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# Decamethylchromocenium Tetracyanoethenide,† $[Cr(C_5Me_5)_2]^{\therefore+}[TCNE]^{\cdot-}$: A Molecular Ferromagnet with $T_c = 3.65$ K

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The electron-transfer salt $^4[Cr(C_5Me_5)_2]^+[TCNE]^{\cdot-}$ (TCNE = tetracyanoethylene) has been prepared and structurally characterized by single-crystal X-ray diffraction. It possesses a solid-state motif of parallel 1D chains of alternating radical cations and anions similar to, but not isostructural to, the ferromagnet $[Fe(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$. $^4[Cr(C_5Me_5)_2]^+[TCNE]^{\cdot-}$ is a soft ferromagnet with no hysteretic effects observed and $T_c = 3.65$ K.

**Keywords:** *Electron-transfer salt*; *Ferromagnet*

The $[FeCp^*_2]^{\cdot+}[TCNE]^{\cdot-}$ (Cp* = pentamethylcyclopentadienide) and subsequently prepared $[MnCp^*_2]^{\cdot+}[TCNE]^{\cdot-}$ electron-transfer salts have been reported to exhibit bulk ferromagnetic behaviour with a Curie temperature, $T_c$, of 4.8[1] and 8.8 K,[2] respectively. From mean-field models the critical temperature, $T_c$, is proportional to the intra- and inter-chain exchange integral, $J_{\parallel}$ and $J_{\perp}$, and the spin, $S$.[3–5] Thus, for similarly structured materials with presumably similar values of $J$, a material with a larger value of $S$ is predicted to result in a higher Curie temperature. This is observed for the $S = 1/2$ Fe$^{III}$ and $S = 1$ Mn$^{III}$ salts. Hence, $[CrCp^*_2]^{\therefore+}[TCNE]^{\cdot-}$ with an $S = 3/2$ cation was targeted for preparation to extend this expected trend. Equally important, was the determination of the magnetic coupling. McConnell's configuration admixing model whereby a virtual triplet charge-transfer excited state is admixed with the ground state to stabilize ferro- or antiferro-magnetic coupling for chains comprising alternating donors and acceptors predicted antiferromagnetic coupling leading to ferrimagnetic behaviour for $[CrCp^*_2]^{\therefore+}[TCNE]^{\cdot-}$.[1b,4–6] Likewise, ferrimagnetic behaviour was predicted for $[CrCp^*_2]^{\therefore+}[TCNQ]^{\cdot-}$, but ferromagnetic behaviour was observed.[7] Preliminary attempts to prepare $[CrCp^*_2]^{\therefore+}[TCNE]^{\cdot-}$ were hampered by its extreme oxygen and water sensitivities and led to isolation of a material with reduced magnetic properties. Herein, we report its synthesis, structure, and magnetic properties.

## Structure Determination

The reaction of $CrCp^*_2$ and TCNE in dichloromethane, tetrahydrofuran or MeCN affords ferromagnetic $[CrCp^*_2]^+[TCNE]^{\cdot-}$. The sharp $\nu_{C\equiv N}$ infrared (IR) absorptions at 2143 and 2189 cm$^{-1}$ are characteristic of isolated $[TCNE]^{\cdot-}$.[8,9] Found: C, 69.33; H, 6.52; N, 11.76. Calc. for $C_{26}H_{30}CrN_4$: C, 69.31; H, 6.71; N, 12.44%. Crystals suitable for single-crystal X-ray analysis were grown from toluene–$CH_2Cl_2$ and the structure was determined. A 0.24 mm × 0.05 mm × 0.50 mm crystal of $[CrCp^*_2][TCNE]$ (MW = 450.55) was grown from toluene–$CH_2Cl_2$ and belongs to the triclinic $P2_1/n$ (No. 14) space group, parameters $a = 10.953(3)$ Å, $b = 14.170(5)$ Å, $c = 15.900(6)$ Å, $\beta = 92.63(2)°$, $V = 2465.1$ Å$^3$; $Z = 4$; $\rho_{calc} = 1.214$ g cm$^{-3}$; $\mu_{Mo} = 4.7$ cm$^{-1}$ at −70 °C. Using an Enraf–Nonius CAD4 diffractometer, 2898 reflections were measured using a graphite-monochromated Mo-K$\alpha$ radiation. With 178 variables the structure was refined using 714 data for which $I > 3\sigma(I)$ to convergence of $R = 0.083$ and $R_w = 0.057$ (see Table 1)‡. $[CrCp^*_2]^+[TCNE]^{\cdot-}$ belongs to the $P2_1/n$ monoclinic space group that is not isomorphous to the $C2/c$ monoclinic phase of $[FeCp^*_2]^{\cdot+}[TCNE]^{\cdot-}\cdot MeCN$.[9] However, like either monoclinic $[FeCp^*_2]^{\cdot+}[TCNE]^{\cdot-}\cdot MeCN$ or orthorhombic $[FeCp^*_2]^{\cdot+}[TCNE]^{\cdot-}$,[9] $[CrCp^*_2]^+$ $[TCNE]^{\cdot-}$ has a structure comprising parallel in- and out-of-registry $\cdots D^{\cdot+}A^{\cdot-}D^{\cdot+}A^{\cdot-}\cdots$ chains,[1b,5,9] but it is not isostructural to $[FeCp^*_2]^{\cdot+}[TCNE]^{\cdot-}$ and some differences exist which may be important in understanding the magnetic properties.

**Table 1** Crystallographic details for $[CrCp^*_2][TCNE]$

| | |
|---|---|
| formula | $C_{26}H_{30}N_4Cr$ |
| formula mass | 450.55 |
| space group | $P2_1/n$ (no. 14) |
| $a$/Å | 10.953 (3) |
| $b$/Å | 14.170 (5) |
| $c$/Å | 15.900 (6) |
| $\beta$/degrees | 92.63 (2) |
| $V$/Å$^3$ | 2465.1 |
| $Z$ | 4 |
| $\rho$(calc.)/g cm$^{-3}$ | 1.214 |
| crystal dimensions/mm | 0.24 × 0.05 × 0.50 |
| radiation | Mo-K$\alpha$ |
| absorption coefficient/cm$^{-1}$ | 4.7 |
| $T$/°C | −70 |
| scan mode | $\omega$ |
| $2\theta_{max}$/degrees | 42.0 |
| total data measured | 2898 |
| unique data with $F_0^2 > 3\sigma F_0^2$ | 714 |
| final number variables | 178 |
| weighting scheme | $\propto[\sigma(I)^2 + 0.0009I^2]^{1/2}$ |
| $R$,[a] | 0.083 |
| $R_w$,[b] | 0.057 |
| largest residual/e Å$^{-3}$ | 0.51 [C(14)] |

$$^aR = \frac{\sum(|F_0 - |F_c|)}{\sum|F_o|}; \quad ^bR_w = \left[\frac{\sum_w[|F_o| - |F_c|]^2}{\sum_w|F_o|^2}\right]^{1/2}$$

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† Bis($\eta$-pentamethylcyclopentadienyl)chromium(II) tetracyanoethylide.

‡ Supplementary data available from the Cambridge Crystallographic Data Centre: See Information for Authors, *J. Mater. Chem.*, 1993, Issue 1.

This is the best structurally determined example of $[\mathrm{MCp}^*_2][\mathrm{TCNE}]$ and the structure determination confirms the presence of isolated $[\mathrm{TCNE}]^{\cdot-}$. It is, however, disordered over two orientations rotated by 90°. Thus it is not meaningful to compare intra-$[\mathrm{TCNE}]^{\cdot-}$ bond distances and angles with more accurately determined structures of $[\mathrm{TCNE}]^{\cdot-}$.[9] The $[\mathrm{CrCp}^*_2]^+$ cation has been structurally characterized for the first time and it is essentially identical to that of $[\mathrm{FeCp}^*_2]^{\cdot+}$ except that the Cr—C ring centroids are 1.833 and 1.902 Å and average 1.87 Å which is substantially greater than the 1.70 Å for Fe—C ring centroid. Likewise, the Cr—C distances range from 2.137 to 2.278 Å and average 2.197 Å which is also greater than the comparable distance of 2.09 Å for $[\mathrm{FeCp}^*_2]^{\cdot+}$.[9]

The solid-state motif comprises parallel 1D$\cdots$D$^+$A$^{\cdot-}$D$^+$A$^{\cdot-}\cdots$ chains (D = $\mathrm{CrCp}^*_2$; A = TCNE). The arrangement and key distances of the adjacent chains is presented in Fig. 1. A comparison of the metal–metal separations for $[\mathrm{MCp}^*_2]^+[\mathrm{TCNE}]^{\cdot-}$ (M = Fe, Cr) is given in Table 2. The data indicate that while the intrachain separation is longer by 0.33 Å, the interchain separations are shorter for the Cr$^{\mathrm{III}}$ salt than the ferromagnetic (orthorhombic) phase of $[\mathrm{FeCp}^*_2]^{\cdot+}[\mathrm{TCNE}]^{\cdot-}$.

## Magnetic Measurements

The 2–320 K Faraday balance[10] magnetic susceptibility of $[\mathrm{CrCp}^*_2]^{\cdot+}[\mathrm{TCNE}]^{\cdot-}$ may be fit by the Curie–Weiss expression, $\chi_M = C/(T-\theta)$ above *ca.* 60 K, with $C$ and $\theta$ being the Curie and Curie–Weiss constants. The effective moment, $\mu_{\mathrm{eff}}[\equiv(8\chi T)^{1/2}]$, and $\theta$ values for independently prepared samples are 4.22, 4.24, and 4.24 $\mu_B$ and +22.3, 23.2, and 21.8 K, and average 4.24 $\mu_B$ and 22.2 K, respectively, see Fig. 2. The moment is as expected (*i.e.*, 4.24 $\mu_B$) from a randomly oriented

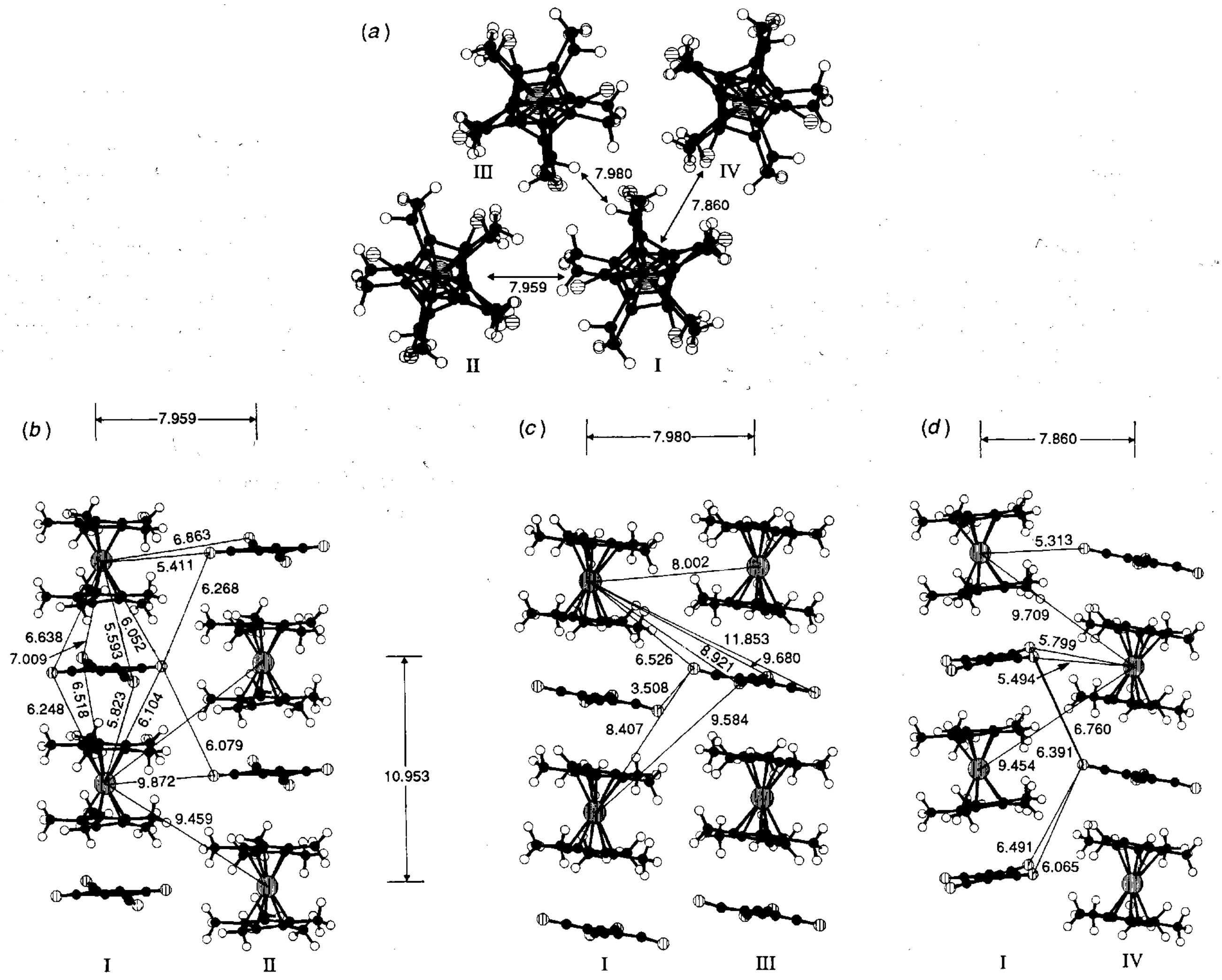

**Fig. 1** View of chains showing the unique chains: **I**, **II**, **III**, and **IV** for $[\mathrm{CrCp}^*_2][\mathrm{TCNE}]$. Distances in Å

**Table 2** Key metal–metal separations for $[\mathrm{MCp}^*_2]^+[\mathrm{TCNE}]^{\cdot+}$ (M = Fe, Cr)

| | | | interchain M···M separation/Å | | | interchain separation/Å | |
|---|---|---|---|---|---|---|---|
| cation | phase | intrachain M···M separation/Å | in-registration | out-of-registration | | in-registration | out-of-registration |
| $[\mathrm{FeCp}^*_2]^{\cdot-}$ | orthorhombic | 10.621 | 8.689 | 9.618 | 9.649 | | |
| $[\mathrm{FeCp}^*_2]^{\cdot+}$ | monoclinic | 10.415 | 8.722 | 9.473 | 10.028 | 8.732 | 8.232 |
| $[\mathrm{CrCp}^*_2]^{\cdot+}$ | monoclinic | 10.953 | 8.002 | 9.454 | 9.709 | 7.980 | 7.860 |
| | | | | 9.459 | 9.872 | | 7.959 |

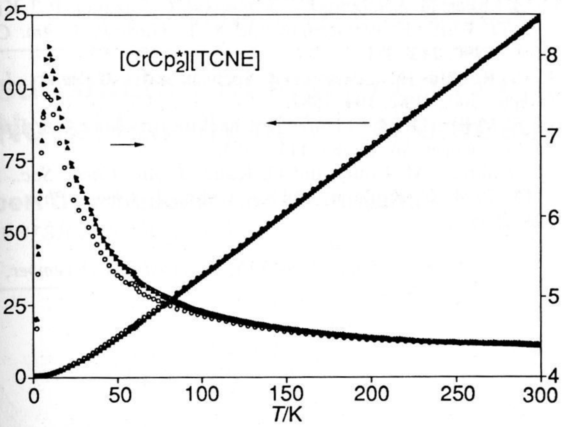

**Fig. 2** Reciprocal molar magnetic susceptibility, $\chi^{-1}$, (*a*) and moment (*b*) as function of temperature for three independently prepared samples of $[\mathrm{CrCp}^*_2][\mathrm{TCNE}]$

sample[11] of $g=2.00$ $[\mathrm{CrCp}^*_2]^{\cdot+}$ and $[\mathrm{TCNE}]^{\cdot-}$. The positive Curie–Weiss $\theta$ of 22.2 K suggests significant ferromagnetic interactions. This value of $\theta$ is less than the 30 K reported for $[\mathrm{FeCp}^*_2]^{\cdot+}[\mathrm{TCNE}]^{\cdot-}$ aligned parallel to the $C_5$ axis[1] and 22.6 K value reported for $[\mathrm{MnCp}^*_2]^{\cdot+}[\mathrm{TCNE}]^{\cdot-}$,[2] but exceeds the 16.8 K value[5] for random powders of $[\mathrm{FeCp}^*_2]^{\cdot+}[\mathrm{TCNE}]^{\cdot-}$ and 12.8 K value[7] reported for $[\mathrm{CrCp}^*_2]^{+}[\mathrm{TCNQ}]^{\cdot-}$.

Field-dependent magnetization was observed below 18 K for applied fields up to 19.5 kG for microcrystals of $[\mathrm{CrCp}^*_2]^{\cdot+}[\mathrm{TCNE}]^{\cdot-}$. The observed saturation magnetization, $M_s$, is *ca.* 24 000 emuG mol$^{-1}$ which is slightly greater than the expected value of 22 300 emuG mol$^{-1}$ for ferromagnetic alignment of the spins (or 11 150 emuG mol$^{-1}$ for antiferromagnetic alignment). A Curie temperature, $T_c$, of 3.65 K is determined from $M(T)$ data taken at 0.15 G, Fig. 3. This is substantially less than 8.8 and 4.8 K for the $S=1[\mathrm{MnCp}^*_2]^{\cdot+}$ and $S=1/2[\mathrm{FeCp}^*_2]^{\cdot+}$ containing $[\mathrm{TCNE}]^{\cdot-}$ salts, but is comparable to the 3.1 K reported[7] for $[\mathrm{CrCp}^*_2]^{\cdot+}[\mathrm{TCNQ}]^{\cdot-}$. The longer intrachain separations suggest that the $\mathrm{Cr^{III}}$ salts have significantly lower values of $J_{\parallel}$ than the $\mathrm{Mn^{III}}$ and $\mathrm{Fe^{III}}$ salts; however, the shorter interchain spacings suggest that $J_{\perp}$ is larger than that for the $\mathrm{Mn^{III}}$ and $\mathrm{Fe^{III}}$ salts.

The magnetic data characterize $[\mathrm{CrCp}^*_2]^{\cdot+}[\mathrm{TCNE}]^{\cdot-}$ as a ferromagnet. McConnell's configuration admixing of a virtual triplet charge-transfer excited state with the ground state to stabilize ferro- or antiferro-magnetic coupling for chains comprising alternating donors and acceptors predicts antiferromagnetic coupling, see Fig. 4 (top) and predicts ferrimagnetic behaviour for $[\mathrm{CrCp}^*_2]^{\cdot+}[\mathrm{TCNE}]^{\cdot-}$.[1b,5,6] Thus the observed ferromagnetic coupling suggests that the model is inadequate. The model, however, is consistent with the observed data if the acceptor←donor (A←D), Fig. 4 (bottom right-hand side) [or alternatively D←A, Fig. 4 (bottom left hand side)] charge-transfer excitation results from the POMO to the next-lowest unoccupied molecular orbital (NLUMO). [Identically, the charge-transfer excitation may be NHOMO to POMO (A←D or D←A).] This extension to the model was invoked to explain the observed ferromagnetic coupling for $[\mathrm{Cr(C_6Me_xH_{6-x})_2}]^{\cdot+}[\mathrm{TCNE}]^{\cdot-}$ ($x=3$, 6) ($\theta>11$ K) as well as $[\mathrm{TTF}]^{\cdot+}\{\mathrm{Pt[S_2C_2(CF_3)_2]_2}\}^{\cdot-}$ ($\theta=16$ K).[5,12] Recently, this was quantified *via* extensive molecular orbital calculations for $[\mathrm{CrCp}^*_2]^{\cdot+}[\mathrm{TCNE}]^{\cdot-}$ by Kahn and coworkers.[13] The relatively low $T_c$ for $[\mathrm{CrCp}^*_2][\mathrm{TCNE}]$ compared with the $T_c$s of $[\mathrm{FeCp}^*_2][\mathrm{TCNE}]$ and $[\mathrm{MnCp}^*_2][\mathrm{TCNE}]$ and the non-monotonic variation of $T_c$ suggests that for differing metallocene electron-transfer salts, different configuration interaction terms may dominate.

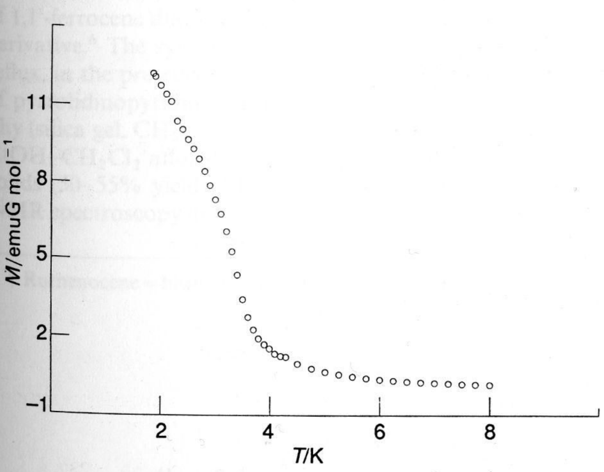

**Fig. 3** Molar magnetization as a function of temperature at 0.15 G for $[\mathrm{CrCp}^*_2][\mathrm{TCNE}]$

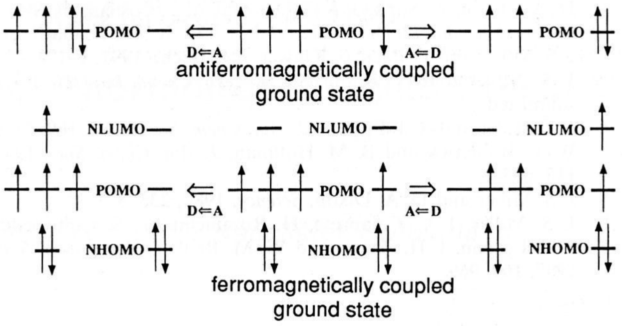

**Fig. 4** Schematic illustration of the stabilization of antiferromagnetic coupling (top) by configurational interaction (CI) only involving POMOs on adjacent sites (D and A) for the case where the $[\mathrm{CrCp}^*_2]^{\cdot+}$ D has three accidentally degenerate orbitals with three unpaired electrons and the $[\mathrm{TCNE}]^{\cdot-}$ A has one unpaired electron residing in a nondegenerate orbital for either A←D (right-hand side) or D←A (left-hand side) charge transfer. Stabilization of ferromagnetic coupling (bottom) by CI involving only virtual excitation from a POMO on D to a virtual NLUMO on A (right-hand side), or from a POMO on A to a virtual NLUMO on D (left-hand side)

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