# A New Class of Electrically Conducting Organometallic Salts with an Unprecedented Metallocene Stack. Preparation and Crystal Structures of $\eta^5$-Cyclopentadienyl-$\eta^6$-tri- and hexa-methylbenzeneiron(II) Tetracyano-*p*-quinomethanides

**Rose-Marie Lequan,[a] Minh Lequan,[a]* Gerard Jaouen,[a] Lahcene Ouahab,[b] Patrick Batail,[b]* Jean Padiou,[b] and Ronald G. Sutherland[c]**

[a] *Ecole Nationale Supérieure de Chimie de Paris, URA CNRS 403, 75231 Paris, France*
[b] *Laboratoire de Chimie du Solide et Inorganique Moléculaire, LA CNRS 254, Université de Rennes, 35042 Rennes, France*
[c] *Department of Chemistry, University of Saskatchewan, Saskatoon, Canada S7N 0W0*

Redox reactions between $[(cp)FeAr]^+I^-$ (cp = $\eta^5$-$C_5H_5$; Ar = 2,4,6-$Me_3C_6H_3$ or $C_6Me_6$; readily prepared from the parent $PF_6$ salts by exchange with KI on anionic resin) and tetracyanoquinodimethane (TCNQ), afford electrically conducting, single crystals of the title compounds whose structures reveal, as a consequence of the difference in size of the two parallel planar ligands, one-dimensional segregated stacks of organometallic cations and $TCNQ^{\frac{1}{2}-}$ anions, a situation unique in metallocene complexes with electron acceptors.

Charge-transfer reactions between metallocenes and organic electron-acceptors have produced compounds with a variety of interesting properties.[1] Few of the materials, however, are conducting and/or are obtained as good quality single-crystals. This paper reports the high-yield syntheses and crystal structures of previously unknown conducting closed-shell iron(II) mixed sandwich tetracyano-*p*-quinodimethane salts.

Redox reactions[2] between $[(cp)FeAr]^+I^-$ (**1**) readily prepared[3] from the parent $PF_6$ salts[4] by exchange with KI on Amberlyst A-26 resin in acetonitrile, and TCNQ in boiling acetonitrile affords the corresponding tetracyanoquinodimethanide salts (**2a**) and (**2b**)† [equation (1)] as large dark-green needles by slow cooling of the solution mixture to room temperature.

$$\underset{(\mathbf{1})}{[(cp)FeAr]^+I^-} \xrightarrow[\text{MeCN}]{\text{TCNQ}} \underset{(\mathbf{2})}{[(cp)FeAr]^+[(TCNQ)_2]^-} \qquad (1)$$

cp = $\eta^5$-$C_5H_5$ **a**; Ar = 2,4,6-$C_6H_3Me_3$
**b**; Ar = $C_6Me_6$

---

† Satisfactory elemental analyses were obtained.

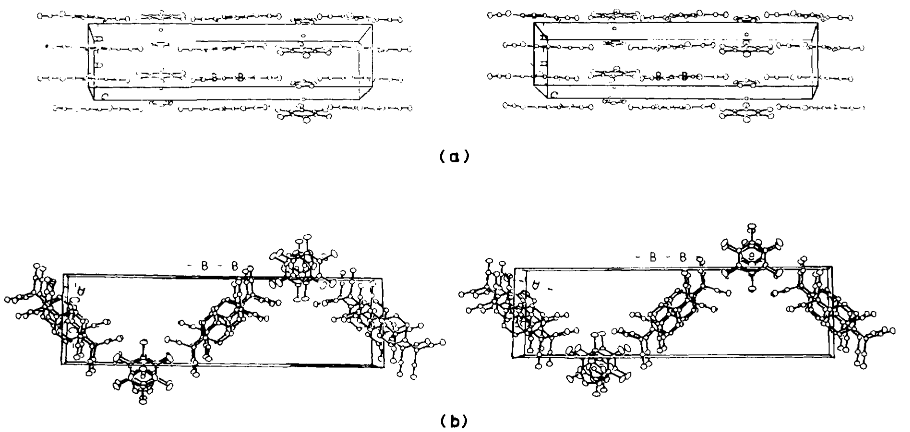

**Figure 1.** Stereoviews of the crystal structure of (**2b**) (a) showing the stack direction and (b) looking along the stack.

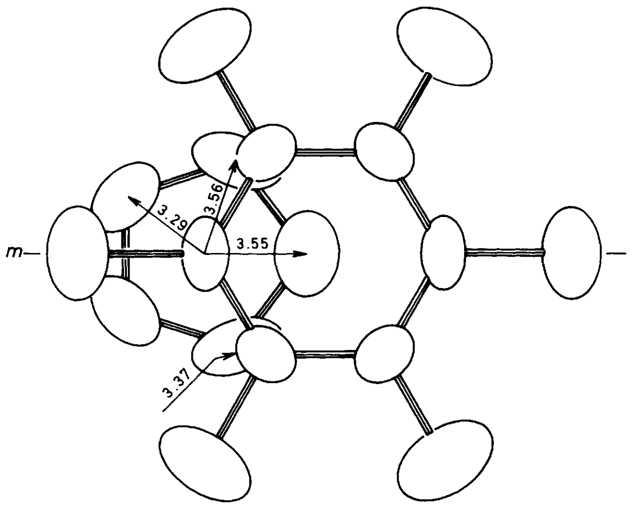

**Figure 2.** The cp–C$_6$Me$_6$ inter-complex overlap (50% probability ellipsoids; distances in Å). For comparison, the average intra-complex C(cp) $\cdots$ C(C$_6$Me$_6$) distance is 3.26 Å.

Powder diffraction showed that compounds (**2a**) and (**2b**) are isostructural and a single-crystal *X*-ray structure determination was carried out on (**2b**) only.‡ The crystal structure (Figure 1) is composed of one-dimensional segregated stacks (along the needle axis *a*) of organometallic cations and TCNQ$^{\frac{1}{2}-}$ anions.[5] Within the TCNQ stack, the mode of overlap is of the usual ring-over-exocyclic bond type. However, an unusual zig-zag configuration,[6] which matches neatly the dissymetric organometallic cation, is observed rather than the common slipped sequence found for most TCNQ salts. The TCNQ molecule is slightly nonplanar with both C(CN)$_2$ groups bent over the same side of the central ring. The spacings between the central TCNQ rings are uniform (3.35 and 3.37 Å) as are those between the C$_8$ rings (including the quinonoid carbons; 3.34 and 3.37 Å) yet are larger than in TTF (tetrathiafulvalene)–TCNQ (3.17 Å).[7] This is significantly different from other 1 : 2 TCNQ salts[8] which all have dimerized stacks. Consistently the materials exhibit fairly high activated d.c. electrical conductivities [$E_a = 0.08$ and 0.14 eV for (**2a**) and (**2b**)] of 0.21 and 4.13 $\Omega^{-1}$ cm$^{-1}$ respectively at room temperature with no maxima in the temperature dependence of the conductivities§ as in related 1 : 2 TCNQ salts.

The metallocenes are located on sites of *m* symmetry with the successive cyclopentadienyl and hexamethylbenzene rings on top of each other. The cp–Fe–C$_6$Me$_6$ axis is essentially colinear (15°) with the stacking axis. This contrasts with the usual ferricenium cation–TCNQ complexes where large tilting (45°) precludes any inter-complex ring-to-ring interaction.[1c] The intra-complex inter-ring distance is 3.211(1) Å with Fe–ring centre distances of 1.665(1) Å (cp) and 1.546(1) Å (C$_6$Me$_6$) similar to the corresponding distance reported for the isoelectronic complex (cp)Fe($\eta^5$-C$_6$Me$_5$CH$_2$).[9] This demonstrates that in the metallocene the metal retains its closed-shell d$^6$ configuration.

The cp–C$_6$Me$_6$ inter-complex ring-to-ring separation is 3.36 Å, the expected thickness of aromatic rings,[10] which brings the rings closer than in the pseudo-stack described for 1,1′-dimethylferricenium(TCNQ)$_2$ (3.63 Å).[1e,6] The carbon atoms are at van der Waals distances and the overlap of the rings (Figure 2) is not at an optimum, yet the structural requirement for developing a one-dimensional band structure

---

‡ *Crystal data*: (**2a**), C$_{38}$H$_{25}$N$_8$Fe, $M = 649.52$, monoclinic, space group $P2_1/m$, $a = 6.693(8)$, $b = 30.052(9)$, $c = 8.630(9)$ Å, $\beta = 101.23(5)°$, $U = 1702.5$ Å$^3$, $D_c = 1.27$ g cm$^{-3}$, $Z = 2$. (**2b**), C$_{41}$H$_{31}$N$_8$Fe, $M = 691.60$, monoclinic, space group $P2_1/m$, $a = 6.718(6)$, $b = 30.032(9)$, $c = 8.649(7)$ Å, $\beta = 101.02(4)°$, $U = 1712.9$ Å$^3$, $D_c = 1.34$ g cm$^{-3}$, $Z = 2$, $\mu$(Mo-$K_\alpha$) = 4.79 cm$^{-1}$, $R = 0.045$, $R_w = 0.048$ for 1261 independent intensities with $I \geqslant 3\sigma(I)$. Diffraction data were collected using an Enraf-Nonius CAD4 diffractometer. The structure was solved by a combination of conventional heavy-atom methods and the program MULTAN. Atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ The conductivities were measured by a standard four-probe method along the stacking direction between room temperature and 260 and 175 K for (**2a**) and (**2b**) respectively. Below those temperatures cracks repeatedly occurred in the crystals.

out of vacant $\pi^*$ ligand orbitals of the individual metallocenes has been met.

*Received, 15th June 1984; Com. 838*

## References

1 (a) U. T. Mueller-Westherhoff and P. J. Eilbracht, *J. Am. Chem. Soc.*, 1972, **94**, 9271; (b) S. Z. Goldberg, B. Spivack, G. Stanley, R. Eisenberg, D. M. Braitsch, J. S. Miller, and M. Abkowitz, *ibid.*, 1977, **99**, 110; (c) C. Willi, A. H. Reis, Jr., E. Gebert, and J. S. Miller, *Inorg. Chem.*, 1981, **20**, 313; (d) C.-P. Lau, P. Sinh, S. J. Cline, R. Seiders, M. Brookhart, W. E. Marsh, D. J. Hodson, and W. E. Hatfield, *Mol. Cryst. Liq. Cryst.*, 1982, **86**, 131; (e) B. W. Sullivan and B. M. Foxman, *Organometallics*, 1983, **2**, 187.

2 For a discussion of the crystallization of TCNQ salts from acetonitrile when association equilibria are present see: L. Komorowski and G. Malachowicz, *J. Phys. (Paris)*, 1983, **C3**, 44, 1207.

3 A general route to iodides of a great number of high purity organic or organometallic derivatives: M. Lequan, R. M. Lequan, P. Batail, J. F. Halet, and L. Ouahab, *Tetrahedron Lett.*, 1983, **24**, 3107.

4 R. G. Sutherland, *J. Organomet. Chem.*, 1977, **3**, 311 and references therein.

5 The charge on the anion is deduced from an empirical scheme based on the concomitant respective lengthening and shortening of the formal double and single bonds of the TCNQ structure as it becomes more benzenoid: T. J. Kistenmacher, T. J. Emge, A. N. Bloch, and D. O. Cowan, *Acta Crystallogr., Sect. B*, 1982, **38**, 1193.

6 S. R. Wilson, J. P. Corvan, R. P. Seiders, D. J. Hodgson, M. Brookhart, W. E. Hatfield, J. S. Miller, A. H. Reis, P. K. Rogan, E. Gebert, and A. J. Epstein, 'Molecular Metals,' ed. W. E. Hatfield, Plenum, New York, 1979, p. 407.

7 T. J. Kistenmacher, T. E. Phillips, and D. O. Cowan, *Acta Crystallogr., Sect. B*, 1974, **30**, 763.

8 P. Goldstein, K. Seff, and K. N. Trueblood, *Acta Crystallogr., Sect. B*, 1968, **24**, 778; A. T. McPhail, G. M. Semeniuk, and D. B. Chesnut, *J. Chem. Soc. A*, 1971, 2174.

9 J. R. Hamon, D. Astruc, E. Roman, P. Batail, and J. J. Mayerle, *J. Am. Chem. Soc.*, 1981, **103**, 2431.

10 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, 1960, p. 262.