Electrically conducting TCNQ Derivatives of Copper Sulphur/Nitrogen Chelates; Structure of a Novel Semiconducting Complex $[Cu(pdto)(TCNQ)]_2$ which contains N-bonded TCNQ (pdto = 1,8-di-2-pyridyl-3,6-dithiaoctane; TCNQ = 7,7,8,8-tetracyanoquinodimethane)

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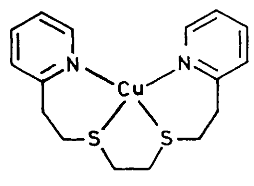
Reaction in water of $Cu(pdto)(ClO_4)_2$ with Li(TCNQ)/TCNQ mixtures yields solid crystalline materials of formulae $Cu(pdto)(TCNQ)_x$ (x = 2, 2.5, or 3) which display high electrical conductivities; reaction of $Cu(pdto)(ClO_4)$ with Li(TCNQ) yields Cu(pdto)(TCNQ), a poor conductor which has been shown by *X*-ray crystallography to have a novel dimeric structure involving π–π interaction between TCNQ units and which possesses Cu–TCNQ bonding.

As part of a project studying new electrically conducting solid materials of the charge-transfer and conducting polymer types, we are investigating TCNQ (7,7,8,8-tetracyanoquinodimethane) derivatives of mono- and bi-nuclear copper chelates. The pioneering work of Melby,[1] and subsequent studies by groups such as those of Endres[2] and Inoue,[3] have generally employed metal–N donor mononuclear complexes in reactions with TCNQ. One aim of our work has been to vary the nature of the donor atoms in the metal-complex partner of the charge-transfer complex in order to vary the redox potential and, possibly, to vary the structural features of the metal-complex donor. Such variations are intended to produce molecular materials which will show enhanced conductivity, preferably of magnitude appropriate to the metallic region. We are particularly interested in mixed sulphur–nitrogen donor sets such as that found in the pyridyl-thioether ligand, pdto, the copper complex of which (Figure 1) shows a positive Cu^{II}/Cu^{I} potential[4,5] in relation to that of $TCNQ/TCNQ^-$ and a planar S_2N_2 co-ordination in the solid state.[6]

Reactions in deoxygenated water of $Cu(pdto)(ClO_4)_2$ with Li(TCNQ)/TCNQ mixtures yielded green–black needle-shaped crystals of formula $Cu(pdto)(TCNQ)_x$, where the value of x depends on the ratio of $Cu/TCNQ^-/TCNQ$ used (Figure 1).

Despite repeated attempts to obtain non-twinned crystals suitable for structural elucidation, twinned crystals have thus far been obtained in the case of (**1**) and (**2**). Nevertheless,



$Cu(pdto)(TCNQ)_2$ (**1**)
$Cu(pdto)(TCNQ)_{2.5}$ (**2**)
$Cu(pdto)(TCNQ)_3$ (**3**)
$[Cu(pdto)(TCNQ)]_2$ (**4**)

Figure 1

Table 1. Electrical conductivities and spectral properties of Cu(pdto)(TCNQ)$_x$ and related species.

Compound	Conductivity, σ (295 K)/ Ω^{-1} cm^{-1}	E_a/eV	C–H bending frequency/ cm^{-1}	(ε 394 nm) / (ε 842 nm) MeCN soln.	Ref.[a]
Cu(pdto)(TCNQ)$_2$ (**1**)	1.3×10^{-2}	0.09	844	1.57	t.w.
Cu(pdto)(TCNQ)$_{2.5}$ (**2**)	7.1×10^{-1}	0.09	844	2.83	t.w.
Cu(pdto)(TCNQ)$_3$ (**3**)	6.8×10^{-2}	0.08	865, 841	2.06	t.w.
[Cu(pdto)(TCNQ)]$_2$ (**4**)	1.1×10^{-5}	—	827	0.47	t.w.
Cu(dpa)$_2$(TCNQ)$_2$·H$_2$O	1.1	0.05	838	1.70	3 & t.w.
Li(TCNQ)	5×10^{-6}	—	829	0.58	t.w.
TCNQ	—	—	862	—	t.w.

[a] t.w. = this work.

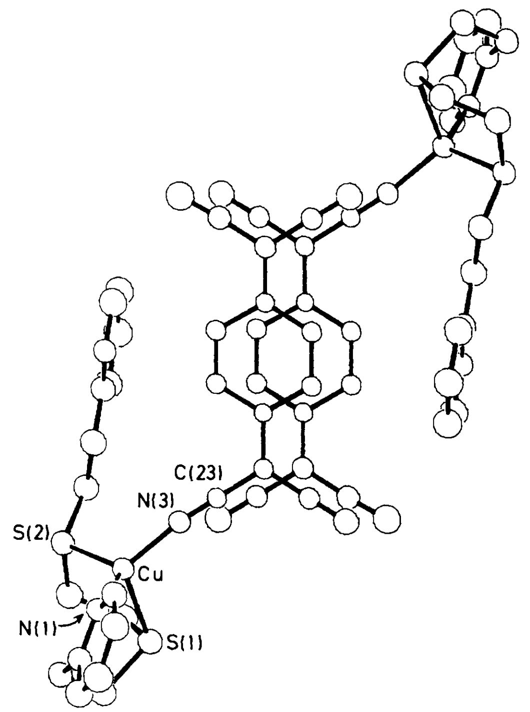


Figure 2. Molecular structure of [Cu(pdto)(TCNQ)]$_2$, (**4**). Selected bond distances (Å) and angles (°): Cu–S(1) 2.362(2); Cu–S(2) 2.286(2); Cu–N(1) 2.057(5); Cu–N(3) 1.951(5); N(1)–Cu–S(1) 97.5(1); S(1)–Cu–S(2) 93.3(1); S(2)–Cu–N(3) 120.2(2); N(3)–Cu–N(1) 109.6(2); Cu–N(3)–C(23) 166.1(5); TCNQ · · · · TCNQ interplanar separation 3.12 Å. TCNQ$^-$ average bond lengths (see ref. 9): *a* 1.358, *b* 1.420, *c* 1.418, *d* 1.410 Å.

these materials show room temperature powder conductivity values typical of good semiconductors and close to the metallic region (Table 1). Variable temperature 4-probe resistivity measurements yield linear ln σ *vs.* $1/T$ plots over the range T = 77—300 K from which activation energies of *ca.* 0.1 eV were deduced. As shown in Table 1, these σ and E_A values are rather similar to those of the dipyridylamine (dpa) complex of Inoue *et al.*,[3] Cu(dpa)$_2$(TCNQ)$_2$·H$_2$O, which has been shown to display one of the highest conductivities of this class of TCNQ adduct. Compounds (**1**)—(**3**) exhibit u.v.–visible and i.r. spectral features (Table 1) which are characteristic[1,2] of partially oxidised TCNQ units within a stacked structure. Thus, (**1**) and (**2**) show a C–H bending vibration at values intermediate between those of TCNQ$^-$ and TCNQ, as well as broad bands at *ca.* 1300 and 1100 cm^{-1}, features characteristic of equivalent, partially charged, TCNQ units. Compound (**3**) shows a weak extra band at 865 cm^{-1}, indicative of neutral TCNQ molecules held within the lattice structure. Compound (**3**) readily yields a mixture of crystals of (**2**) and TCNQ on recrystallization from acetonitrile.

Charge transfer between Cu^{II} and TCNQ$^-$ in equilibrium

$$\mathrm{Cu^{II}(pdto)(TCNQ^-)_x} \rightleftharpoons \mathrm{Cu^{I}(pdto)[(TCNQ)_x]^-} \quad (1)$$

(1) lies predominantly to the right as judged by e.s.r. studies of powdered samples. These spectra yield no evidence for localized Cu^{II} signals of the kind found in the precursor complex Cu^{II} (pdto)(ClO$_4$)$_2$.[4,5] Only sharp narrow lines at g = 2.003 were observed arising from delocalized TCNQ$^-$ electrons. Preliminary magnetic susceptibility studies on (**1**) over the range 4.2—300 K using a 10 kOe‡ applied field showed a very small, temperature-independent Pauli susceptibility of the type expected for conducting electrons. However, this compound, as well as (**2**), (**3**), and Cu(dpa)$_2$(TCNQ)$_2$·H$_2$O displays a surprising field dependence of the magnetic moment at room temperature. Compound (**2**), for example, shows μ = 1.67 μ_B under H_{appl} = 2 kOe and μ = 0.81 μ_B at 7 kOe. This field dependence does not appear to have been recognised in related studies, and was not commented on by Inoue *et al.*[3] in their magnetic studies of Cu(dpa)$_2$ (TCNQ)$_2$·H$_2$O, the results for which we can reproduce. Further magnetic studies are warranted.

One of the most interesting results to emerge from this study is the structure† of (**4**), a purple complex prepared by the reaction of colourless Cu^{I}(pdto)(ClO$_4$) with Li(TCNQ) in MeCN. All the properties of this diamagnetic compound (Table 1), including its weak semiconductivity, are compatible

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‡ 1 A/M = 4π × 10^{-3} Oe.

† *Crystal data* for C$_{28}$H$_{24}$CuN$_6$S$_2$: M = 572.2, monoclinic, space group $P2_1/a$, a = 13.663(3), b = 15.900(3), c = 12.171(3) Å, β = 99.42(2)°, U = 2608(1) Å^3, Z = 4, D_c = 1.46, D_m = 1.45(1) g cm^{-3}, F(000) = 1180, μ(Mo-K_α) = 10.2 cm^{-1}, T = 293 K. Crystal dimensions 0.32 × 0.27 × 0.12 mm; data were collected in the range 6° < 2θ ≤ 60° in the ω scan mode; intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELX-76) and refined by full-matrix least-squares procedures. A total of 2792 unique reflections with $I > 3\sigma(I)$ were refined to conventional values of R (R_w) of 0.059 (0.055). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

with its being a localized 'salt.' However, as is evident in Figure 1, the structure makes it one of the rare examples to possess direct metal–TCNQ co-ordination. Each Cu^I is tetrahedrally co-ordinated to two thioether S, one pyridyl N, and one N atom of TCNQ, the latter having displaced the other pyridine group, which was co-ordinated in the precursor complex.[4,6] This dangling pyridine group is disposed at *ca.* 90° to the TCNQ ring. The Cu(pdto)(TCNQ) molecules are dimerized *via* π–π interactions (spacing 3.12 Å) between adjacent TCNQ units, and this leads to a very symmetrical overall structure containing a centre of inversion. Other recent examples of TCNQ-like co-ordination include the compounds $[M(2,5\text{-}Me_2\text{-}DCNQI)]_2$ (where M = Cu or Ag and $2,5\text{-}Me_2$-DCNQI = 2,5-dimethyl-*N*,*N*′-dicyanobenzoquinonediimine). These compounds do not contain a co-ligand, but do display metallic conductivity over extended temperature ranges, no doubt due to the uniform stacked structure of $2,5\text{-}Me_2$-DCNQI units. The role of the metal ion in the conductivity mechanism in these materials is unclear. As in the present complex (**4**), the metal ions adopt a tetrahedral co-ordination geometry.[7,8]

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