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Crown ether alkali metal TCNQ complexes revisited – the impact of smaller cation complexes on their solid-state architecture and properties

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The solid-state behaviour of four alkali metal TCNQ complexes: (15-crown-5)Li(TCNQ) (1), (15-crown-5)Na(TCNQ) (2), (15-crown-5)Li(TCNQ)·H₂O (3.·H₂O) and (15-crown-5)Na(TCNQ)·H₂O (4.·H₂O) has been explored by single crystal X-ray diffraction, Infrared (IR), Raman and Electron Paramagnetic Resonance (EPR) measurements. The presence of a small cation and ionophore leads to subtle changes in behaviour compared with their larger alkali metal analogues and in the hydrated salts water bridges form links between the crown-encapsulated cations and neighbouring TCNQ stacks.

Introduction

7,7',8,8'-Tetracyano-p-quinodimethane (TCNQ) is a good one electron acceptor which forms stable radical-anion salts (M⁺TCNQ⁻⁻) with various metal, organometallic and organic cations. In the solid-state, these salts often exhibit a range of electrical and magnetic properties, which are associated with the organisation of the paramagnetic TCNQ⁻⁻ moieties within the crystal architecture.

In particular, the TCNQ⁻⁻ units have a tendency to form face-to-face π-stacked dimers and infinite columns in the solid-state in which peripheral counter-cations are associated with the terminal cyano groups. Furthermore, these anion stacks can incorporate neutral TCNQ units which can result in a significant change in their solid-state electronic properties. The local geometry of the TCNQ dimer and its organisation within the crystal as a result of interaction with the counter-ion play an important role in determining the solid-state behaviour of such materials. One approach for controlling this is through the use of ionophores such as crown ethers and cryptands. Nogami and co-workers reported the synthesis of a large number of ionophore-complexed metal TCNQ salts but no detailed structural characterisation was undertaken. We subsequently explored the solid-state behaviour of 18-crown-6 complexes of the K⁺, Rb⁺ and Tl⁺ salts of TCNQ⁻⁻ and that of (15-crown-5)KTCNQ (4).

In the present study, we report the solid-state behaviour of the 15-crown-5 complexes of Li and Na TCNQ (1-4), and the effect of the presence of additional TCNQ and water molecules on this.

Experimental

General procedures

All experiments were performed under a nitrogen atmosphere unless stated otherwise. Acetonitrile was dried over calcium hydride and distilled before use. Diethyl ether was dried over sodium wire and was freshly decanted before use. All chemicals were commercially available and used as received, unless otherwise stated.
Physical measurements
Melting points were determined on an electrochemical melting point apparatus and are uncorrected. Elemental analyses were performed by Medac Ltd, Chobham Business Centre, Chertsey Road, Chobham, Surrey, GU24 8JB. IR spectra (as KBr discs) were obtained using a Golden Gate sampling attachment on a Mattson Satellite 3000 FT-IR. Raman spectra were collected using a Renishaw In-Via system with a high powered near Infrared (HPNIR) 785 nm laser and microscope using a 50x objective. ESI mass spectra were obtained using a Solarix (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with a 4.7 T magnet and FT-ICR cell.

Single crystal X-ray diffraction
A suitable crystal was selected and measured following a standard method on a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of a FR-E-SuperBright molybdenum (0.71075 Å) rotating anode generator with Varimax optics (70µm focus) (1, 3, 4) or (100µm focus) (2, 5) at 100K. Cell determinations and data collections were carried out using CrysAlisPro Expert 3.1b27–270 with data reduction, cell refinement and absorption correction carried out using CrysAlisPro (v1.171.39.46)270. Structures were solved in Olex228 and refined using SHELXL29 and refined using SHELXL29.

Electron paramagnetic resonance
All of the measurements were performed at X-band (~9.4 GHz) on a Bruker EMX EPR spectrometer using a cylindrical cavity (Bruker ER 4119HS or ER 4122 SHQE) and equipped with a programmable goniometer (ER 218PG1). Temperature control was achieved using nitrogen gas flow from a B-VT 2000 temperature controller with a quartz dewar insert (ER 169DIS). Microwave power was optimised to ensure signal response in the linear regime, typically requiring <1 mW. In some samples the presence of distinct species giving rise to signals of vastly different intensity and linewidth necessitated deliberate over-modulation of the narrower line.

General procedure for preparation of complexes (1) and (2)
A solution of the metal TCNQ salt (1 mol equiv) and 15-crown-5 (1 mol equiv) in anhydrous acetonitrile (50 ml) was boiled for 5 minutes, filtered whilst hot and then left to cool. The solvent was allowed to evaporate slowly at room temperature over a period of several days. During this time, a solid formed which was separated by filtration, washed with dry diethyl ether (50 ml), and then dried in vacuum to give the resulting small crystals.

Preparation of (15-crown-5)LiTCNQ (1)
Reaction of LiTCNQ (0.280g, 0.1mmol) and 15-crown-5 (0.291g, 1.32mmol) afforded small crystals of 1 as a purple solid (0.459g, 81%). MS (solution) (MeCN) (ESI–) m/z: 243.2 (Crown + Na+). IR νmax/cm–1: 2930, 2878 (saturated CH stretch), 2195, 2174, 2153 (CN stretch), 1579 (C=C(CN)2 stretch), 1503 (C=C ring stretch), 1347 (CH bend), 1179 (C-CN and C-C ring stretch), 985 (C-C ring stretch), 829, 717 (CH out of plane bend). Raman νmax/cm–1: 2216 (CN stretch), 1605 (C=C ring stretch), 1379 (C-CN stretch), 1208 (C=C-H bending). M.p. 202°C (dec.). Elemental analysis: Calculated: C: 62.5%, H: 6.4%, N: 12.98%. Found: C: 61.98%, H: 5.51%, N: 12.29%.

Preparation of (15-crown-5)NaTCNQ (2)
Reaction of NaTCNQ (0.450g, 2mmol) and 15-crown-5 (0.440g, 2mmol) gave small purple crystals of 2 (0.426g, 47.7%). MS (solution) (MeCN) (ESI+) m/z: 204.1 (TCNQ2–). (ESI+) m/z: 243.2 (Crown + Na+). IR νmax/cm–1: 2908, 2875 (saturated CH stretch), 2179, 2152 (CN stretch), 1576 (C=C(CN)2 stretch), 1504 (C=C ring stretch), 1343 (CH bend), 1177 (C-CN and C-C ring stretch), 986 (C-C ring stretch), 820, 717 (CH out of plane bend). Raman νmax/cm–1: 2207 (CN stretch), 1602 (C-C ring stretch), 1380 (C-CN stretch), 1205 (C=C-H bending). M.p. 160°C (lit.22 150°C). Elemental analysis: Calculated: C: 59.06%, H: 5.41%, N: 12.52%. Found: C: 58.76%, H: 5.02%, N: 12.32%.

Preparation of (15-crown-5)Li(TCNQ)2H2O (3.2H2O)
Reaction of LiTCNQ (0.021g, 0.1mmol), TCNQO (0.020g, 0.1mmol) and 15-crown-5 (0.044g, 0.2mmol) gave 3.2H2O as blue crystalline plates (0.035g, 56%). MS (solution) (MeCN) (ESI+) m/z: 204.1 (TCNQ2–). (ESI+) m/z: 243.2 (Crown + Na+). IR νmax/cm–1: ~3500 (OH stretch), 2878 (saturated CH stretch), 2201, 2173 (CN stretch), 1560 (C=C(CN)2 stretch), 1507 (C=C ring stretch), 1340 (CH bend), 1100 (C-CN and C-C ring stretch), 954 (C-C ring stretch), 836, 700 (CH out of plane bend). Raman νmax/cm–1: 2216 (CN stretch), 1606 (C=C ring stretch), 1384 (C-CN stretch), 1206 (C=C-H bending). M.p. 270°C (dec.). Elemental analysis: Calculated: C: 62.48%, H: 4.63%, N: 17.14%. Found: C: 62.47%, H: 4.45%, N: 17.38%.

Preparation of (15-crown-5)Na(TCNQ)2H2O (4.4H2O)
Reaction of NaTCNQ (0.028g, 0.1mmol), TCNQO (0.020g, 0.1mmol) and 15-crown-5 (0.044g, 0.2mmol) afforded 4.4H2O as blue crystalline plates (0.039g, 60%). MS (solution) (MeCN) (ESI+) m/z: 204.1 (TCNQ2–). (ESI+) m/z: 243.2 (Crown + Na+). IR νmax/cm–1: ~3500 (OH stretch), 2872 (saturated CH stretch), 2277, 2195, 2165 (CN stretch), 1560 (C=C(CN)2 stretch), 1508 (C=C ring stretch), 1343 (CH bend), 1112 (C-CN and C-C ring stretch), 948 (C-C ring stretch), 836, 697 (CH out of plane bend). Raman νmax/cm–1: 2206 (CN stretch), 1603 (C=C ring stretch), 1384 (C-CN stretch), 1206 (C=C-H bending). M.p. 252°C (dec.). Elemental analysis: Calculated: C: 60.98%, H: 4.52%, N: 16.73%. Found: C: 61.28%, H: 4.30%, N: 16.69%.

Preparation of (18-crown-6)Li(TCNQ) (5)
This was prepared following the procedure reported previously to give 5 in 56% yield. M.p. 202°C (dec.) (lit.22 m.p. 203-205°C).

Results and discussion
Complexes of “simple” TCNQ2– salts (1 and 2)
Crystallisation of Li or NaTCNQ from anhydrous acetonitrile in the presence of 15-crown-5 afforded dark purple single crystals suitable for X-ray structural study (at 100 K). In each case, a 1:1 complex of the metal TCNQ with the crown ether was formed. The sodium salt showed solid-state behaviour similar to that seen previously for the 18-crown-6...
complexes of K and RbTCNQ (5 and 6 respectively), but that of the corresponding lithium salt showed significant differences. In order to facilitate analysis of the structural data, the structure of (18-crown-6)KTCNQ 5 was also re-determined at 100 K.

In the solid-state structure of (15-crown-5)NaTCNQ (2), the TCNQ$^{−}$ counterions form dimers in which diagonally opposite cyano groups on each TCNQ$^{−}$ unit are both co-ordinated to a sodium cation, this latter also being complexed within a crown ether cavity. The crown ether lies almost perpendicular to the TCNQ$^{−}$ molecular plane (see Fig 2). The top view of the TCNQ dimer (see Fig 2b) reveals that the TCNQ$^{−}$ dimer is significantly short-axis and slightly long-axis slipped (see Table 1 and Fig. 6 for key structural details).

The dimers assemble into long-axis slipped extended columns (see Fig 3) similar to those previously observed in the 18-crown-6 complexes of K and RbTCNQ. However in the present structure, neighbouring TCNQ dimers within a column are closer to each other in comparison with their 18-crown-6 analogues reflecting the smaller volume of each dimer complex arising from the presence of the smaller crown ether. Perpendicular to these columns, the dimers form layers. The closest inter-dimer contact is 7.205(2) Å between the centroids of neighbouring TCNQ$^{−}$ dimer units within this structure [c.f. 8.1777(1) Å for the corresponding distance in (18-crown-6)KTCNQ 5 at 100 K].

For the (18-crown-6)K$^+$ complex 5, neighbouring dimers within a layer are herringbone packed and the stacking axes of the associated TCNQ$^{−}$ columns are twisted relative to each other (by 60.86°). However, in the sodium complex 2, all of the neighbouring dimer planes and their stacking axes lie parallel with each other.

The solid-state behaviour of (15-crown-5)LiTNCQ 1 shows marked differences arising from the presence of the smaller lithium cation. Once again, a TCNQ$^{−}$ dimer is formed (see Fig 4) but in this case each TCNQ$^{−}$ is only directly co-ordinated to one lithium cation. Each TCNQ$^{−}$ unit has a slightly non-planar geometry with the non-coordinated C(CN)$_2$ termini twisted away from their dimer neighbours. The dimer components are significantly short-axis slipped (see Table 1 for key structural details).

Another consequence of the reduced level of co-ordination to the TCNQ$^{−}$ dimer is that the location of the crown ether moieties is different; they now extend significantly above and below the plane of the TCNQ$^{−}$ dimer (see Fig 4a). The dimers assemble in sheets of parallel columns (see Fig 5a) but with the planes between neighbouring TCNQ dimers tilted at an angle of 48.63(7)° in a herringbone pattern (see Fig 5b).

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Crystallisation of both Li$^+$ and Na$^+$ TCNQ$^{−}$ from anhydrous
acetonitrile in the presence of 15-crown-5 and one molar equivalent of TCNQ\(^2\) afforded crystals of the complex salt (15-

Table 1. Key structural data for TCNQ dimers in the complexes discussed here with comparative literature data (see Fig.6 for definitions of long- and short-axis slip). Note that 3.H\(_2\)O forms two different stacks (indicated as AA in green and BB in magenta in Figure 7).

<table>
<thead>
<tr>
<th>Complex</th>
<th>π-π separation / Å</th>
<th>Long-axis slip / Å</th>
<th>Short-axis slip / Å</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (at 100 K)</td>
<td>3.150(13)</td>
<td>0.250(5)</td>
<td>0.964(5)</td>
<td>This work</td>
</tr>
<tr>
<td>2 (at 100 K)</td>
<td>3.264(17)</td>
<td>0.176(8)</td>
<td>0.600(8)</td>
<td>This work</td>
</tr>
<tr>
<td>3.H(_2)O (AA) (at 100 K)</td>
<td>3.095(3)</td>
<td>2.141(11)</td>
<td>0.039(11)</td>
<td>This work</td>
</tr>
<tr>
<td>3.H(_2)O (BB) (at 100 K)</td>
<td>3.100(3)</td>
<td>1.946(10)</td>
<td>0.076(10)</td>
<td>This work</td>
</tr>
<tr>
<td>4.H(_2)O (at 100 K)</td>
<td>3.086(4)</td>
<td>2.058(16)</td>
<td>0.074(16)</td>
<td>This work</td>
</tr>
<tr>
<td>5 (at 100 K)</td>
<td>3.1559(7)</td>
<td>0.083(3)</td>
<td>0.532(3)</td>
<td>This work</td>
</tr>
<tr>
<td>5 (at Room temp)</td>
<td>3.2251(14)</td>
<td>0.080(6)</td>
<td>0.332(6)</td>
<td>Ref(^{17})</td>
</tr>
<tr>
<td>6 (at Room temp)</td>
<td>3.187(5)</td>
<td>0.081(19)</td>
<td>0.509(19)</td>
<td>Ref(^{24})</td>
</tr>
</tbody>
</table>

crown-5)M(TCNQ\(^{2-}\))(TCNQ\(^0\))\(_2\)H\(_2\)O (M = Li or Na) 3.H\(_2\)O and 4.H\(_2\)O respectively. Attempts to prepare crystalline samples of the anhydrous analogue of each of these materials failed. In the solid-state, the lithium complex (3.H\(_2\)O) forms a structure consisting of columns of TCNQ dimers in the channels between which lie (15-crown-5)Li(H\(_2\)O\(^+\)) complexes. Each water molecule forms two significantly non-linear [C≡N⋯(H)O angle = 154.9(2)°] hydrogen-bonding contacts (2.00(5) and 2.05(5) Å) between TCNQ units in neighbouring columns (see Fig 7), only one cyano group from each TCNQ unit being involved. Similar behaviour has been observed in several hydrated lanthanide TCNQ salts.\(^{31-34}\) These TCNQ columns consist of a 1:1 mixture of TCNQ\(^0\) and TCNQ\(^{2-}\). The similarity of the bond lengths within the two TCNQ units and intra-/inter-dimer spacings makes it difficult to distinguish between the TCNQ\(^{2-}\) and TCNQ\(^0\) components.

In contrast with the other structures reported here, in the solid-state structure of the complex salt (15-crown-5)Na(TCNQ\(^{2-}\))(TCNQ\(^0\))\(_2\)H\(_2\)O (4.H\(_2\)O) the crown ether is disordered [as has been seen previously for [(15-crown-5)]K\(^+\) TCNQ\(^{2-}\)]. Once again, a water molecule is co-ordinated to the metal ion within the crown ether complex and forms a hydrogen-bonding contact with the nitrogen atoms of a TCNQ cyano group.

![Figure 6. Definitions of short and long axis slip](image1)

The TCNQ units are dimerised within extended face-to-face π-stacked dimers which assemble into extended tetrermers.

![Figure 7. Water-bridged TCNQ columns formed by (15-crown-5)Li(TCNQ\(_2\)).H\(_2\)O (3.H\(_2\)O) (A stack in green and B stack in magenta)](image2)

![Figure 8. Side (a) and top (b) views of a TCNQ dimer unit showing in (15-crown-5)Li(TCNQ\(_2\)).H\(_2\)O (3.H\(_2\)O) showing hydrogen bonding contacts to adjacent Li\(^+\)-coordinated water molecules](image3)
forming parallel sheets throughout the structure separated by the crown ether complexes (see Fig 9).

Table 2. Infrared and Raman data for the TCNQ complexes reported in this work together with selected comparative literature data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Infrared data / cm$^{-1}$</th>
<th>Raman data / cm$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C≡N stretch</td>
<td>C=C stretch</td>
<td>C≡N stretch</td>
</tr>
<tr>
<td>TCNQ$^a$</td>
<td>2228, 2225</td>
<td>1545</td>
<td>2225</td>
</tr>
<tr>
<td>TCNQ$^b$</td>
<td>2224, 2220</td>
<td>1545</td>
<td>2230</td>
</tr>
<tr>
<td>NaTCNQ</td>
<td>2197, 2184, 2160</td>
<td>1505</td>
<td>2204</td>
</tr>
<tr>
<td>1</td>
<td>2195, 2174, 2153</td>
<td>1505</td>
<td>2216</td>
</tr>
<tr>
<td>2</td>
<td>2179, 2152</td>
<td>1504</td>
<td>2207</td>
</tr>
<tr>
<td>3.H$_2$O</td>
<td>2197, 2170</td>
<td>1507</td>
<td>2216</td>
</tr>
<tr>
<td>4.H$_2$O</td>
<td>2196, 2167</td>
<td>1508</td>
<td>2206</td>
</tr>
<tr>
<td>5</td>
<td>2201, 2187, 2177, 2158</td>
<td>1505</td>
<td>2197</td>
</tr>
<tr>
<td>6</td>
<td>2202, 2187, 2177, 2158</td>
<td>1504</td>
<td>2197</td>
</tr>
</tbody>
</table>

Within each TCNQ dimer, the individual molecules are significantly long-axis slipped (see Fig 9) with a π-π separation of 3.086(4) Å (see Table 1). Once again, the water molecules apparently act as hydrogen-bonding bridges between neighbouring TCNQ columns thereby forming infinite hydrogen-bonded threads through the structure (see Fig 10).

Vibrational spectra of Ionophore-encapsulated MTCNQ complexes 1-4

Infrared and Raman spectroscopy have previously been used to gain insight into the redox state of the TCNQ moiety.35 Table 2 presents key data for complexes 1-6 together with some corresponding literature data for comparison. The spectra and number of bands reported here are consistent with previous literature reports.36-39 We note the lack of sensitivity of the C≡N stretching vibrations to the changes in co-ordination environment observed in the crystal structures. This is easily accounted for by consideration of the angles of contact involved. To have a significant effect on v(C≡N) a linear C≡N-—M head-on contact is required. Variations in the number of cyano-bands observed is partially accounted for by the varying number of co-ordination environments seen in these structures.

Preliminary Electron Paramagnetic Resonance of Ionophore encapsulated MTCNQ salts

The behaviour of the complexes 1, 2, 3.H$_2$O and 4.H$_2$O has been studied by single crystal EPR Spectroscopy. The EPR spectra of TCNQ salt 1 were recorded on multiple single crystals at temperatures up to 400 K. Two different spectral components were identified, one being a series of sharp lines observed at ambient temperature (see Fig S5), and of greater significance for the present discussion a strongly temperature dependent doublet as shown in Figure 11. The outer doublet is characteristic of a thermally populated triplet exciton, the two transitions of the $S = 1$ state being separated due to the fine structure splitting. Whilst these features are so broad that they are barely discernible at ambient temperature, the splitting decreases and the lines progressively narrow on heating until coalescing in a strong spectral singlet that dominates at high temperature, as seen previously for Frenkel-type triplet excitons.10,40 A second behaviour characteristic of triplet exciton spectra is the change in line-width seen at certain orientations (see Fig S6). This has been attributed to interchain jumping of excitons between two crystallographically distinct chains at orientations in which they are magnetically equivalent in agreement42 with our finding of two distinct dimer columns (see Fig 6).
The EPR behaviour of TCNQ salt 2 has also been explored over a temperature range 298–375 K. At ambient temperature, a central peak is observed whose field position is not orientation dependent, likely arising from a migrating exciton. As the temperature is increased to 315 K, a small doublet signal becomes apparent which was very weak at lower temperatures. The positions of these weak satellites signals change rapidly with crystal rotation exhibiting characteristics of a localised, thermally activated triplet state within the isolated TCNQ$^{**}$-dimer.1, 17, 18, 25 Figure 12 shows the resulting roadmap as a function of angular displacement of TCNQ salt 2 at 315 K. This behaviour is similar to that previously reported for other crown ether-MTCNQ salt complexes, however only one doublet is observed for TCNQ salt 2 reflecting the presence of a single localised exciton due to the coplanar arrangement of the TCNQ dimers (see Fig 4). As illustrated for TCNQ salt 5 in Figure S7 for the previously reported 18-crown-6 K$^+$ and Rb$^+$ analogues, two independent doublets were observed due to the tilt angle between TCNQ dimer planes in neighbouring columns.18 The orientation dependent splitting arises from the dipolar fine structure (zero-field splitting) of an excited triplet exciton state, and whilst a full determination of the spin-spin interaction tensor would require further data we can place a lower bound on the axial zero-field splitting parameter $|D_{zz}| \geq 426$ MHz making the value comparable to that for TCNQ salts 5 and 6.

The electronic behaviour of TCNQ salts 3.H$_2$O and 4.H$_2$O has also been explored by variable-temperature EPR spectral experiments. In both cases, only a central feature can be observed with some weak anisotropy. As the temperature is increased signal intensity decreases, as expected for observation of a ground state doublet spin system obeying the Curie Law, in contrast to TCNQ salts 1 and 2 which showed the opposite behaviour with higher temperatures increasing the thermal population of triplet excited states and hence their signal intensity. There is no evidence for localised triplet excited states in either of TCNQ salts 3.H$_2$O and 4.H$_2$O, behaviour typical for other complex TCNQ salts in which there are extended mixed TCNQ stacks (i.e. containing both TCNQ$^{-}$ and TCNQ$^{**}$).

Conclusions

In the complexes involving simple (1:1) salts (1 and 2), the TCNQ$^{**}$ units form isolated [TCNQ$^{**}$]$^{2-}$ $\pi$-stacked dimers terminated by crown-encapsulated metal ions. Despite the reduced bulk of the Na$^{+}$(15-crown-5) complex, the solid-state behaviour of the sodium salt 2 mimics that of its 18-crown-6 potassium and rubidium analogues 5 and 6 respectively. In marked contrast, the behaviour of the lithium salt 1 is dominated by the limited co-ordination environment of the lithium cation with the result that each (15-crown-5)Li$^+$ unit is only associated with one cyano group of the TCNQ dimer. As Huang and co-workers21 note, there are very few examples in the Cambridge Structural Database of assemblies of “isolated” TCNQ dimers such as those observed here for the simple TCNQ$^{**}$ salts 1 and 2 and the results obtained provide further insight into the behaviour of such dimers as the counter-cation co-ordination environment is modified. In marked contrast, the solid-state behaviour of the complex salts 3.H$_2$O and 4.H$_2$O is dominated by the presence of water-bridged hydrogen bonding to the TCNQ units there being no direct contact between these latter and the alkali-metal counter cation.

Notes and references


Water molecules play a key structure-organising rôle in the crystallisation of 15-crown-5 complexes of Lithium and Sodium TCNQ in the presence of excess TCNQ.