Thallium Tetracyanoquinodimethanide (TCNQ$^-$) and its 18-Crown-6 Complex

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The preparation of Tl^{I}TCNQ and its 18-crown-6 complex are reported together with an X-ray structural study of the latter which provides the first example of a crown ether-complexed Tl$^+$ salt in which the lone pair plays an active stereochemical role in the solid state.

Despite extensive studies of the properties of simple (*i.e.* 1:1 stoichiometry) metal cation TCNQ$^{\cdot -}$ salts (MTCNQ, where M = Li, Na, K, Rb, Cs, Ag, *etc.*)[1,2] and a few dialkyl-Tl^{III} salts[3] the preparation of Tl^{I}TCNQ itself has never been reported. Our recent investigations[4–7] have shown that the complexes K(18-crown-6)TCNQ **1a** and Rb(18-crown-6)-TCNQ **1b** have almost identical structural, but somewhat different electronic, behaviour. In view of the similar size but potentially different coordination requirements of Tl$^+$ arising from its pair of antibonding s electrons,[8,9] and the current interest in the effect of coordination on the solid-state properties of TCNQ salts[10] we have undertaken the preparation of Tl(18-crown-6)TCNQ **1c**.

Whilst 'normal' conditions[1] failed to give TlTCNQ, a metathesis reaction between TlNO$_3$ and LiTCNQ in boiling water produced material of excellent purity in high (89%) yield.† Treatment of this salt with 18-crown-6 in boiling acetonitrile followed by slow solvent evaporation at room temperature gave high quality† crystals of Tl(18-crown-6)-TCNQ.

Nine crystal structures are documented in which thallium is encapsulated by an ionophore (in each case a substituted crown ether or cryptand),[11,12] four of which concern dimethyl-Tl^{III} salts.[11] In the solid state Tl(18-crown-6)TCNQ **1c** favours a TCNQ dimer structure‡ (Fig. 1) analogous to that found in its K$^+$ and Rb$^+$ analogues **1a** and **1b**, the Tl$^+$ ion being coordinated to six crown ether oxygens and two nitriles from different TCNQ units. In **1c** the metal cation is significantly shifted towards the TCNQ dimer long axis [Fig. 1(*a*)] and lies further away from the cyanide nitrogens when compared with **1a** or **1b** (in which the metal ion lies along the CN bond axis of the TCNQ dimer). We conclude from this that the lone pair of the Tl$^+$ cation is playing an active stereochemical role in the solid-state structure of **1c**;[13] such behaviour has also been tentatively suggested for Tl^I(benzo-15-crown-5) picrate.[9] The

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† TlTCNQ forms dark-blue microcrystals, m.p. 224 °C (decomp.), 10^{-3} λ_{max}/cm^{-1} 13.7 and 23.5 cm^{-1}; ν_{max}/cm^{-1} (KBr disc) 3 peak envelope at 2180 (CN), 1568 [C=C(CN)$_2$], 1505 (C=C ring), 1364 (CH bend), 1329 (C–C ring), 1168 (C–CN and C–C ring), 985w (C–C ring), 824m and 718w (CH out-of-plane bend).

Tl(18-crown-6) TCNQ forms blue-black rod-like crystals, m.p. 180 °C decomp., 10^{-3} λ_{max}/cm^{-1} (Nujol mull) 10.5, 14.3 and 25.6; ν_{max}/cm^{-1} (KBr disc) 2889m (saturated CH), 2181 and 2154 (CN), 1583m [C=C(CN)$_2$], 1503 (C=C ring), 1360 (CH bend), 1179m (C–CN and C–C ring), 986w (C–C ring), 828m and 718w (CH out-of-plane bend).

Satisfactory elemental analyses were obtained for both compounds.

‡ *Crystal data*: $C_{24}H_{28}N_4O_6Tl$, M = 672.9. Monoclinic, a = 14.019(1), b = 8.187(1), c = 22.994(3) Å, β = 97.82 (1)°, V = 2614.49 Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 1.5418 Å), space group $P2_1/c$ (No. 14), Z = 4, D_c = 1.71 g cm^{-3}. Blue-black rods. Crystal dimensions: 0.07 × 0.13 × 0.27 mm, μ(Cu-Kα) = 122.2261 cm^{-1}.

Data collection and processing: CAD4 diffractometer, ω–2θ with ω scan width = 0.67 + 0.15 tanθ, ω scan speed 1.1–6.7 deg min^{-1}, graphite-monochromated Cu-Kα radiation; 7607 reflections measured ($1 \leqslant \theta \leqslant 75°$), 5151 unique [merging R = 5.03% after correction for Lorentz and polarisation effects (max., min. transmission factors = 1.76, 4.35)], giving 3056 with $I > 3\sigma(I)$. Intensity controls stable.

Structure analysis and refinement: Direct methods (using Hg as a substitute for Tl) followed by difference Fourier techniques. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions (C–H 0.97 Å), constrained to 'ride' on the attached atoms. DIFABS correction followed by corrections for anomalous scattering and extinction and a two-term Chebychev polynomial weighting scheme (0.991, −0.0149).[17] The hydrogens were refined isotropically in two groups U_{iso}[= 0.038(8) Å^2] for the TCNQ hydrogens and U_{iso}[= 0.082(5) Å^2] for the crown ether hydrogens. Final R and R_w values are 3.57 and 3.19% respectively. Programs used and sources of scattering factor data are given in ref. 18.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

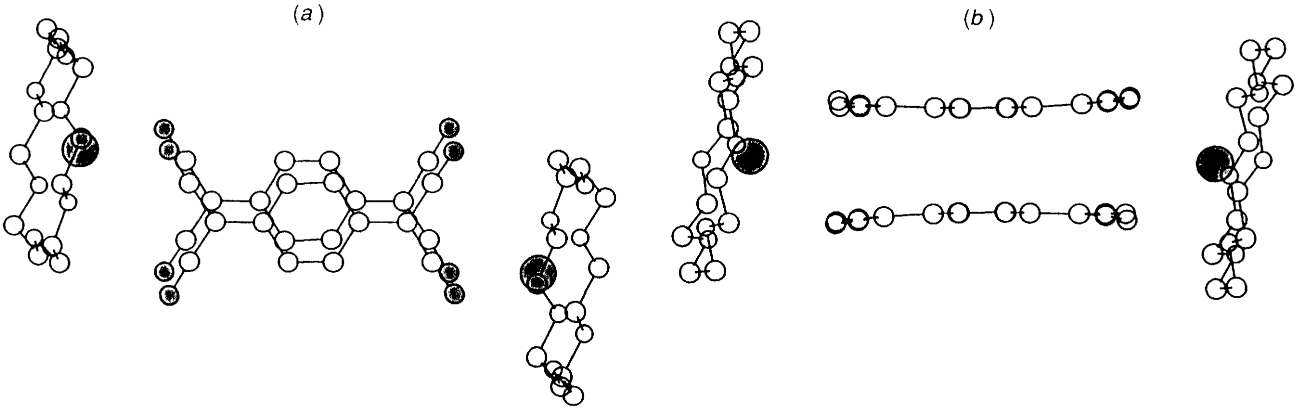

Fig. 1 (*a*). A top view of the TCNQ dimer unit present in Tl(18-crown-6)TCNQ showing a preference for short-axis slip over long-axis and the deviation of the metal away from the line along the CN bond axis. (*b*). A side view of the TCNQ dimer unit present in Tl((18-crown-6)TCNQ showing the TCNQ boat conformation and how the crown-ethers tilt away from the normal to the TCNQ ring.

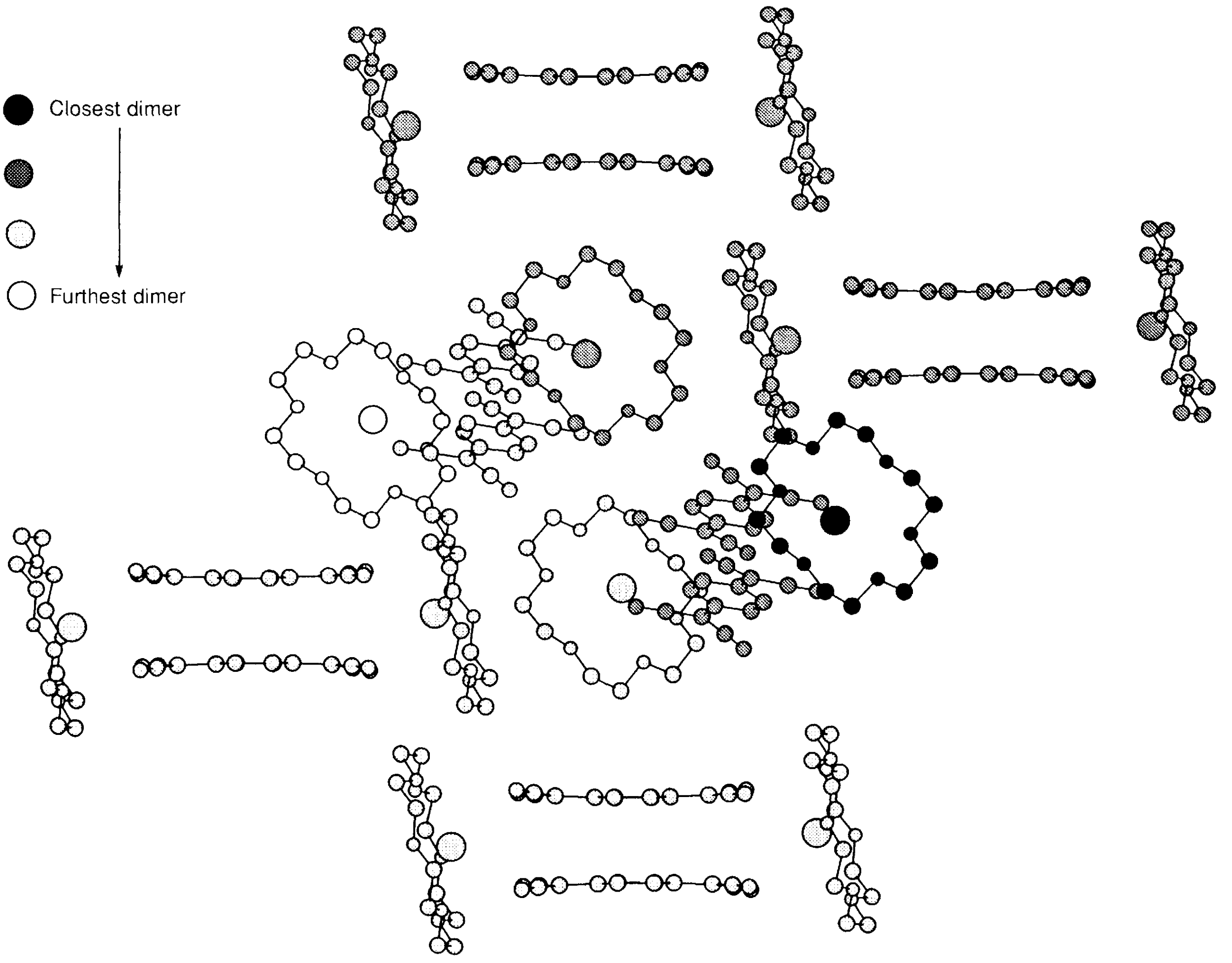

Fig. 2 The packing in the Tl(18-crown-6)TCNQ salt showing the two very distinct isolated TCNQ dimer columns

Tl^+ cation sits 0.89 Å above the crown ether plane (defined by the oxygen atoms), a value intermediate between those observed for K^+ (0.76 Å)[5] and Rb^+ (0.94 Å)[4] and consistent with its size.

The individual $TCNQ^{\cdot -}$ units within a dimer favour a boat geometry [Fig. 1(*b*)] rather than the paddle conformation seen in **1a** and **1b**. The dimer is significantly short-axis-slipped [by 0.691 Å (12.38°), the long axis slip being 0.095 Å (1.73°)] with an intradimer mean perpendicular spacing (3.15 Å) somewhat less than those previously reported (3.23 Å for K^+; 3.19 Å for Rb^+).[7] As such it is probably the closest *perpendicular* spacing yet reported for a TCNQ dimer and comparable with that seen in the low temperature form of RbTCNQ (polymorph I, 3.16 Å).[14] Repulsion between the highly charged nitrogens[14,15] probably encourages a boat conformation similar to that in RbTCNQ (polymorph I).[14]

A notable feature of this structure, however, is the packing of the crown–TCNQ dimer units (Fig. 2), there being no trace of the herringbone-packed columns of dimers seen in the K^+ and Rb^+ analogues;[4,5] rather total isolation of the TCNQ dimers is found, adjacent dimers being rotated or tilted to a much greater degree than hitherto observed.

Preliminary investigations of the ESR behaviour of a single crystal of the 18-crown-6 salt **1c** correlate well with the structure. Recorded spectra show the presence of a central feature which is temperature-, but not orientation-, dependent and thus shows all the characteristics of a migrating triplet exciton.[7] In addition there are two outer lines which are both orientation- and temperature-dependent and can thus be assigned to two static triplet excitons arising it is believed[7] from the two equivalent but geometrically different TCNQ dimers present in this structure. These phenomena are being investigated further.

The ambient molar magnetic susceptibility (χ_m) of TlTCNQ is 3.00×10^{-10} m^3 mol^{-1} and this salt is therefore slightly paramagnetic whereas KTCNQ is diamagnetic.[16] The 18-crown-6 complex **1c** is as expected diamagnetic, having $\chi_m = -3.20 \times 10^{-9}$ m^3 mol^{-1}. Further studies of the electrical and magnetic behaviour of these materials are in progress.

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