

# Decamethylnickelocenium hydrogen-7,7,8,8-tetracyanoperfluoro-*p*-quinodimethandiide: isolation of the protonated weak base [HTCNQF<sub>4</sub>]<sup>-</sup>

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**Unprecedentedly stable hydrogen-7,7,8,8-tetracyanoperfluoro-*p*-quinodimethandiide, [HTCNQF<sub>4</sub>]<sup>-</sup>, is isolated and crystallographically characterized.**

The discoveries of the metamagnetic behaviour<sup>1</sup> of a one-dimensional phase [Fe(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup>[TCNQ]<sup>-</sup> (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) and the ferromagnetic behaviour<sup>2</sup> of [Fe(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup>[TCNE]<sup>-</sup> (TCNE = tetracyanoethylene) led to extensive studies of the electron-transfer salts comprising metallocenium cations and polycyano anions.<sup>3,4</sup> As part of our program to understand the magnetic properties of metallocenium salts of radical anion acceptors, the reaction of decamethylnickelocene, [Ni(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>], with perfluoro-TCNQ, TCNQF<sub>4</sub>,<sup>5</sup> has been studied. TCNQF<sub>4</sub> is a strong electron acceptor, however, unlike TCNQ, its isolated radical anion has never been observed in the solid state, only as its *S* = 0 dimer, [TCNQF<sub>4</sub>]<sub>2</sub><sup>2-</sup>.<sup>6</sup> Seven metallocene-based electron-transfer salts incorporating reduced TCNQF<sub>4</sub> as [TCNQF<sub>4</sub>]<sub>2</sub><sup>2-</sup> have been reported.<sup>6a,c,e,f</sup> [Ni(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] undergoes two reversible one-electron oxidations at -0.73 and 0.37 V,<sup>7</sup> while TCNQF<sub>4</sub> undergoes two reversible one-electron reductions at 0.53 and 0.02 V<sup>8</sup> (vs. SCE in MeCN). Thus, there are 0.90 and 0.39 V driving forces for forming [Ni(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup>[TCNQF<sub>4</sub>]<sup>-</sup> and {[Ni(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup>]<sub>2</sub>[TCNQF<sub>4</sub>]<sub>2</sub><sup>2-</sup>, respectively.

Recrystallisation from MeCN of the precipitate formed upon the reaction of [Ni(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] and TCNQF<sub>4</sub> (1 : 1) in thf led to the isolation of two phases. The β-phase precipitates first and has a characteristic IR (Nujol): ν(CN) 2181 ± 1 m and 2151 ± 1 m cm<sup>-1</sup> (at 26 K: 2182s and 2150s cm<sup>-1</sup>) (yield: 41%). After the β-phase was isolated, the remaining mother liquor was concentrated and cooled at -40 °C for several days, affording the α-phase in two crops (yield: 24%). IR (Nujol): ν(CN) 2182 ± 1 m and 2155 ± 1 m cm<sup>-1</sup> (at 26 K: 2195w, 2183s, 2155s cm<sup>-1</sup>).

Crystals of α-phase suitable for single-crystal X-ray diffraction were obtained upon refrigerating a MeCN solution at -40 °C. The structure determination<sup>†</sup> confirms [Ni(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup> and an unexpected polymeric anion. The cation, Fig. 1, has approximate *D*<sub>5d</sub> molecular symmetry with Ni-C distances ranging between 2.082(7) and 2.117(7) Å and averaging 2.105 Å; 0.06 Å shorter than in [Ni(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>].<sup>9</sup> The C<sub>5</sub> rings have C-C distances averaging 1.420 Å. The Ni-C<sub>5</sub> ring centroid distance is 1.7235 ± 0.0035 Å while the angle between ring centroids and Ni is 178.9°. This is the second reported structure of [Ni(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup>, the first being [Ni(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup>[C<sub>60</sub>]<sup>-</sup>,<sup>10</sup> however, structural details of the cation were not reported.

The polymeric anion is [HTCNQF<sub>4</sub>]<sup>-</sup> (Fig. 1) which is reported for the first time and possesses a planar (NC)<sub>2</sub>CC<sub>6</sub>F<sub>4</sub> moiety typical of previously reported TCNQ<sup>11</sup> and TCNQF<sub>4</sub>.<sup>6,12</sup> compounds with an unprecedented nonplanar C(CN)<sub>2</sub>H group. The ring C-C distances average 1.387 Å. The four CN groups average 1.138 Å. The unique feature is the sp<sup>3</sup> C(27) with a C<sub>6</sub>-ring C(21)-C(27) distance of 1.501(10) Å and C(27)-CN distances of 1.482 ± 0.012 Å which are distinctly longer than the those for sp<sup>2</sup> C(30). For example, the C(30)-C(24)

bond is 1.414(9) Å and the C(27)-H(27) bond distance is 1.00(7) Å. The bond angles of C(21)-C(27)-C(28), C(21)-C(27)-C(29) and C(28)-C(27)-C(29) sum to 331.9° characteristic of sp<sup>3</sup> bonding about C(27). In contrast, the sum of the angles about C(30) is 360.1° characteristic of sp<sup>2</sup> bonding. Furthermore, the mean distance of the C(27)-C(28) and C(27)-C(29) bonds (1.482 Å) is significantly longer than that of the C(30)-C(31) and C(30)-C(32) bonds (1.428 Å). Except for the H atom and the CN groups bonded to C(27), all the atoms are essentially coplanar.

The solid is comprised of one-dimensional ...D<sup>+</sup>A<sup>-</sup>D<sup>+</sup>A<sup>-</sup>... chains {D<sup>+</sup> = [Ni(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup>, A<sup>-</sup> = [HTCNQF<sub>4</sub>]<sup>-</sup>} where the C<sub>6</sub>-ring is essentially parallel to the C<sub>5</sub>Me<sub>5</sub> plane, as observed for many [M(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup>[A]<sup>-</sup> electron-transfer salts that exhibit cooperative magnetic interactions.<sup>1-4</sup> The intrachain Ni...Ni separation is 10.888 Å, while the interchain separations are 9.570, 9.733, 9.822, 10.025 and 11.579 Å. Unlike previously reported ...D<sup>+</sup>A<sup>-</sup>D<sup>+</sup>A<sup>-</sup>... structured salts, this salt has hydrogen-bonded chains of [HTCNQF<sub>4</sub>]<sup>-</sup> anions in the solid. Each C(27)-H(27) hydrogen bonds to N(3) on another [HTCNQF<sub>4</sub>]<sup>-</sup> with an sp<sup>2</sup>-C(27)...N(3) separation of 3.14 Å and a C(27)-N(3) distance of 2.084 Å which is significantly less than the sum of the N and H van der Waals radii,<sup>13</sup> Fig. 2.

A detailed study of the ν(CH) region of the IR spectra (Fluorolube) reveals a room-temperature absorption at 2854m cm<sup>-1</sup> for the α-phase which is not present for either the β-phase or [Ni<sup>III</sup>(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup> and is assigned to the (NC)<sub>2</sub>C-H stretch. Comparable absorptions have been reported for CH<sub>2</sub>(CN)<sub>2</sub>,<sup>14a</sup> H<sub>2</sub>TCNQ,<sup>14b</sup> HC(CN)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)C(CN)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)NMe<sub>2</sub>,<sup>14a</sup> HC(CN)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)C(CN)NC<sub>6</sub>H<sub>4</sub>OMe,<sup>14c</sup> and H<sub>2</sub>TCNE. At 26 K this band shifts to lower energy and splits into three absorbances

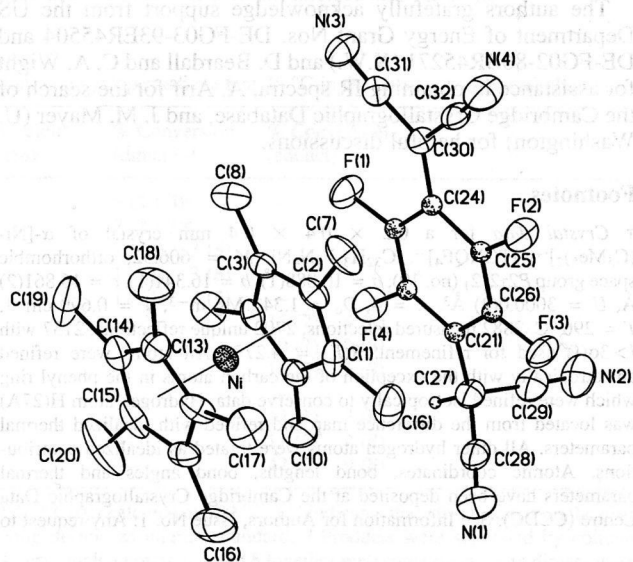


Fig. 1 ORTEP drawing depicting the atom labelling of [Ni(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup>[HTCNQF<sub>4</sub>]<sup>-</sup>; atoms shown as 30% probability ellipsoids

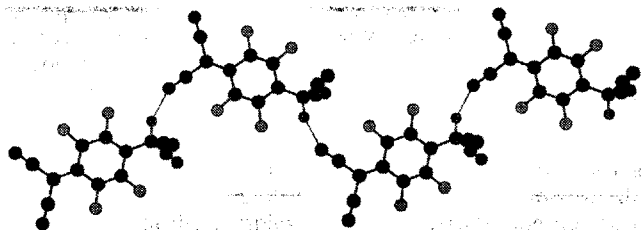


Fig. 2 Hydrogen-bonded chains of [HTCNQF<sub>4</sub>]<sup>-</sup>

at 2846m, 2837m and 2823w cm<sup>-1</sup> consistent with a phase transition that is indicative from preliminary magnetic studies.

The hydrogen source is either H<sup>+</sup> or H<sup>•</sup>; the former requiring protonation of [TCNQF<sub>4</sub>]<sup>2-</sup> and the latter requiring H<sup>•</sup> addition to [TCNQF<sub>4</sub>]<sup>•-</sup>. H<sub>2</sub>TCNQF<sub>4</sub> is an intermediate in the preparation of TCNQF<sub>4</sub>,<sup>5</sup> but unlike H<sub>2</sub>TCNQ,<sup>14b</sup> it has neither been isolated or characterized.<sup>5</sup> The computationally determined pK<sub>a1</sub> and pK<sub>a2</sub> are 4.0 and 7.2 for H<sub>2</sub>TCNQF<sub>4</sub>;<sup>15</sup> hence strong acids are needed to protonate [TCNQF<sub>4</sub>]<sup>2-</sup>. Therefore, although formation of {[Ni(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup>]<sub>2</sub>[TCNQF<sub>4</sub>]<sup>2-</sup> is energetically allowed, it requires 2 equiv. of the donor<sup>16†</sup> and a sufficiently strong acid to protonate [TCNQF<sub>4</sub>]<sup>2-</sup>;§ both of which are not present.

Since the first step is probably the formation of [Ni<sup>III</sup>(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup>[TCNQF<sub>4</sub>]<sup>•-</sup>, H<sup>•</sup> addition to [TCNQF<sub>4</sub>]<sup>•-</sup> to form [HTCNQF<sub>4</sub>]<sup>-</sup> is plausible even though formation of the sp<sup>3</sup>-C breaks the extended conjugation and stability of the radical anion.¶ The H<sup>•</sup> source is most likely the thf solvent. This is consistent with the observation that only the β-phase is isolated from acetonitrile and that the α-phase requires thf.

The β-phase has not as yet yielded crystals of sufficient size to determine its structure. The β-phase undergoes a reversible phase transition at 42.5 °C (ΔH = 1.81 kJ mol<sup>-1</sup>) without a change in the ν(CN) absorptions. Therefore, the β-phase is not a metastable phase that has the same chemical composition as the α-phase. This is in accord with the IR spectra in the ν(CH) region which lacks the 2854 cm<sup>-1</sup> absorption and the ν(CN) region of the two phases which are similar, but not identical. Consequently, based upon elemental analyses and IR data, the β-phase is formulated as [Ni<sup>III</sup>(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>][TCNQF<sub>4</sub>]. However, the ν(CN) region of the two phases are different from those of previously characterized TCNQF<sub>4</sub>, {[TCNQF<sub>4</sub>]<sub>2</sub>}<sup>2-</sup> and [TCNQF<sub>4</sub>]<sup>•-</sup>.<sup>6</sup> This suggests that some interactions between the acceptor and the donor exist, but requires a structural determination to elucidate.

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## Footnotes

† Crystal data for a 0.2 × 0.4 × 0.4 mm crystal of α-[Ni(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup>[HTCNQF<sub>4</sub>]<sup>-</sup>, C<sub>32</sub>H<sub>31</sub>F<sub>4</sub>N<sub>4</sub>Ni, M = 606.32, orthorhombic space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (no. 19); a = 10.888(1), b = 16.341(1), c = 16.861(2) Å, U = 3000.0(3) Å<sup>3</sup>, Z = 4, D<sub>c</sub> = 1.342 Mg m<sup>-3</sup>, μ = 0.699 cm<sup>-1</sup>, T = 296 °C. 2882 measured reflections, 2702 unique reflections, 2137 with I > 3σ(I) used for refinement. R(F) = 4.27%. All atoms were refined anisotropically with the exception of the carbon atoms in the phenyl ring which were refined isotropically to conserve data. Hydrogen atom H(27A) was located from the difference map and refined with idealized thermal parameters. All other hydrogen atoms were treated as idealized contributions. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to

the CCDC for this material should quote the full literature citation and the reference number 182/152.

‡ The reaction of [Ni(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] and TCNQF<sub>4</sub> (2:1) in MeCN form-[Ni(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup>[TCNQF<sub>4</sub>]<sup>2-</sup> with ν(CN) at 2167s and 2131s cm<sup>-1</sup> characteristic of unbound [TCNQF<sub>4</sub>]<sup>2-</sup>.<sup>6b</sup>

§ A potential H<sup>+</sup> source might be the disproportionation of [Ni<sup>III</sup>(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup> to [Ni<sup>II</sup>(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] and [Ni<sup>IV</sup>(C<sub>5</sub>Me<sub>5</sub>)(C<sub>5</sub>Me<sub>4</sub>)(=CH<sub>2</sub>)] + H<sup>+</sup> as reported for [Ru<sup>III</sup>(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup><sup>17a</sup> and [Rh<sup>III</sup>Cp(C<sub>5</sub>Me<sub>5</sub>)]<sup>+</sup>.<sup>17b</sup>

¶ The homolytic C-H bond strength is estimated to be 74 kcal mol<sup>-1</sup> (cal = 4.184 J) using the method developed by Bordwell *et al.* (see footnote 1b).

|| This is 16 kcal mol<sup>-1</sup> weaker than that reported for H<sub>2</sub>C(CN)<sub>2</sub>,<sup>18b</sup> but comparable to those reported for 4-RC<sub>6</sub>H<sub>4</sub>CH(CN)<sub>2</sub>.<sup>18c</sup> It is, however, 18 kcal mol<sup>-1</sup> less than that of thf,<sup>18d</sup> the putative hydrogen source. The MeCN reduction potential (0.02 V vs. SCE) for [TCNQF<sub>4</sub>]<sup>•-</sup>-[TCNQF<sub>4</sub>]<sup>2-</sup> is -0.40 V vs. ferrocene-ferrocenium in Me<sub>2</sub>SO and since pK<sub>a</sub> values for Me<sub>2</sub>SO are unavailable, the computed value<sup>15</sup> is used. The comparable value for [HTCNQ]<sup>-</sup> is 69 kcal mol<sup>-1</sup>.

## References

- G. A. Candela, L. J. Swartzendruber, J. S. Miller and M. J. Rice, *J. Am. Chem. Soc.* 1979, **101**, 2755.
- J. S. Miller, J. C. Calabrese, H. Rommelmann, S. R. Chittipeddi, J. H. Zhang, W. M. Reiff and A. J. Epstein, *J. Am. Chem. Soc.*, 1987, **109**, 769.
- J. S. Miller and A. J. Epstein, *Adv. Chem. Ser.*, 1995, **245**, 161; D. Gatteschi, *Adv. Mater.*, 1994, **6**, 635. O. Kahn, *Molecular Magnetism*, VCH, New York, 1993; J. S. Miller and A. J. Epstein, *Chem. Eng. News*, 1995, **73**(40), 30.
- J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 385; *Angew. Chem.*, 1994, **106**, 399.
- R. C. Wheland and E. L. Martin, *J. Org. Chem.*, 1975, **40**, 3101.
- (a) J. S. Miller, J. H. Zhang and W. M. Reiff, *Inorg. Chem.*, 1987, **26**, 600; (b) D. A. Dixon, J. C. Calabrese and J. S. Miller, *J. Phys. Chem.*, 1989, **93**, 2284; (c) J. S. Miller, unpublished work. These are isomorphous to {[Fe(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup>]<sub>2</sub>[TCNQF<sub>4</sub>]<sup>2-</sup> [J. S. Miller, J. H. Zhang, W. M. Reiff, L. D. Preston, A. H. Reis, Jr. E. Gerbert, M. Exline, J. Troup and M. D. Ward, *J. Phys. Chem.*, 1987, **91**, 4344]; (d) M. D. Ward and D. C. Johnson, *Inorg. Chem.*, 1987, **26**, 4213; (e) D. Stein, H. Sitzmann, R. Boese, E. Dormann and H. Winter, *J. Organomet. Chem.*, 1991, **412**, 143; (f) D. Stein, H. Sitzmann and R. Boese, *J. Organomet. Chem.*, 1991, **421**, 275.
- J. L. Robbins, N. Edelstein, B. Spencer and J. C. Smart, *J. Am. Chem. Soc.*, 1982, **104**, 1882.
- C. Vazquez, J. C. Calabrese, D. A. Dixon and J. S. Miller, *J. Org. Chem.*, 1993, **58**, 65.
- P. Seiler and J. D. Dunitz, *Acta Crystallogr., Sect. B*, 1980, **36**, 2255.
- W. H. Wan, X. Liu, G. M. Sweeny and W. E. Broderick, *J. Am. Chem. Soc.*, 1995, **117**, 9580.
- Over 550 TCNQ-based structures have been reported in the Cambridge Crystallographic Database version 5.10 (Oct. 1995).
- E.g. R. C. S. Hotta and H. Kobayashi, *Synth. Met.*, 1994, **66**, 117.
- CRC Handbook of Chemistry and Physics*, ed. R. C. Weast, 57th edn., Boca Raton, FL, pp. D-178.
- (a) *Aldrich Library of Infrared Spectra*, 2nd edn., ed. C. J. Pouchert, 1975, pp. 446; (b) D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, 1962, **84**, 3370; pK<sub>a1</sub> and pK<sub>a2</sub> values are computed to be 7.1 and 10.3 for H<sub>2</sub>TCNQ;<sup>15</sup> (c) W. R. Hertler, H. D. Hartzler, D. S. Acker and D. E. Benson, *J. Am. Chem. Soc.*, 1962, **84**, 3387.
- T. Akutagawa and G. Saito, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 1753.
- J. S. Miller and D. A. Dixon, *Science*, 1987, **235**, 871; D. A. Dixon, J. C. Calabrese and J. S. Miller, *J. Phys. Chem.*, 1988, **93**, 2284.
- (a) U. Kolle and J. Grub, *J. Organomet. Chem.*, 1985, **289**, 133; (b) J. A. Miguel-Garcia, H. Adams, N. A. Bailey and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1992, 131.
- (a) F. G. Bordwell, J.-P. Cheng, G.-Z. Ji, A. V. Satish and X. Zhang, *J. Am. Chem. Soc.*, 1991, **113**, 9790; (b) X. J. Zhang and F. G. Bordwell, *Phys. Org. Chem.*, 1994, **7**, 751; (c) F. G. Bordwell, X. Zhang, A. V. Satish and J.-P. Cheng, *J. Am. Chem. Soc.*, 1994, **116**, 6605; (d) *Lange's Handbook of Chemistry*, ed. J. A. Dean, 14th edn., McGraw-Hill, New York, p. 4.29.

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