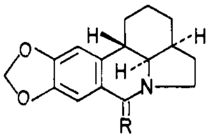
crude alcohol to **5b**, mp 136–137 °C, in 50–55% overall yield. Conversion of **5b** into **6** could be accomplished in high yield under carefully defined conditions (i.e., 0.176 mmol of **5b** in 5 mL of THF, 1 mL of MeOH, 2 mL of H_2O, 5 equiv of $NaIO_4$,[12] 6.75 equiv of $NaHCO_3$, for 24 h, and then an additional 5 equiv of $NaIO_4$–2 mL of H_2O, 18 h; 94%). The triene **6** cyclized in 51% yield to a single compound **7**, mp 218–220 °C at 140 °C (0.145 mmol of **6** in 600 mL of chlorobenzene, 2 mg of 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide, 0.5 mL of O,N-bis(trimethylsilyl)acetamide at reflux under argon, in ammonia-treated glassware for 24 h). At 80 MHz, the ^1H NMR spectrum in $CDCl_3$ offered little information concerning the stereochemistry at the ring junction of the adduct. Both the benzylic and amide methine protons were obscured by other resonances. In benzene-d_6 the resonances due to H_a and H_b were separated, allowing observation of J_{bc} = 12 Hz, upon irradiation of the H_a signal. This value, which is in accord with the expected values for galanthan systems,[13] establishes **7** as the structure of the sole adduct obtained. Furthermore, hydrogenation of this substance (EtOAc, 5% Pd/C, 1 atm, 25 °C) afforded the galanthan **8a**, 7-oxo-α-lycorane, mp 169–171 °C, identical in all respects (IR, NMR, mass spectral fragmentation pattern, TLC, and mixture melting point) with material prepared from an authentic sample of (±)-α-lycorane[14] (**8b**) (potassium permanganate–acetone–water, 0 °C, 20 min;[15] 50–60% yield). The simplicity and potential versatility of this route suggests that it will be valuable in the construction of a number of lycorine alkaloids.



8a R=O

8b R=H,H

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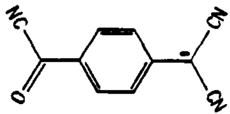
Synthesis and Characterization of the Metamagnetic 1:1 1-D Phase of the Decamethylferrocenium 7,7,8,8-Tetracyano-*p*-quinodimethanide: $Fe[C_5(CH_3)_5]_2{}^{+}\cdot(TCNQ)^{-}\cdot$

Sir:

The reaction of decamethylferrocene (DMeFc) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) results in the formation of several interesting substances, namely, phase I and phase II 1:1 charge-transfer salts and a third substance of 1:2 composition, $(DMeFc)(TCNQ)_2$.[1] In a previous paper we reported the structure of the paramagnetic phase I substance, i.e., $(DMeFc^{+})_2\cdot(TCNQ)_2{}^{2-}$, which exists as isolated dimers in the solid state.[2] Large crystals (~18 mg) of the phase I material are isolated upon long standing from an acetonitrile solution of DMeFc and TCNQ (1:1). Quick crystal growth (~2 h), however, results in the reproducible formation of a phase II polymorph of identical composition, but with an enhanced oxygen sensitivity. Furthermore, the phase II substance exhibits unusual magnetic properties,[3] i.e., metamagnetism.

Initially only one 1:1 substance was assumed; however, the optical absorptions characteristic of an isolated $TCNQ^{-}\cdot$ (Figure 1), which differ markedly from that predicted for the $TCNQ^{-}$ dimer[4] present in the dimeric phase I polymorph, and the observation of simple Curie-like paramagnetism for large single crystals led us to suspect a second phase. Furthermore, in contrast to crystals of the dimeric substance, on standing in the ambient atmosphere sublimed thin films turned red and gave a red-yellow solution in acetonitrile (λ_{max} ~480 nm). These differences in reactivity again suggested the presence of two distinct phases. Herein we report the characterization of the metamagnetic phase II material, $(DMeFc^{+}\cdot)(TCNQ^{-}\cdot)$. We also show structural evidence for the formation of α,α-dicyano-*p*-toluoylcyanide anions, formed from the solid-state reaction of $(DMeFc^{+}\cdot)(TCNQ^{-}\cdot)$ and air.

The large phase I crystals are stable with respect to reaction with oxygen presumably owing to the unreactiveness of the tight $(TCNQ)_2{}^{2-}$ dimer which is formed. A freshly sublimed thin film of the phase I dimer exhibits an ESCA spectrum containing a single N_{1s} peak at 398.2 eV. Upon exposure to the atmosphere for 24 h, the film had a pronounced O_{1s} peak at 532.8 eV and the N_{1s} peak split into a double at 400.3 and 398.3 eV. These data confirmed that oxygen reacted with the $TCNQ^{-}\cdot$. A possible reaction product consistent with the ESCA data is the α,α-dicyano-*p*-toluoylcyanide anion ($DCTC^{-}\cdot$, **1**), which has been previously reported to result from the oxygenation of $TCNQ^{2-}$.[5a] Resonance Raman spectra taken on aged bulk crystals of the phase II polymorph by using 514.5-nm radiation confirmed the presence of **1**. This radiation enhanced the $DCTC^{-}\cdot$ absorptions at 1624, 1331, 1282, and 1172 cm^{-1}. Additionally using 459.9-nm radiation, a frequency of 1392 cm^{-1} characteristic of $TCNQ^{-}\cdot$ (ν_4) absorption was observed.[5b]



1

The green phase II material crystallizes as rectangular block crystals in the monoclinic, centrosymmetric, space group, $P2_1/n$ (C_{2h}, No. 14) with unit cell constants a = 10.840 (5), b = 30.999 (13), c = 8.628 (3) Å; β = 99.20 (3)°; Z = 4; ρ_{calcd} = 1.238 g cm^{-3} (ρ_{obsd} = 1.238 (5) g cm^{-3} by flotation in cyclohexane–1,2-dibromoethane). The only crystal found suitable for X-ray studies was unfortunately kept unprotected from the atmosphere for 18 months. Attempts to grow larger crystals

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Table I. X-Ray Diffraction Powder Patterns of $Fe(C_5(CH_3)_5)_2^{+}\cdot(TCNQ^{-}\cdot)$[a–c]

powder under argon	powdered single crystal after exposure to air
5.0 (vw)	5.0 (vw)
5.6 (vs)	5.6 (vs)
	5.8 (m)
6.2 (s)	6.2 (m)
6.9 (vw)	6.7 (w)
8.4 (m)	8.3 (m)
9.5 (vw)	9.5 (vw)
10.5 (vw)	
12.9 (s)	12.8 (s)

[a] Diffraction lines are reported in degrees θ. [b] vs = very strong; s = strong; m = medium; w = weak; vw = very weak. [c] Patterns were taken with Cu K$\bar{\alpha}$ radiation, 1.5418 Å.

led to the isolation of large crystals of only the phase I polymorph. Diffractometer ω scans showed the mosaic spread of the crystals to be on the order of 0.65° (fwhm) which is considerably larger than normal (~0.30° fwhm) and is an indication of significant disorder or decomposition. Although 5068 unique reflections were collected on a Syntex $P2_1$ automated diffractometer to a 2θ limit of 50° (Mo K$\bar{\alpha}$), only 935 reflections were considered observable. To confirm that the structure of the materials before and after reaction with air were the same, powder diffraction data were recorded on freshly prepared phase II powder and powdered phase II single crystals exposed to air. The observed spacings of both of these materials are essentially the same (Table I); however, there are several intensity variations. This result shows that the materials are isomorphous with only small structural differences. All of the above observations indicate a possible O_2 reaction over extended periods of time which results in a significant structural disorder and little change in cell parameters.

The structure was determined by a combination of Patterson, direct methods, Fourier, and least-squares refinement techniques. At this stage of the refinement with all atoms refined with isotropic thermal parameters, except Fe where anisotropic thermal parameters have been included, the $R_F{}^2$ = 0.118 for all observable data. The larger than normal discrepancy index is a result of considerable disorder within the $TCNQ^{-}\cdot$ anions and the $DMeFe^{+}\cdot$ cations.

The crystalline lattice consists of parallel one-dimensional (1-D) chains comprised of alternating $DMeFe^{+}\cdot$ cations and $TCNQ^{-}\cdot$ anions (Figure 2). This structural array differs markedly from the phase I material, which is dominated by tight a_u, $[TCNQ]_2{}^{2-}$ dimers, and is similar to the donor–acceptor complexes reported for ferrocene and tetracyanoethylene,[6] *N,N,N′,N′*-tetramethyl-*p*-diaminobenzene and TCNQ[7] and proposed for bis(arene)iron(II)$^{2+}$ and ferrocene.[8] Recently, we have observed this structural arrangement in DMeFc-2,3-dichloro-5,6-dicyano-1,4-benzoquinone.[9] Additionally, this type of structure has been reported for the spin Peierls compounds, namely, the 1:1 tetrathiofulvalenium salts of $M[S_2C_2(CF_3)_2]_2$ (M = Cu, Au).[10] The distances between the cation and anion within a chain are 3.67 (2) and 3.66 (3) Å compared with 3.554 Å in the phase I material[2] and 3.14 Å in the ferrocene–tetracyanoethylene complex.[6] The expansion is primarily due to the interaction of the anion and the methyl groups of the C_5 rings.

The C_5 rings of the $DMeFc^{+}\cdot$ ion are eclipsed, which is similar to the results found for the phase I dimer[2] and for $[Fe(C_5H_5)_2][BiCl_4]$.[11] The average Fe–C, C–C, and C–Me distances are 2.07 (3), 1.39 (4), and 1.56 (4) Å, respectively. As is common among ferrocene complexes, each C_5 ring is structurally disordered, which, when resolved, would cause potential staggering of the C_5 rings.

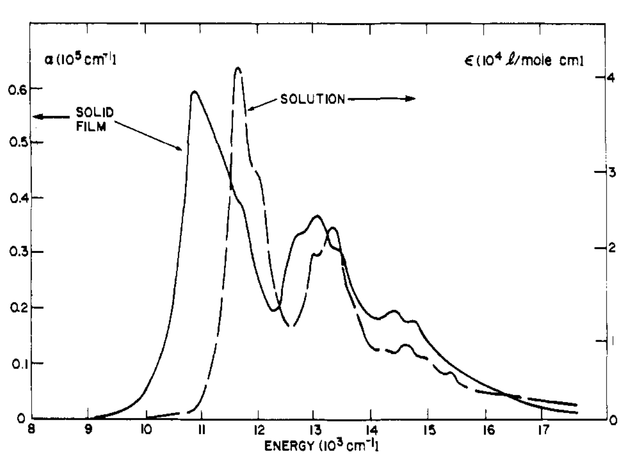

Figure 1. The solution (acetonitrile) and thin-film solid-state adsorption spectra of (DMeFc)(TCNQ).

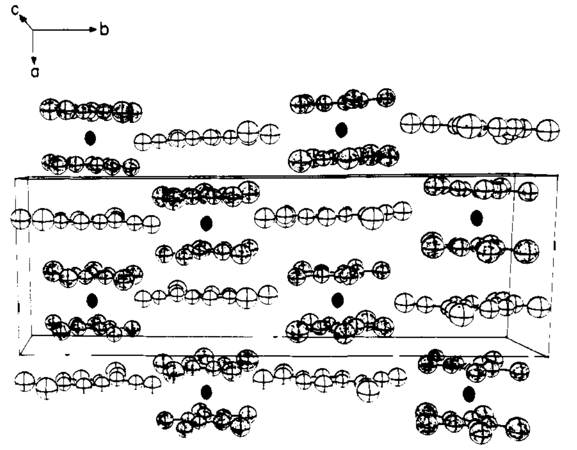

Figure 2. Unit cell of (DMeFc)(TCNQ) viewed down the *c* axis. One of the CN groups of TCNQ has been replaced by O showing the $DCTC^{-}\cdot$ ion. The $DMeFc^{+}\cdot$ cation is shaded.

Within the preceding discussion the anion was assumed to be spin ½ $TCNQ^{-}$. Based on spectroscopic and crystallographic evidence, what is realistically observed appears to be a combination of $TCNQ^{-}\cdot$ and $DCTC^{-}\cdot$ (**1**) ions. The isotropic thermal parameters of the anion are much larger than normal, being on the order of 6–10 Å^2 for the C atoms compared with 2–4 Å^2 in other $TCNQ^{-}\cdot$ anion structures, and are extremely large, 11–15 Å^2, for the N atoms indicating severe disorder of these groups. An explanation of this disorder is the reaction of the $TCNQ^{-}\cdot$ with air forming $DCTC^{-}\cdot$ ions. We have refined a model where the more disordered cyano groups is replaced by oxygen. The bond distances within the anion appear to be combinations of distances expected for $DCTC^{-}\cdot$ and the unreacted $TCNQ^{-}\cdot$. Because of the poor quality of the crystals after reaction with air, the extent of the disorder is unlikely to be determined.

Within an isolated 1-D $DMeFc^{+}\cdot TCNQ^{-}\cdot$ chain, the S = ½ Fe^{III} sites are 10.840 (5) Å apart. These intrachain separations permit cooperative magnetic interactions to manifest themselves. Coupling between parallel 1-D chains appears to be minimal owing to a lack of direct orbital interactions.

In conclusion, we determined the structure of the reaction product between metamagnetic phase II $(DMeFc^{+}\cdot)(TCNQ^{-}\cdot)$ and oxygen and have shown that it is isomorphic with the unreacted 1:1 phase and it is comprised of isolated S = ½ $DMeFc^{+}\cdot$ and S = ½ $TCNQ^{-}\cdot$ ions. The oxidized $TCNQ^{-}$ forms **1** which was confirmed spectroscopically and crystallographically. Furthermore, the absorption spectra with vibrational fine structure of detailed isolated $TCNQ^{-\cdot}$ in the solid state is reported here for the first time.

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Electrochemistry of Cytochrome *c*. Comparison of the Electron Transfer at a Surface-Modified Gold Electrode with That to Cytochrome Oxidase

Sir:

As we have recently shown,[1] rapid direct electron transfer between cytochrome *c* and a gold electrode takes place in the presence of 4,4′-bipyridyl and 1,2-bis(4-pyridyl)ethylene, which form an adsorbed layer on the electrode surface thus facilitating the electron-transfer reaction. We report here some striking analogies between the reaction of cytochrome *c* at this electrode and its reaction with cytochrome oxidase with respect to the effect of chemical modification of the cytochrome *c* lysine residues and the effect of poly-L-lysine on the electrode reaction. The results suggest that cytochrome *c* binds to the 4,4′-bipyridyl-modified gold electrode surface prior to electron transfer in a manner similar to its interaction with the oxidase.

The electron-transfer reaction between cytochrome *c* and cytochrome oxidase proceeds via a protein complex in which the ϵ-amino groups of the cytochrome *c* lysine residues are believed[2] to play an important role. Chemical modification of these lysines is well known[3] to affect the cytochrome *c*-oxidase electron-transfer reaction. The importance of lysine residues in the protein-protein interaction is further illustrated by the effect[4] of poly-L-lysine, a competitive inhibitor of the cytochrome *c*-oxidase reaction which acts by binding[5] to the oxidase.

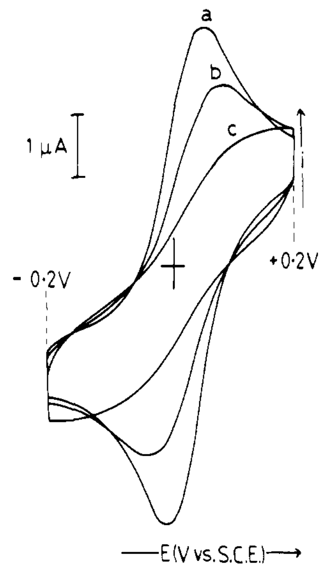

Figure 1. dc cyclic voltammogram of horse heart ferricytochrome *c*, 0.4 mM in 0.1 M NaClO$_4$, 0.02 M phosphate buffer, pH 7, saturated solution of 1,2-bis(4-pyridyl)ethylene in the potential range of +0.2 to −0.2 V vs. SCE with poly-L-lysine: (a) 0 mg/mL^{-1}, (b) 1 mg mL^{-1}, (c) 1.5 mg mL^{-1}. dc potential scan rate, 100 mV s^{-1}.

We have investigated the effect of acetimidilation,[6] guanidinilation,[7] trifluoracetylation,[8] and maleylation[9] of cytochrome *c* and the effect of poly-L-lysine on the electrode reaction studied by cyclic voltammetry as previously described,[1] and find the following: Both *N*-acetimidyllysyl[10] and *N*-guanidinyllysyl[11] horse heart cytochrome *c* are found to be electroactive[12] at the gold electrode in the presence of 4,4′-bipyridyl or 1,2-bis(4-pyridyl)ethylene, giving rise to quasi-reversible diffusion-controlled dc and ac voltammograms indistinguishable from those (Figure 1a) of the native protein,[1] with a half-wave potential, $E_{1/2}{}^{r}$ = 0.25 V vs. NHE. Similarly both are enzymatically active[5,6] in the cytochrome-oxidase system. However, the enzymatically inactive *N*-trifluoroacetyl[13] and *N*-maleyl[14] derivatives are both electroinactive.

Poly-L-lysine[15] is found to inhibit the electrode reaction of native horse heart cytochrome *c*, as shown by its effect on the dc voltammetry (Figure 1), again analogous to its inhibiting effect on the cytochrome *c*-oxidase reaction. The effect on the ac cyclic voltammetry peak current, i_p(ac), is more marked. The variation with poly-L-lysine concentration (Figure 2) is consistent with adsorption of poly-L-lysine onto the electrode surface, decreasing the effective free electrode area.

The electron-transfer reaction of the native protein has been studied by ac impedance measurements[16] and we find the heterogeneous electron-transfer rate to be as fast as that determined[17] for the ferri/ferrocyanide couple (0.3–3.0 × 10^{-4} m s^{-1}). The measured in-phase and quadrature-phase components of the ac current, treated as described[18] by De Levie and Pospisil, yield a plot of real, Z_F', against imaginary, Z_F'', component of faradaic impedance which is a straight line of unit slope, with an intercept on the real axis as expected for the quasi-reversible case. From this the heterogeneous rate constant, k_s, can be calculated[18] as 1.86 × 10^{-4} m s^{-1}. The cotangent of phase angle shows a linear relationship with the square root of ac modulation frequency, consistent[19] with the quasi-reversible nature of the reaction. The value of k_s = 1.4 × 10^{-4} m s^{-1} thus derived[19] is in good agreement with the value obtained above.

Preliminary investigations[20] using the methods of double-potential-step chronocoulometry, rotating disk and ac rotating

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