One-electron Oxidation of $[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2\{\mu\text{-}Ph_2PN(Et)PPh_2\}]$ by 7,7,8,8-Tetracyano-*p*-quinodimethane: Formation of a Charge-transfer Salt with a Novel Solid-state Stoichiometry and Structure

Sharon E. Bell, John S. Field and Raymond J. Haines*

Unit of Metal Cluster Chemistry, Department of Chemistry, University of Natal, PO Box 375, Pietermaritzburg 3200, Republic of South Africa

Treatment of $[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2\{\mu\text{-}Ph_2PN(Et)PPh_2\}]$ with 7,7,8,8-tetracyano-*p*-quinodimethane, TCNQ, affords, on crystallization from acetonitrile, a charge-transfer salt, $[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2\{\mu\text{-}Ph_2PN(Et)PPh_2\}]_2(TCNQ)_3\cdot 2MeCN$, with a novel 2 : 3 stoichiometry; the cations and anions in this species are distributed in segregated stacks, the TCNQ anions packing as trimers along the stack with an intratrimer separation of 3.24(1) Å and an intertrimer separation of 3.39(1) Å.

We have established previously that the di-tertiary-phosphine-bridged derivatives $[Fe_2(cp)_2(\mu\text{-}CO)_2(\mu\text{-}Ph_2PYPPh_2)]$ (cp = $\eta\text{-}C_5H_5$; Y = CH_2, C_2H_4, C_3H_6 or NEt) are electron rich and as such are readily oxidized by chemical oxidants such as iodine and silver salts to afford the paramagnetic one-electron oxidized species $[Fe_2(cp)_2(\mu\text{-}CO)_2(\mu\text{-}Ph_2PYPPh_2)]^+$, readily isolated as the tetrafluoroborate, perchlorate, hexafluorophosphate, hexafluoroantimonate or tetraphenylborate salts.[1–3] These cationic species exhibit anomalous magnetic and ESR and Mössbauer spectroscopic properties which vary with the linking group Y. Thus, while the iron atoms in $[Fe_2(cp)_2(\mu\text{-}CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)]SbF_6$ are equivalent down to temperatures of 4 K, the Mössbauer spectral data for the crystal form of $[Fe_2(cp)_2(\mu\text{-}CO)_2(\mu\text{-}Ph_2PC_2H_4PPh_2)]SbF_6$, crystallized from CH_2Cl_2–light petroleum, are consistent with the iron atoms being non-equivalent at very low temperatures.[4] As part of a programme involving the synthesis of charge-transfer salts derived from dinuclear and metal cluster compounds, we have investigated the reaction of the diiron derivatives $[Fe_2(cp)_2(\mu\text{-}CO)_2(\mu\text{-}Ph_2PYPPh_2)]$ with the electron acceptor ligand, 7,7,8,8,-tetracyano-*p*-quinodimethane, TCNQ.

Treatment of $[Fe_2(cp)_2(\mu\text{-}CO)_2(\mu\text{-}Ph_2PYPPh_2)]$ (Y = CH_2, C_2H_4 or NEt) with an equimolar amount of TCNQ in toluene at 0 °C was found to lead to the separation of a green-black material which in the case of the $Ph_2PN(Et)PPh_2$-bridged derivative could be isolated in a crystalline form suitable for an X-ray diffraction study. This species, crystallized from acetonitrile, was established to have the stoichiometry $[Fe_2(cp)_2(\mu\text{-}CO)_2\{\mu\text{-}Ph_2PN(Et)PPh_2\}]_2(TCNQ)_3\cdot 2MeCN$. The stereochemistry of the cation $[Fe_2(cp)_2(\mu\text{-}CO)_2\{\mu\text{-}Ph_2PN(Et)PPh_2\}]^+$, as established X-ray crystallographically† and illustrated in Fig. 1, is very similar to that of the neutral parent complex.[5] The Fe–Fe distance of 2.495(1) Å is very slightly shorter (0.013 Å) than that of the parent, indicating that the oxidation process involves an electron in an orbital which is essentially nonbonding with respect to the two iron atoms. A similar decrease in the Fe–Fe distance has been observed on oxidation of $[Fe_2(cp)_2(\mu\text{-}CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)]$ to $[Fe_2(cp)_2(\mu\text{-}CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)]^+$.[6] Significantly, Hall and Sherwood have similarly proposed that oxidation of neutral $[Fe_2(cp)_2(\mu\text{-}CO)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}]$ (n = 1 or 2) involves the removal of an Fe–Fe nonbonding electron on the basis of ESCA studies and molecular orbital calculations on

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† *Crystal data*: $C_{58}H_{44}Fe_2N_8O_2P_2$, M = 1058.6, triclinic, space group $P\bar{1}$ (No. 2), a = 10.089(2), b = 15.967(3), c = 16.227(3) Å, α = 83.64(4), β = 78.17(4), γ = 74.04(4)°, U = 2455.9 Å^3, D_c = 1.431 g cm^{-3}, Z = 2, Mo-Kα radiation, λ = 0.71069 Å, μ = 7.30 cm^{-1}. Nonius CAD4 diffractometer, 5581 unique absorption corrected intensities with $I > 3\sigma(I)$ in the range $3 \leqslant \theta \leqslant 23°$. R_{int} = 0.014. Structure solved from a Patterson synthesis and successive Fourier maps and refined to R = 0.085 (309 parameters). 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.

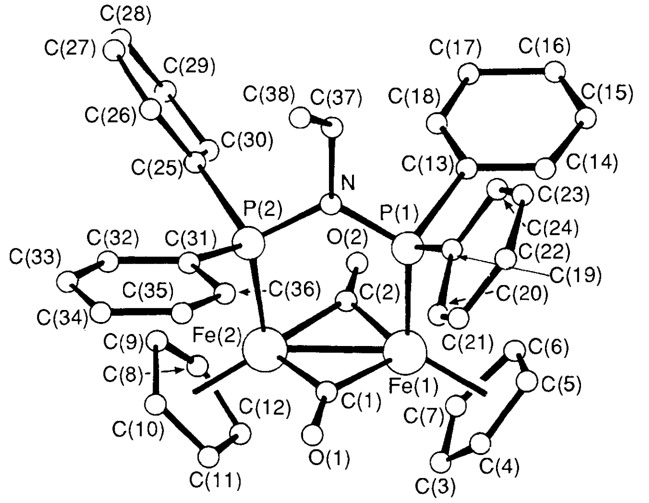

Fig. 1 Perspective view of the $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2\{\mu\text{-}Ph_2PN(Et)PPh_2\}}]^+$ cation. Relevant interatomic distances: Fe(1)–Fe(2) 2.495(1); Fe(1)–P(1) 2.195(2); Fe(2)–P(2) 2.209(2) Å.

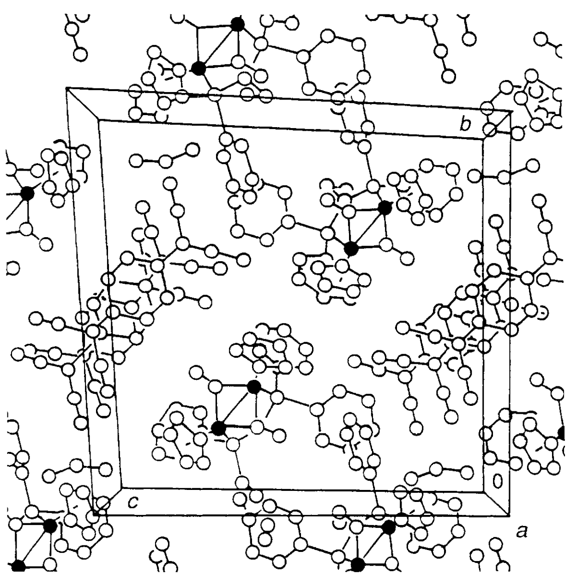

Fig. 2 The crystal structure of $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2\{\mu\text{-}Ph_2PN(Et)PPh_2\}}]_2\mathrm{(TCNQ)_3\cdot 2MeCN}$ viewed along the *a* axis

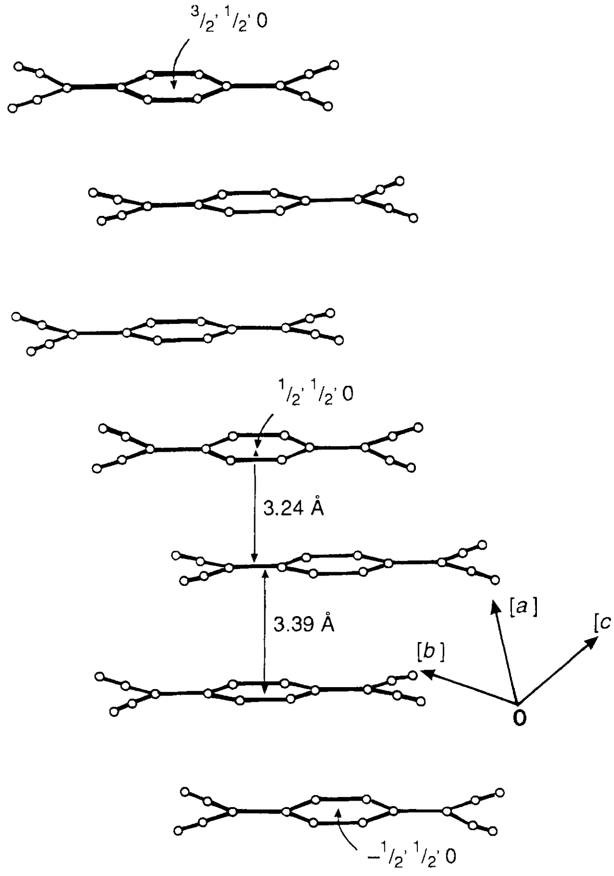

Fig. 3 One stack of TCNQ anions in $[\mathrm{Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2\{Ph_2PN(Et)PPh_2\}}]\cdot\mathrm{2MeCN}$. The coordinates of the crystallographic centres of symmetry through which the stacking axis passes are indicated.

the series of compounds of formula $[\mathrm{Fe_2(cp)_2(\mu\text{-}CO)_2\{\mu\text{-}Ph_2P(CH_2)_{\mathit{n}}PPh_2\}}]^{m+}$ (n = 1 or 2; m = 0 or 1).[7] The Fe–P distances are less invariant to oxidation with the average distance for the cation being 0.045 Å longer than that for the neutral parent.

The packing of the cations and anions of this salt warrants particular comment. A view of the unit cell of this species, along the *a*-axis, is illustrated in Fig. 2. There are two cations, three TCNQ anions and two acetonitrile molecules per unit cell; two of the TCNQ anions occupy general equivalent positions while the third is situated on a crystallographic centre of symmetry. As indicated by Fig. 2, the organometallic cations and the TCNQ anions form segregated stacks with the acetonitrile molecules occupying interstitial spaces. Fig. 3 illustrates the stacking of the TCNQ anions; these anions are essentially planar and almost parallel to each other, the dihedral angle between the least-squares planes of the TCNQ anions not related by crystal symmetry being 3.6(6)°. The packing sequence is best described as a series of TCNQ trimers, the central member of each trimer being situated on a crystallographic inversion centre; indeed the stacking axis passes through these inversion centres and as a result is parallel to the *a*-axis. The outer TCNQ units of each trimer lie on either side of the stacking axis and, moreover, the lines joining the midpoints of the benzene rings of the TCNQ units making up the trimer are all parallel to each other. A further feature of the packing of the TCNQ anions is that their planes are not perpendicular to the stacking axis but rather make angles of 78.1(5) and 77.9(5)° to it, the net result being a highly unusual packing sequence.[8] The intratrimer separation is 3.24(1) Å while the perpendicular distance between adjacent TCNQ units belonging to different trimers is slightly greater [3.39(1) Å; see Fig. 3]. These interplanar spacing are somewhat greater than the spacing between TCNQ units found in TFF (tetrathiafulvalene)–TCNQ (3.17 Å)[9] and the radical-anion salt of 2,2′-bi-1,3-dithiole and TCNQ (3.17 Å).[10] However, the intratrimer spacing is significantly shorter and the intertrimer separation very similar to the uniform spacing between the central TCNQ rings (3.35 and 3.37 Å) found in the 1:2 organometallic charge-transfer salt $[\mathrm{(cp)FeAr}]\mathrm{(TCNQ)_2}$ (Ar = 2,4,6-$\mathrm{C_6H_3Me_3}$)[11] which, with the closely related salt where Ar = $\mathrm{C_6Me_6}$, exhibits semi-conductor properties.[12] Furthermore, within the TCNQ stack, the mode of overlap is of the usual ring-over-exocyclic double bond type typically found in highly conducting salts of TCNQ.[13]

On the basis that the TCNQ anions stack as trimers and on the assumption that charge transfer is complete {ν(C–O) for $[\mathrm{Fe_2(cp)_2(\mu\text{-}CO)_2\{\mu\text{-}Ph_2PN(Et)PPh_2\}}]_2\mathrm{(TCNQ)_3\cdot 2MeCN}$ in the solid state is the same as that found for $[\mathrm{Fe_2(cp)_2(\mu\text{-}CO)_2\{\mu\text{-}Ph_2PN(Et)PPh_2\}}]\mathrm{BPh_4}$[14]}, each TCNQ anion must be formally assigned a fractional charge of $-\frac{2}{3}$ for this 2 : 3 salt. This is highly unusual because only one other 2:3 organometallic charge-transfer salt is known *viz.* the ferrocenium salt of 7,7,8,8-tetracyanoperfluoro-*p*-quinodimethane, $[Fe(cp)_2]_2$-$[TCNQF_4]_3$, and in this case the $TCNQF_4$ anions stack quite differently; two $TCNQF_4$ units form a $[TCNQF_4]_2^{2-}$ dimer while the third $TCNQF_4$ unit exists as a neutral molecule at right angles to the dimer.[15]

The charge-transfer salt isolated from the reaction of $[Fe_2(cp)_2(\mu\text{-}CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)]$ with TCNQ was established to have a 1 : 1 stoichiometry but attempts to isolate it in a crystalline form suitable for an X-ray diffraction study in order to ascertain its packing pattern proved unsuccessful. The product isolated from the reaction of $[Fe_2(cp)_2(\mu\text{-}CO)_2(\mu\text{-}Ph_2PC_2H_4PPh_2)]$ with TCNQ was found to contain mononuclear derivatives as well as the one-electron oxidized species $[Fe_2(cp)_2(\mu\text{-}CO)_2(\mu\text{-}Ph_2PC_2H_4PPh_2)]^+$ and could not be purified further.

Studies involving the synthesis and properties of organometallic charge transfer salts derived from electron-rich dinuclear donor and electron-acceptors such as TCNQ are continuing.

The authors express their sincere thanks to the Foundation for Research Development and the University of Natal for financial support and to Mr S. Naidoo of the University of Durban-Westville for the gift of $[Fe_2(cp)_2(\mu\text{-}CO)_2\{\mu\text{-}Ph_2PN(Et)PPh_2\}]$.

Received, 22nd November 1990; Com. 0/05265E

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