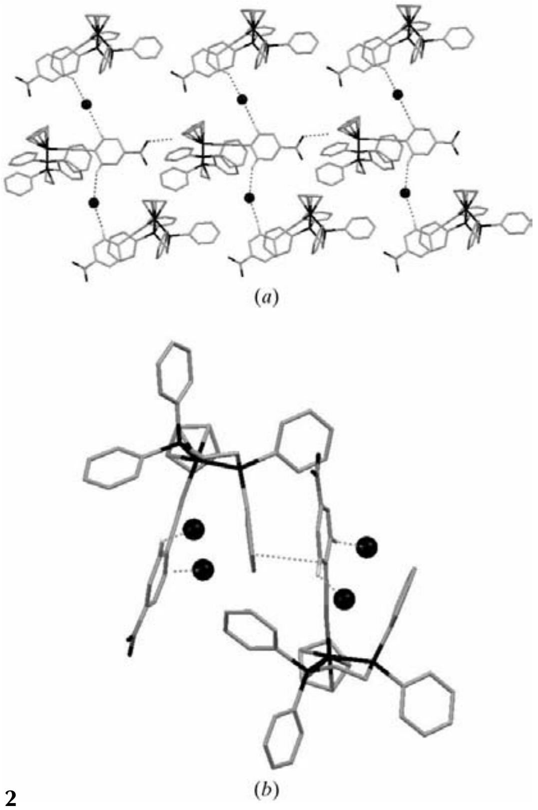

Figure 2
(*a*) A view of the packing, showing the cationic chain along the [$\overline{1}$10] direction. (*b*) A view of the crystal packing of (I) along a direction perpendicular to the *ac* plane.

$H_4NO_2)]PF_6$ (Garcia, Robalo *et al.*, 2001) (Table 1; Garcia, Robalo *et al.*, 2001). These X-ray data corroborate the spectroscopic IR and NMR data obtained for the complex. The nitrile group shows an almost linear geometry, with Fe—N1—C1 and N1—C1—C2 angles of 175.6 (11) and 177.9 (16)°, respectively, indicating that the Fe atom and the benzonitrile ligand are in the same plane. These features provide evidence for the existence of π back-donation in the solid state. With the aim of enhancing the molecular NLO properties in the solid state and considering the different crystallization results obtained using PF_6^- and I^- as counter-ions, which have probably induced centrosymmetric and asymmetric crystallization, respectively, we proposed to analyse the crystal packing obtained in both cases and draw conclusions on the role of the anion in the process.

Complex (I) has a non-centrosymmetric packing arrangement. A short hydrogen-bond interaction, involving the O atom of the nitrile moiety and a Cp H atom [$C14\cdots O1^i$ = 3.51 (3) Å, $H14\cdots O1^i$ = 2.64 (3) Å and $C14—H14\cdots O1^i$ = 157 (1)°; symmetry code: (i) $-\frac{1}{2}+x, -\frac{1}{2}+y, z$] promotes the formation of a cationic chain along the $[\bar{1}10]$ direction (Fig. 2*a*). Each cationic chain is aligned in a direction almost opposite to that of the molecules in adjacent chains, making an angle of 35.2°, as they are connected by an iodide anion [$C3—H3\cdots I1$ = 3.03 (4) Å and $C7—H7\cdots I1$ = 3.06 (4) Å], resulting in alternating chains of anions and cations along the diagonal of the *ac* plane. The effect of the iodide anion is the quasi-cancellation of the dipoles.

Finally, a π–π stacking interaction (3.32 Å) between the benzene group of the nitrile and a phosphine phenyl ring is observed between cations, as can be seen in Fig. 2(*b*), along a direction perpendicular to the *ac* plane, which strengthens the relative position of the cations in two adjacent planes.

The crystal packing analysis of complex [FeCp(dppe)(*p*-$NCC_6H_4NO_2$)]PF_6, whose molecular structure we reported previously (Garcia, Robalo *et al.*, 2001), shows the cancellation of molecular dipoles resulting from the formation of a hydrogen bond between the O atoms of the nitrile groups and the H atoms of the CH_2 group of the phosphines of two other molecules, thus forming a tetramer, depicted in Fig. 3(*a*). This tetramer promotes two dipole cancellations, the first between the molecules connected through the H atoms acting as bridges, and the other between the two molecules to which the H atoms belong. This geometry is strengthened by intermolecular π–π interactions between the benzene rings of two nitrile moieties, as well as with a phenyl ring of a phosphine (Fig. 3*b*).

In this structure, there are two types of PF_6 molecules, each with half occupancy; one interacts with four different cations, with short contacts ranging from 3.150 to 3.355 Å, while the other only interacts with two cationic fragments, with distances in the range 3.174–3.124 Å. As can be seen in Fig. 3(*b*), the cationic molecules form a column along *a*, while the PF_6^- anions occupy the channels along *b*.

From these results, we can conclude that the introduction of different counter-ions, of different size and geometry allowing specific and directional intermolecular interactions, can be a determining factor for the formation of a particular type of crystal packing. Although interactions of the same type (short contacts between the counter-ion and cationic molecules, π–π stacking interactions and hydrogen bonding between the O atoms of the terminal nitro group and neighbouring molecules) were found in both cases, they interact synergistically, promoting different arrangments in the crystal packing.

Further studies are in progress to introduce new counter-ions, and second-harmonic generation measurements on the final materials are being carried out.

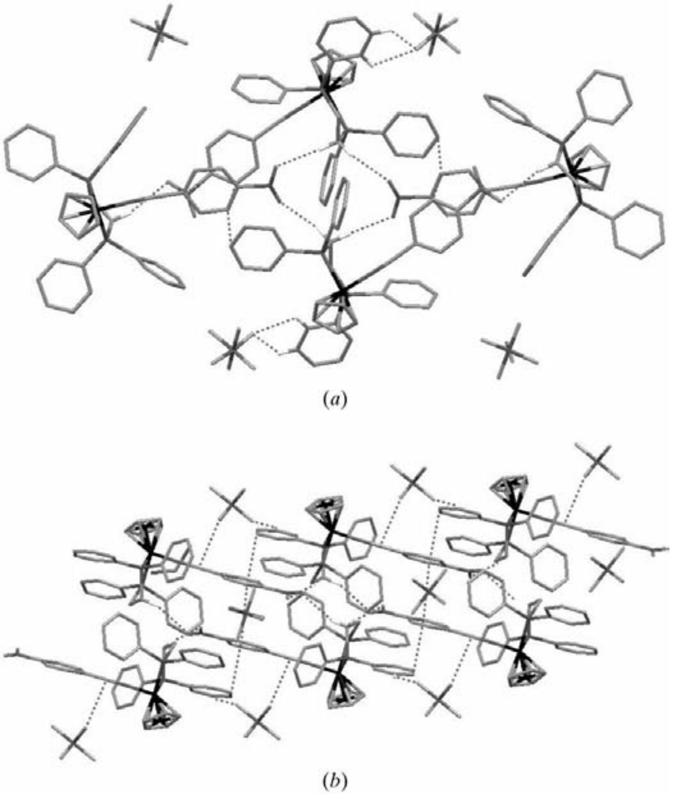

Figure 3
(*a*) A view of the tetramer motif formed in the crystal packing of the complex [CpFe(dppe)(*p*-$NCC_6H_4NO_2$)]PF_6. (*b*) A view of the dipole cancellation enhancing the π–π stacking interactions.

Experimental

To a solution of [Fe(η^5-C_5H_5)I(dppe)] (Garcia, Robalo *et al.*, 2001) (0.3 mmol) in dichloromethane (20 ml) was added 4-nitrobenzonitrile (0.33 mmol, 1.1 equivalents) at room temperature. The mixture was stirred at room temperature for 22 h. A change in the colour of the solution was observed from purple to dark red. The red solution was filtered, evaporated under vacuum to dryness and washed several times with diethyl ether. The dark-red residue was further purified by vapour diffusion of diethyl ether into a concentrated dichloromethane solution, affording dark-red crystals of (I) [yield 167 mg, 70%; m.p. 433 K (decomposition)]. Analysis calculated for $C_{38}H_{33}FeIN_2O_2P_2$: C 57.46, H 4.19, N 3.53%; found: C 56.91, H 4.27, N 3.49%. IR (KBr, ν, cm^{-1}): 2215 ($C\equiv N$), 1513 and 1335 (NO_2); ^1H NMR (300 MHz, $CDCl_3$): δ 2.65 (*m*, 4H, CH_2, dppe), 4.65 (*s*, 5H, η^5-C_5H_5), 7.02 (*d*, 2H, *J* = 8.4 Hz, H_2, H_6), 7.20–7.80 (*m*, 20H, C_6H_5, dppe), 7.97 (*d*, 2H, *J* = 8.4 Hz, H_3, H_5); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 28.48 (*t*, J_{CP} = 20.4 Hz, CH_2, dppe), 80.57 (η^5-C_5H_5), 116.91 (C1), 123.68 (C3, C5), 129.28 (*m*, J_{CP} = 4.4 Hz, C_6H_5-dppe), 129.64 (*m*, C_6H_5-dppe), 130.69 (C2, C6), 131.04 (C_6H_5-dppe), 131.31 (NC), 133.05 (C_6H_5-dppe), 133.81 (C_6H_5-dppe), 136.41 (*t*, J_{CP} = 20.9 Hz, C-*ipso*, C_6H_5-dppe), 149.04 (C4); $^{31}P\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 97.64 (dppe); UV–vis ($CHCl_3$, λ_{max}, nm): 256 (ε = 3920 M^{-1} cm^{-1}) and 464 (ε = 860 M^{-1} cm^{-1}).

Crystal data

$[Fe(C_5H_5)(C_7H_4N_2O_2)(C_{26}H_4P_2)]I$
M_r = 794.35
Monoclinic, *Cc*
a = 10.602 (3) Å
b = 26.834 (7) Å
c = 12.489 (3) Å
β = 102.77 (2)°
V = 3465.2 (16) Å^3

Z = 4
D_x = 1.523 Mg m^{-3}
Mo *K*α radiation
μ = 1.46 mm^{-1}
T = 293 (2) K
Prism, dark red
0.4 × 0.2 × 0.2 mm

Data collection

Enraf–Nonius MACH3 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.508, T_{max} = 0.645 (expected range = 0.589–0.748)
3987 measured reflections

3987 independent reflections
2074 reflections with $I > 2\sigma(I)$
R_{int} = 0
θ_{max} = 27.0°
3 standard reflections every 400 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.071
$wR(F^2)$ = 0.155
S = 0.95
3987 reflections
415 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0682P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.007
$\Delta\rho_{max}$ = 0.66 e Å^{-3}
$\Delta\rho_{min}$ = −0.58 e Å^{-3}
Absolute structure: Flack (1983), with 120 Friedel pairs
Flack parameter: −0.03 (4)

Table 1
Selected geometric parameters (Å, °).

Fe1—N1	1.875 (13)	C4—C3	1.34 (2)
Fe1—P1	2.209 (4)	C4—C5	1.366 (19)
Fe1—P2	2.211 (4)	C2—C7	1.370 (18)
N1—C1	1.171 (17)	C2—C3	1.40 (2)
C6—C7	1.335 (19)	C5—N2	1.462 (18)
C6—C5	1.388 (19)	O1—N2	1.207 (19)
C1—C2	1.390 (19)	N2—O2	1.20 (2)
N1—Fe1—P1	90.5 (3)	C1—N1—Fe1	175.6 (11)
N1—Fe1—P2	87.7 (3)	N1—C1—C2	178.0 (16)
P1—Fe1—P2	86.52 (14)		

All phenyl and cyclopentadienyl H atoms were positioned using an idealized aromatic geometry, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C). Methylene H atoms were also placed in idealized positions, with C—H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C). Poor crystal quality precluded the acquisition of more accurate data.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR99* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PLATON* (Spek, 2003) and *enCIFer* (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3019). Services for accessing these data are described at the back of the journal.

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