The tridentate dianionic ligand spans three positions in the basal plane, *via* the charged phenolic O atom, the neutral N atom and the charged thiolate S atom, the fourth position being occupied by the benzenethiolate S atom. The Tc atom, as usual (Table 3), lies above the basal plane towards the O(1) apex (0.66 Å) and with respect to the mean basal plane the four donor atoms are in a slightly puckered (± 0.12 Å) arrangement (Table 2), similar to other compounds of this type (Bryson, Brenner, Lister-James, Jones, Dewan & Davison, 1989; Faggiani, Lock, Epps, Kramer & Brune, 1988; Mahmood, Haplin, Baidoo, Sweigart & Lever, 1990). The angle between the Tc—O(1) bond direction and the normal to the basal plane is 177.2° and the benzenethiolate mean plane is approximately normal (102.4°) to the same plane. There is nothing remarkable about the bond lengths and angles (Bandoli, Mazzi, Roncari & Deutsch, 1982; Clarke & Fackler, 1982; Davison & Jones, 1982; Melnik & Van Lier, 1987).

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Structure of (η^5-Cyclopentadienyl)(η^6-1,3,5-trimethylbenzene)iron–7,7,8,8-Tetracyano-p-quinodimethane (1/2)

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Abstract. [Fe(C_9H_{12})(C_5H_5)]($C_{12}H_4N_4$)$_2$, $M_r = 649.5$, monoclinic, $P2_1/m$, $a = 7.914$ (2), $b = 30.983$ (3), $c = 6.629$ (1) Å, $\beta = 102.38$ (1)°, $V = 1588$ Å^3, $Z = 2$, $D_x = 1.36$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 4.22$ mm^{-1}, $F(000) = 696$, $T = 295$ K, $R = 0.042$ for 2587 observed reflections. The crystal structure of the

1,3,5-trimethylbenzene derivative, [(Cp)Fe(C₆H₃Me₃)]-(TCNQ)₂, consists of layers of TCNQ separated by the ferrocene. The steric effects of the methyl groups do not only manifest themselves on the metallocene but on the TCNQ packing as well.

Introduction. A large number of salts and charge-transfer complexes of metallocenes have been prepared during the last few years in an attempt to induce properties such as electrical conductivity and magnetic long-range order (Miller, Epstein & Reiff, 1988). Among these is a new class of charge-transfer complexes with tetracyanoquinodimethane (TCNQ) as electron acceptors, and a cationic part consisting of a ferrocene derivative which, in the present case, is unsymmetrically coordinated with a cyclopentadienyl ring (Cp) and a substituted benzene ring $C_6H_{6-n}R_n$ (Ar). Various derivatives (R_n = H, Me, Me₃, Me₄, Et₆, ʹBu₃) were synthesized to modulate systematically the electronic properties by steric effect on the arene group, as described by Pucksacki, Pawlak, Graja, Lequan & Lequan (1987). The crystal structure of the Me₆-substituted compound has been reported by Lequan, Lequan, Jaouen, Ouahab, Batail, Padiou & Sutherland (1985), and affords an example for comparison with the structure of the title compound as well as parametrizing the influence of the steric effect of the substituted groups of the benzene moiety on the crystal packing. The room-temperature conductivities are 0.2 and 4 S cm⁻¹ for Me₃ and Me₆, respectively. It was found (Lequan, Lequan, Flandrois, Delhaes, Bravic & Gaultier, 1990) that their magnetic properties can be well described by the Bonner–Fisher model for $S = \frac{1}{2}$ antiferromagnetic Heisenberg chains (Bonner & Fisher, 1964).

Experimental. Black prismatic crystals were obtained by metathesis of [(Cp)Fe(C₆H₃Me₃)]⁺.I⁻, prepared from the parent PF₆ salt by anion exchange with I, and tetracyanoquinodimethane (TCNQ). A single crystal 0.35 × 0.20 × 0.13 mm was mounted on a CAD-4 diffractometer equipped with Cu Kα radiation and a graphite monochromator. Cell dimensions were calculated from positional angles of 17 reflections in the range 12 < θ < 41°. Intensities of 5358 reflections were collected up to θ = 70° (−9 < h < 9, 0 < k < 37, 0 < l < 8) and corrected for Lorentz and polarization effects. Three standards (0,26,0, 421, 104) were used to check crystal orientation and intensity stability; no significant variation of intensity was observed. An empirical absorption correction was applied using the ψ-scan technique [relative transmission factors 0.738 (minimum), 0.999 (maximum)]. After averaging crystallographically equivalent reflections (R_{int} = 0.022), 3062 were unique and 2587 observed [$I \geq 3\sigma(I)$]. The structure was solved

by direct methods using *MITHRIL* (Gilmore, 1984) and refined by block-diagonal least squares based on F, minimizing $\Sigma w(|F_o| - |F_c|)^2$, w defined as $[\sigma^2(F_o) + (0.03F_o)^2]^{-1}$. H atoms were generated geometrically except for those of the methyl groups which were located from difference Fourier maps. All the atoms were refined anisotropically except for the H atoms whose thermal motion was kept isotropic and constant. Scattering factors were taken from Cromer & Waber (1974). Anomalous-dispersion corrections were made for all non-H atoms. The final values of the reliability factors were R = 0.042 and wR = 0.042; S = 1.66; residual electron density between −0.37 and 0.31 e Å⁻³; maximum (Δ/σ) = 0.11. Tables 1 and 2 give the final atomic coordinates and bond lengths and angles. Fig. 1 shows the structure with its atomic numbering.*

Discussion. The projection of the crystal structure along the *a* axis is shown in Fig. 2. The structure consists of TCNQ anion stacks which are separated by discrete (Cp)Fe(C₆H₃Me₃) columns; the anionic columns have a herring-bone structure. The columns are close to one another along the **a** direction so that they form anionic and cationic layers. This arrangement is very similar to that found for the Me₆ derivative (Lequan *et al.*, 1985). The effect of increasing the number of methyl groups on the benzene ring manifests itself mainly on the interchain metallocene distance, and thus on the *a* parameter which increases from 7.914 Å for the tri-substituted (Me₃) to 8.630 Å for the hexa-substituted compound (Me₆). This, in turn, induces a rotation of ± 5° along the *c* axis in the zigzag conformation of the TCNQ columns from two consecutive anionic sheets, so that the value of the *b* cell parameter decreases from 30.983 Å for the Me₃ derivative to 30.032 Å for the Me₆ derivative. The TCNQ stacks are slightly dimerized with two different mean interplanar spacings between adjacent TCNQ molecules (3.25 and 3.36 Å). The mean values of equivalent bond lengths of the TCNQ molecule (C≡C 1.351, C—C 1.435, C—N 1.14 Å) are consistent with those of TCNQ¹ᐟ²⁻ (Flandrois & Chasseau, 1977). One electronic charge equally shared by two TCNQ molecules is not unknown in these acceptor complexes. The angle of the respective orientations of the anionic and cationic rings is 4° for the Me₃ derivative and increases to 14° for the Me₆. Within each metallocene cation, the distance between Fe and the Cp ring is 1.66 Å and between Fe and the Ar ring 1.54 Å, *i.e.* a total distance d_1 of 3.20 Å between Cp

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab\beta_{12} + ac(\cos\beta)\beta_{13} + bc\beta_{23}].$$

	x	y	z	B_{eq}
Fe(1)	0.30905 (6)	0.2500	0.32813 (8)	2.60 (1)
C(11)	0.1110 (4)	0.2500	0.0656 (5)	3.5 (1)
C(12)	0.2029 (3)	0.21104 (7)	0.0782 (4)	3.6 (1)
C(13)	0.3838 (3)	0.21050 (8)	0.1059 (4)	3.8 (1)
C(14)	0.4718 (4)	0.2500	0.1234 (6)	4.1 (2)
C(111)	-0.0803 (5)	0.2500	0.0491 (7)	6.2 (3)
C(131)	0.4802 (5)	0.1681 (1)	0.1311 (6)	7.0 (2)
C(21)	0.4410 (5)	0.2271 (1)	0.6014 (5)	7.7 (2)
C(22)	0.2709 (5)	0.21451 (9)	0.5736 (5)	6.3 (2)
C(23)	0.1722 (5)	0.2500	0.5553 (7)	6.2 (3)
C(31)	-0.1708 (3)	0.06349 (6)	0.7015 (3)	2.78 (8)
C(32)	-0.2479 (3)	0.02163 (7)	0.6981 (4)	3.07 (9)
C(33)	-0.1498 (3)	-0.01454 (6)	0.7279 (3)	3.00 (9)
C(34)	0.0354 (3)	-0.01235 (6)	0.7637 (3)	2.75 (8)
C(35)	0.1130 (3)	0.02989 (6)	0.7700 (3)	2.99 (9)
C(36)	0.0138 (3)	0.06577 (6)	0.7379 (4)	3.02 (9)
C(311)	-0.2725 (3)	0.10064 (7)	0.6676 (4)	3.26 (9)
C(312)	-0.1989 (3)	0.14248 (7)	0.6620 (4)	4.0 (1)
N(313)	-0.1440 (3)	0.17637 (7)	0.6532 (5)	6.3 (1)
C(314)	-0.4559 (3)	0.09954 (7)	0.6376 (4)	3.8 (1)
N(315)	-0.6032 (3)	0.09938 (7)	0.6144 (4)	5.6 (1)
C(341)	0.1366 (3)	-0.04922 (6)	0.7931 (4)	3.06 (9)
C(342)	0.0646 (3)	-0.09162 (7)	0.7859 (4)	3.7 (1)
N(343)	0.0106 (3)	-0.12547 (7)	0.7815 (4)	5.9 (1)
C(344)	0.3203 (3)	-0.04798 (7)	0.8264 (4)	3.51 (9)
N(345)	0.4683 (3)	-0.04799 (7)	0.8535 (4)	5.2 (1)

Table 2. *Bond lengths* (Å) *and angles* (°)

Fe(1)—C(11)	2.077 (2)	C(31)—C(36)	1.431 (3)
Fe(1)—C(12)	2.076 (3)	C(31)—C(311)	1.395 (3)
Fe(1)—C(13)	2.096 (3)	C(32)—C(33)	1.353 (3)
Fe(1)—C(14)	2.062 (3)	C(33)—C(34)	1.435 (3)
Fe(1)—C(21)	2.016 (4)	C(34)—C(35)	1.442 (3)
Fe(1)—C(22)	2.039 (4)	C(34)—C(341)	1.385 (3)
Fe(1)—C(23)	2.035 (3)	C(35)—C(36)	1.351 (3)
C(11)—C(12)	1.402 (4)	C(311)—C(312)	1.425 (4)
C(11)—C(111)	1.494 (4)	C(311)—C(314)	1.423 (4)
C(12)—C(13)	1.404 (4)	C(312)—N(313)	1.143 (4)
C(13)—C(14)	1.401 (4)	C(314)—N(315)	1.143 (4)
C(13)—C(131)	1.510 (5)	C(341)—C(342)	1.429 (3)
C(21)—C(22)	1.375 (5)	C(341)—C(344)	1.423 (3)
C(21)—C(21^i)	1.419 (5)	C(342)—N(343)	1.131 (4)
C(22)—C(23)	1.339 (5)	C(344)—N(345)	1.146 (4)
C(31)—C(32)	1.431 (3)		

C(11)—Fe(1)—C(12)	39.5 (1)	C(12)—C(13)—C(131)	120.1 (3)
C(11)—Fe(1)—C(13)	71.8 (1)	C(14)—C(13)—C(131)	121.4 (3)
C(11)—Fe(1)—C(14)	85.1 (1)	Fe(1)—C(14)—C(13)	71.6 (2)
C(11)—Fe(1)—C(21)	154.8 (1)	C(13)—C(14)—C(13^i)	121.8 (2)
C(11)—Fe(1)—C(22)	117.0 (1)	Fe(1)—C(21)—C(22)	71.1 (2)
C(11)—Fe(1)—C(23)	101.2 (1)	Fe(1)—C(21)—C(21^i)	69.4 (2)
C(12)—Fe(1)—C(13)	39.3 (1)	C(22)—C(21)—C(21^i)	106.5 (3)
C(12)—Fe(1)—C(14)	71.2 (1)	Fe(1)—C(22)—C(21)	69.3 (2)
C(12)—Fe(1)—C(21)	123.7 (1)	Fe(1)—C(22)—C(23)	70.6 (2)
C(12)—Fe(1)—C(22)	102.7 (1)	C(21)—C(22)—C(23)	108.3 (3)
C(12)—Fe(1)—C(23)	113.7 (1)	Fe(1)—C(23)—C(22)	71.0 (2)
C(13)—Fe(1)—C(14)	39.4 (1)	C(22)—C(23)—C(22^i)	110.4 (3)
C(13)—Fe(1)—C(21)	104.8 (1)	C(32)—C(31)—C(36)	117.6 (2)
C(13)—Fe(1)—C(22)	111.0 (1)	C(32)—C(31)—C(311)	121.1 (2)
C(13)—Fe(1)—C(23)	142.7 (1)	C(36)—C(31)—C(311)	121.3 (2)
C(14)—Fe(1)—C(21)	108.4 (1)	C(31)—C(32)—C(33)	121.2 (2)
C(14)—Fe(1)—C(22)	138.2 (1)	C(32)—C(33)—C(34)	121.2 (2)
C(14)—Fe(1)—C(23)	173.7 (1)	C(33)—C(34)—C(35)	117.5 (2)
C(21)—Fe(1)—C(22)	39.6 (1)	C(33)—C(34)—C(341)	121.6 (2)
C(21)—Fe(1)—C(23)	65.8 (1)	C(35)—C(34)—C(341)	121.0 (2)
C(22)—Fe(1)—C(23)	38.4 (1)	C(34)—C(35)—C(36)	120.8 (2)
Fe(1)—C(11)—C(12)	70.2 (1)	C(31)—C(36)—C(35)	121.6 (2)
Fe(1)—C(11)—C(111)	129.2 (2)	C(31)—C(311)—C(312)	122.0 (2)
C(12)—C(11)—C(111)	120.6 (2)	C(31)—C(311)—C(314)	122.6 (2)
C(12)—C(11)—C(12^i)	118.8 (2)	C(312)—C(311)—C(314)	115.4 (2)
Fe(1)—C(12)—C(11)	70.3 (1)	C(311)—C(312)—N(313)	178.0 (3)
Fe(1)—C(12)—C(13)	71.1 (2)	C(311)—C(314)—N(315)	178.8 (3)
C(11)—C(12)—C(13)	121.3 (2)	C(34)—C(341)—C(342)	122.6 (2)
Fe(1)—C(13)—C(12)	69.6 (2)	C(34)—C(341)—C(344)	122.7 (2)
Fe(1)—C(13)—C(14)	69.0 (2)	C(342)—C(341)—C(344)	114.6 (2)
Fe(1)—C(13)—C(131)	130.0 (2)	C(341)—C(342)—N(343)	178.7 (3)
C(12)—C(13)—C(14)	118.4 (2)	C(341)—C(344)—N(345)	178.4 (3)

Symmetry code: (i) x, $\frac{1}{2} - y$, z.

and Ar. The distance between metallocene cations, d_2, is 3.43 Å in the stacks. The sum of these two distances drives the nature of the crystal packing in the metallocene TCNQ complexes. In this case it allows a period along the **a** direction which is also favourable to the stacking of TCNQ dimers in the same direction, creating segregated stacks of donors and acceptors. It may be noticed that in the ferrocene complexe [(CpMe$_5$)$_2$Fe](TCNQ)$_2$ (Miller *et al.*, 1988), the d_1 distance increases to 3.41 Å and then disturbs the possible TCNQ packing: the structure becomes alternated. A similar result was found by Fagan, Ward & Calabrese (1989) and Ward, Fagan, Calabrese & Johnson (1989) in ruthenium metallocene complexes of TCNQ. In the [CpMe$_5$-RuC$_6$Me$_6$] complexe the d_1 distance of 3.55 Å does not permit the segregated packing but in [(CpMe$_5$)$_2$Ru$_2$(1,4-cyclophane)] the dimerization of the arene group reduces the d_2 distance to 2.85 Å, restoring this possibility.

The structure of the trimethylbenzene ferrocene complex of TCNQ, which is isostructural with the hexamethylbenzene derivative, serves to emphasize that the increase in the size of the arene moiety has little effect on the structure, and thus on the electrical and magnetic properties; for example, the exchange constant J is 22 K for the Me$_3$ derivtive and 16.5 K for the Me$_6$.
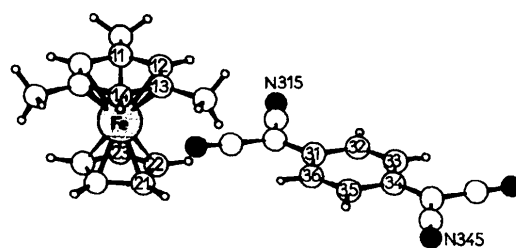
Fig. 1. Molecular conformation and atomic numbering of [(Cp)Fe(C$_6$H$_3$Me$_3$)].
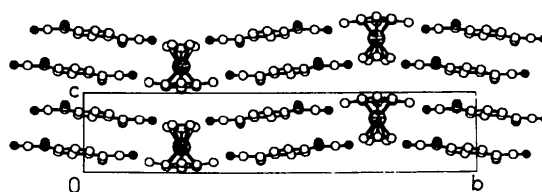
Fig. 2. View of the structure down the *a* axis.

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Structure of Tetraaqua(2,6-pyridinedicarboxylato)neodymium Perchlorate

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Abstract. $[Nd(C_7H_3NO_4)(H_2O)_4]ClO_4$, $M_r = 480.9$, cubic, $Pa\bar{3}$, $a = 20.435\,(11)$ Å, $V = 8533\,(8)$ Å^3, $Z = 24$, $D_m = 2.24$, $D_x = 2.246\,(2)$ Mg m^{-3}, $\lambda(Mo\,K\alpha) = 0.71069$ Å, $\mu = 3.92$ mm^{-1}, $F(000) = 5592$, $T = 300\,(1)$ K, final $R = 0.0374$ for 2708 unique reflections. Each Nd ion is surrounded by one N and four carboxylic O atoms, and by four water molecules. Each dipicolinate anion is bonded to three different Nd cations.

Introduction. Previously, the structures of lanthanide tris(α,α'-dipicolinates) (Albertsson, 1970, 1972) and bis(α,α'-dipicolinates) (Guerriero, Casellato, Sitran, Vigato & Graziani, 1987) have been published. This work reports the structure of a mono(α,α'-dipicolinate)neodymium complex.

Experimental. The title compound was prepared by adding an aqueous solution of $Nd(ClO_4)_3$ with a slight excess of $HClO_4$ to an aqueous solution of sodium 2,6-pyridinedicarboxylate (α,α'-dipicolinate). After a few weeks pink–violet cubes with cut vertices were formed. A specimen $0.15 \times 0.35 \times 0.5$ mm was cut from a larger crystal. D_m was measured by flotation in $C_2H_4Br_2/CHBr_3$. Oscillation and Weissenberg photographs showed the cubic system and space group $Pa\bar{3}$. A Syntex $P2_1$ diffractometer with Mo $K\alpha$ radiation was used for data collection; variable $\omega/2\theta$ scan, $4 < 2\theta < 58°$. Lattice parameters were determined using 15 reflections with $21 < 2\theta < 25°$. Two standards measured every 50 reflections showed mean relative e.s.d. of 2.3%. 9073 intensities were measured, 6841 with $I \geq 3\sigma(I)$, of which 2708

were unique; $R_{int} = 0.035$; index range $h\ 0 \rightarrow 26$, $k\ 0 \rightarrow 27$, $l\ 0 \rightarrow 27$. Absorption corrections, applied using the locally modified program *ABSORB* (Ugozzoli, 1987), were between 0.835 and 1.227. The structure was solved with *SHELXS*86 (Sheldrick, 1986) and the *XTL/XTLE* suite of programs (Syntex, 1976), and refined with *SHELX*76 (Sheldrick, 1976). Neutral-atom scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV); real and imaginary components of anomalous dispersion were included for all non-H atoms. The Nd atom was located from a Patterson map and the remaining non-H atoms from subsequent difference syntheses; C-bonded H atoms and some disordered perchlorate O atoms were placed geometrically; water H atoms were located from difference syntheses (not all were found). Final full-matrix least-squares refinement was based on F {non-H non-disordered atoms anisotropic, H atoms and disordered atoms isotropic with constrained positional parameters and common temperature factors [the following quantities were constrained: Cl1—On1 and On1⋯On'1 ($n, n' = 1, 2, 3, 4$) distances, C—H and O—H bond distances, and the H—H distances within two of four water molecules; common temperature factors were set separately for C-bonded H atoms, for O-bonded H atoms, and for O11 and O41 atoms, except that O24 had its temperature factor set twice as large as that of C14]}. Refinement converged at $R = 0.0374$, $wR = 0.0304$ [$w = 1/\sigma^2(F)$], maximum shift/e.s.d. $= 0.003$; $\Delta\rho$ between -1.09 and 1.01 e Å^{-3} (highest peaks around the Cl atoms), for 240 parameters.