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A Truly Isolated TCNQ$^{\bullet-}$ Dimer?

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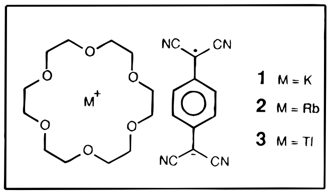
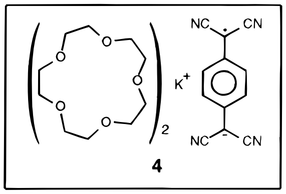
The nature of the countercation is a major factor in determining solid-state architectures and properties of 7,7′,8,8′-tetracyano-*p*-quinodimethane (TCNQ) salts.[1] A number of different types of ion pair association are observed with organic cations,[2] but in the case of metal ion salts cation interaction with the nitrogen lone pairs dominates[3] though the TCNQ radical anion (TCNQ$^{\bullet-}$) is still sometimes regarded as a relatively poor ligand.[4]

Ionophore encapsulation of a cation[5] provides a potentially versatile means of constraining and controlling ion-pair association, particularly in the solid state. For example, while extended TCNQ$^{\bullet-}$ stacks are found in KTCNQ and RbTCNQ,[1] the solid-state structures of their 18-crown-6 complexes **1** and **2** reveal brickwork lattices of dimers. Such structures reflect the need to accommodate both the bulk of the crown ether and tight ion-pair interactions.[6] These complexed salts (and their thallium(I) analogue **3**,[7] in which a stereochemically active lone pair also plays a structural role), show thermally activated triplet exciton behavior which is dependent both on the nature of the counterion and on the solid-state architecture.[8,9] In an attempt to probe such phenomena in more detail, we now report the effect of total cation encapsulation on the properties of the material (15-crown-5)$_2$KTCNQ (**4**). Once again we observe the formation of isolated TCNQ$^{\bullet-}$ dimers with the concomitant presence of thermally activated triplet exciton behavior.[10]



1 M = K
2 M = Rb
3 M = Tl



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Although the solid-state structure of **4** is significantly disordered at room temperature, this study allows a

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(5) A large number of ionophore complexes of metal-ion TCNQ salts have been previously reported, see: Morinaga, M.; Nogami, T.; Kanda, Y.; Matsumoto, T.; Matsuoka, K.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1221−1227. Nogami, T.; Morinaga, M.; Kanda, Y.; Mikawa, H. *Chem. Lett.* **1979**, 111−112.

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(7) Grossel, M. C.; Weston, S. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1510−1512.

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(9) In salts containing TCNQ$^{\bullet-}$ dimers, excited magnetic triplets associated with ground-state singlets have frequently been observed. If the ground states were electronic doublets (arising from isolated TCNQ$^{\bullet-}$ ions), the line intensities should obey the Curie law, whereas excited triplet states should obey the equation,

$$I = \frac{A}{T}\left[\exp\left(\frac{J}{kT}\right) + 3\right]^{-1}$$

where I is the line intensity, T the temperature, k the Boltzman constant, A the preexponential constant, and J the activation energy for triplet production.

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Table 1. Comparison of the Solid-State Structures of TCNQ Salts 1−5

	1	2	3	4	5
TCNQ slip					
short axis (Å)	0.33	0.50	0.69	1.28	1.00
short axis (deg)	5.8	8.9	12.4	22.1	17.65
long axis (Å)	0.08	0.07	0.10	0.00	0.03
long axis (deg)	1.4	1.3	1.7	0.0	0.5
perpendicular intradimer TCNQ spacing (Å)	3.23	3.19	3.15	3.16	3.15
closest cation−TCNQ distance (Å)	2.845(2)[a]	2.980(6)[a]	2.986(6)[a]	5.65[a]	3.63 ($\pi^+\pi^-$)[b]

[a] CN···M$^+$ distance. [b] Vertical π−π interplanar distance.

direct comparison between the physical properties exhibited by this material and its solid-state architecture. The structural determination reveals sheets of TCNQ radical anion dimers surrounded by (15-crown-5)$_2$K$^+$ barrels (Figure 1), a very different situation from that observed for the 1:1:1 (crown:metal:TCNQ) salts, **1**−**3**. The presence of the ionophore inhibits direct cation−anion coordination and gives a structure in which the TCNQ$^{\bullet-}$ dimers can be regarded as effectively *isolated* both from the countercations and from other TCNQ$^{\bullet-}$ dimers. A more detailed examination reveals a pattern constructed from pairs of cation barrels bridged by a TCNQ$^{\bullet-}$ dimer (Figure 2), the counterions within each "building-brick" being arranged so as to optimize electrostatic interactions. Figure 3 depicts the labeling scheme together with the thermal vibration ellipsoids, and it is interesting that the crown ether unit nearest to the TCNQ$^{\bullet-}$ dimer is noticeably more ordered than its more remote partner within each cation sandwich.

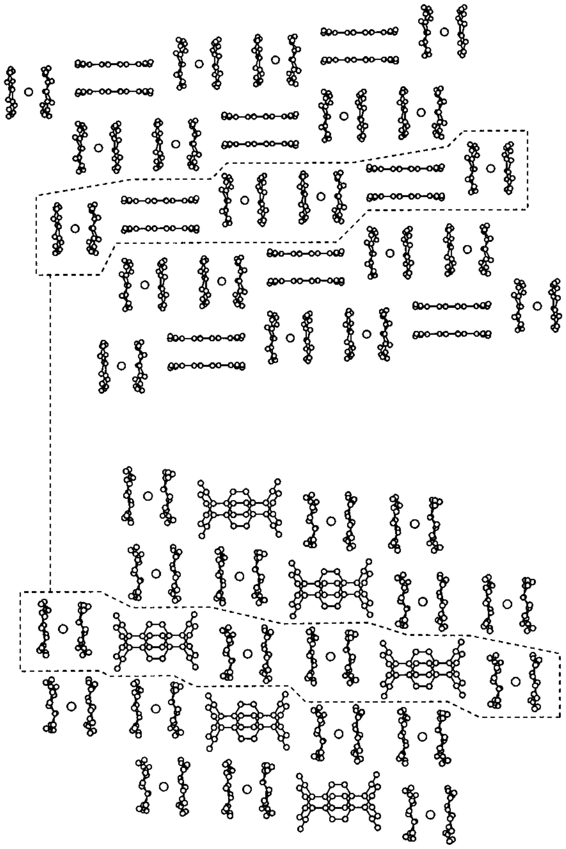

Figure 1. Side and top views of the solid-state structure of (15-crown-5)$_2$KTCNQ (**4**).

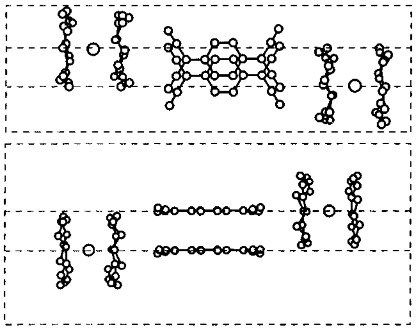

Figure 2. Side and top views of a TCNQ$^{\bullet-}$ dimer unit of **4**; the counterions are arranged so as to optimize electrostatic interactions.

This material provides a unique opportunity to investigate the behavior of an isolated TCNQ$^{\bullet-}$ dimer in the solid-state. Table 1 compares key features of the solid-state structure of **4** with those of the other ionophore MTCNQ complexes **1**−**3**. These data suggest that while there is no clear correlation between perpendicu-

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(10) It should be noted that the presence of relatively isolated TCNQ$^{\bullet-}$ dimers does not always lead to triplet exciton behavior,[2] and that triplet excitons have been observed in extended TCNQ$^{\bullet-}$ stacks.

(11) Crystallization of a CH_3CN solution of KTCNQ in the presence of 1 mol equiv of 15-crown-5 affords a dark purple material with the stoichiometry (15-crown-5)$_2$ KTCNQ (**4**), mp 195 °C dec. (lit.[5] mp 210 °C). IR (KBr disk): ν [cm^{-1}] = two peaks $\approx$2922w (sat. C−H); 2202, 2183, 2154 (CN); 1584m (C=C(CN)$_2$); 1508m (C=C ring); 1362 (C−H bend); 1180m (C−CN and C−C ring). UV/vis/near IR (Nujol) λ_{max} [10^{-3} cm^{-1}] = 9.8, 15.2, 21.1. Found; C, 56.28; H, 6.36; N, 8.12%. $C_{32}H_{44}N_4O_{10}K$ requires C, 56.21; H, 6.49; N, 8.19%. Attempts to prepare the material using a 2:1 molar ratio of 15-crown-5 to KTCNQ resulted in a solution from which no product would crystallize; presumably because of the increased solubility of the metal salt from the extra solvation afforded by the second crown ether.

(12) Data which were collected on an Enraf-Nonius CAD-4F diffractometer using monochromated Cu Kα radiation (full details are given in the supporting information). The unit cell and orientatation matrix were determined using automatic search and centering routines. Data were corrected for Lorentz and polarization effects and an empirical absorption correction based on the χ-scan data of one reflection was applied. There was no substantial crystal decay. The structure was solved by direct methods (SHELXS-86; Sheldrick, G., SHELXS-86 User Guide, Göttingen, FRG, 1986) and difference Fourier techniques were used to find most of the remaining non-hydrogen atoms. At this stage one atom was missing from each crown-ether and to find these the crown-ether moieties were restrained to have equivalent oxygen−oxygen distances (in the −OCH_2CH_2O− fragment) with an allowed esd of 0.01 Å, equivalent oxygen−potassium distances with an allowed esd of 0.01 Å and equivalent oxygen−potassium−oxygen angles (between a potassium and two adjacent oxygens) with an allowed esd of 0.01° (the oxygens used above were the atoms closest to the potassium atom). Under these restraints (which are reasonable for a 15-crown-5 crown-ether sandwich[13]) the missing atoms were found with difference Fourier maps and the oxygens assigned to the atoms closest to the potassium atom with the correct geometry. K(15-crown-5)$_2$TCNQ (**4**): $C_{32}H_{44}N_4O_{10}K_1$, $M = 683.819$, triclinic space group $P\bar{1}$, $a = 9.462(1)$, $b = 13.650(1)$, $c = 14.213(3)$Å, $\alpha = 98.61(1)°$, $\beta = 80.48(1)°$, $\gamma = 80.48(1)°$, $U = 1790.01$ Å^3, $Z = 2$, $D_{calc} = 1.2687$ g cm^{-3}, $F(000) = 726$. Data were collected using a crystal of 0.14 × 0.38 × 0.53 mm. A total of 7306 unique reflections were measured. The refinement converged to give a final $R = 0.130$, $R_w = 0.121$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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(14) Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK), on quoting the full journal citation.

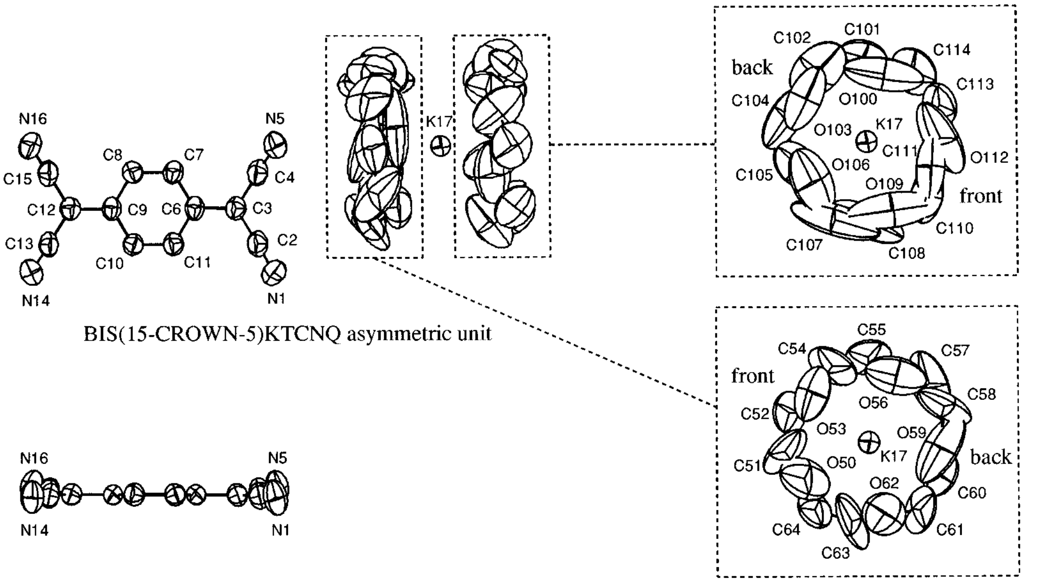

Figure 3. Thermal vibration ellipsoid plot.

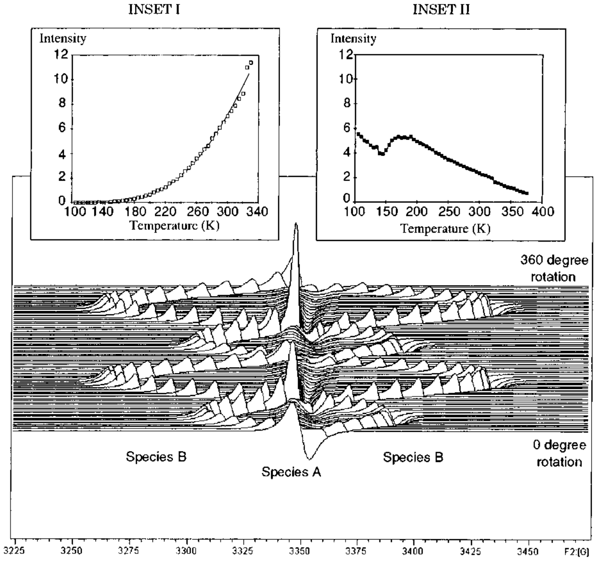

Figure 4. Angular dependence of the ESR spectrum of a single crystal of **4**; inset I shows the temperature dependence (boxes) of species B and the fit to the singlet−triplet model (line); inset II shows the temperature dependence of the “impurity-line”[15] species A.

lar intra-TCNQ$^{\bullet-}$ dimer spacing and the nature of cation association with the TCNQ$^{\bullet-}$ moieties, short axis slip is greatest (22.1°) in the least coordinated structure (**4**) a situation previously noted in TCNQ salts of organic cations.[2]

Further insight into the electronic behavior of crystals of **4** has been obtained from variable-temperature ESR experiments. The angular dependence of ESR spectra of a single crystal of **4** were recorded for a 360° rotation (5° increments) at several different crystal orientations over a wide temperature range (105−455 K). Figure 4 shows the spectral variation for one such rotation and has inset the temperature dependence of the line intensities.

In general two species are observed of which the central feature A is invariant in position but has a somewhat anisotropic line width. The resonance for species B is, however, highly anisotropic and very temperature dependent. Such behavior is typical of the dipolar fine structure (zero-field splitting) of an excited triplet exciton state.[8] Fitting the intensity versus line integral data between 105 and 330 K to the equation in ref 9 using nonlinear regression techniques leads to an activation energy for triplet production (J) of 0.15(3) eV. This value is significantly lower than those observed (≈0.38 eV) for the 18-crown-6 complexes **1** and **2** and suggests that metal-ion coordination to the TCNQ$^{\bullet-}$ dimer dramatically increases the activation energy for localized triplet exciton formation. Species A shows behavior typical of doublet impurity (crystal defects leading to the presence of isolated TCNQ$^{\bullet-}$ monomers); this interpretation is supported by the observation that the presence of the “impurity-line”[15] species A is very sample dependent, whereas the magnitude of J for species B has been found to be almost identical for a number of samples. No hyperfine splittings are observed in any part of the spectrum. Above 330 K the population of the triplet state becomes saturated and no further increase in line intensity is seen, but at the highest temperatures accessible without decomposition the onset of coalescence phenomena is evident, such spectral changes being reversible. This coalescence is attributed to exciton−exciton collision broadening.[16]

In crystals of **4** there is a notable absence of the diffuse (Wannier) triplet exciton behavior, a phenomenon often present in the alkali-metal TCNQ$^{\bullet-}$ salts[17] and their 18-crown-6 complexes, e.g., **1**−**3**.[6−8] This observation emphasises the isolated nature of the TCNQ$^{\bullet-}$ dimer units in **4**.

As expected from its solid-state structure, **4** is insulating (compressed powder $\sigma_{293} = 8.6 \times 10^{-11}$ S/cm) with an activation energy ($E_a = 0.62(4)$ eV) which is markedly greater than that for triplet exciton production. Mag-

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(15) Minute paramagnetic impurities (≈0.1%) can cause large ESR signals, in comparison with observed triplet lines. This is because the triplet state is only partially populated (probably less than 5%), whereas the paramagnetic impurity is observed in its entirety. Chestnut, D. B.; Foster, H.; Phillips, W. D. *J. Chem. Phys.* **1961**, *34*, 684−685.

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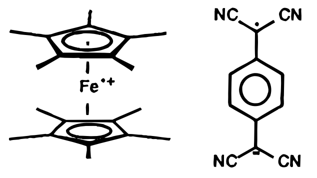
netic susceptibility measurements reveal that **4** shows diamagnetic behavior at room temperature.

Another material of particular interest in the present context is the dimeric (paramagnetic) phase of decamethylferricenium−TCNQ$^{\bullet-}$[18] (**5**) in which the cylindrical nature of the cation is directly analogous to the structure (15-crown-5)$_2$K$^+$ in **4**. Structure **5** might also be expected to contain isolated TCNQ$^{\bullet-}$ dimers, but a reexamination of its solid-state architecture[19] suggests that there are {C−H···N} hydrogen-bond-like electrostatic ordering interactions between the methyl groups (on the ordered cyclopentadienyl ring) and the TCNQ$^{\bullet-}$ nitrile substituents. The extent of short-axis slip in **5** lies intermediate between those seen for the strongly metal-ion-coordinated structures **1**−**3** and that found in [(15-crown-5)$_2$KTCNQ] (**4**) emphasizing the isolated nature of the TCNQ$^{\bullet-}$ dimer in **4**.



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The salt **4** provides the first example of a structure in which there is no evidence for direct cation···TCNQ dimer association through direct metal-ion coordination, close heteroatom contact (such as the S···N interaction in TTF−TCNQ), π−π face-to-face association, or hydrogen bonding.[2] The disordered nature of the crown ether rings and the absence of closer than van der Waals contacts between TCNQ nitrogen and crown-ether carbon atoms[20] suggest that **4** does indeed provide a reasonable model for a truly isolated TCNQ dimer.

Acknowledgment. Thanks are due to Dr. Keith Prout (Chemical Crystallography Laboratory, University of Oxford) for help with the crystal structure solution and to the British Engineering and Physical Science Research Council for a postdoctoral research fellowship (to S.C.W.) and a grant for a Brüker ESR spectrometer.

Supporting Information Available: Full details of the structure solution for **4**, including tables of fractional atomic coordinates, selected interatomic distances, bond and torsion angles, and anisotropic temperature factors together with additional figures showing the numbering scheme used for each structural fragment of **4** and views of the CN···H close contacts in **5** (11 pages); observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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(19) Figures and distances for **5** are included in the supporting information.

(20) Closest C≡N··C(H$_2$) contacts are 3.42 and 3.44 Å, significantly greater than the expected (C)N···(H)···C van der Waals contact distance of 3.25−3.30 Å.