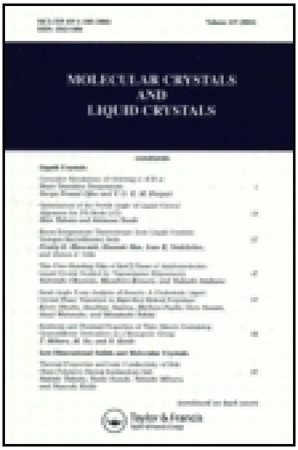

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ELEVEN SALTS ISOSTRUCTURAL WITH $(DEPE)_{0.88}(TCNQ)_4(H_2O)_x$*

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The electrical and structural properties of twelve bis-4-pyridinium TCNQ salts are reported, each having an isostructural TCNQ lattice and a "pseudocrystalline" cation lattice. The electrical properties are dependent upon the degree of cation disorder with σ_{300K} = 0.05 to 500 Scm^{-1}.

INTRODUCTION

$(DEPE)_{0.88}(TCNQ)_4(H_2O)_x$ has unusual electrical properties which are sample dependent[1-3]. This salt was previously assigned a stoichiometry of 1:4, as were its isostructural congeners[2] with the cations 1,2-bis(1-ethyl-4-pyridinium)ethane and 1,3-bis(1-methyl-4-pyridinium)propane. These materials are now known to be nonstoichiometric with cation : TCNQ ratios of ~0.9:4 which can be alternatively written as 1:~4.5 (see Table 1). By systematically varying the size and geometry of the cation the stoichiometry may be changed. In this work twelve TCNQ salts are reported with stoichiometries of 1:3, 1:4, 1:~4.5 and 1:5. In these salts the TCNQ lattice is isostructural and the cation lattice is inherently disordered.

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PREPARATION OF TCNQ SALTS

Bis-4-pyridinium TCNQ salts were synthesised by either reacting aqueous solutions of the cation dihalide with stoichiometric quantities of TCNQ and LiTCNQ in acetonitrile, or by reacting the diiodide with neutral TCNQ. Twelve TCNQ salts were prepared by using the cations shown below. They were obtained as microcrystals, elongated plates and as needles.

1,2-bis(4-pyridinium)ethane^{2+}	DHPA
1,2-bis(4-pyridinium)ethylene^{2+}	DHPE
1,3-bis(4-pyridinium)propane^{2+}	DHPP
1,2-bis(1-methyl-4-pyridinium)ethane^{2+}	DMPA
1,2-bis(1-methyl-4-pyridinium)ethylene^{2+}	DMPE
1,3-bis(1-methyl-4-pyridinium)propane^{2+}	DMPP
1,2-bis(1-ethyl-4-pyridinium)ethane^{2+}	DEPA
1,2-bis(1-ethyl-4-pyridinium)ethylene^{2+}	DEPE
1,3-bis(1-ethyl-4-pyridinium)propane^{2+}	DEPP
1,2-bis(1-n propyl-4-pyridinium)ethane^{2+}	DPPA
1,2-bis(1-n propyl-4-pyridinium)ethylene^{2+}	DPPE
1,3-bis(1-n propyl-4-pyridinium)propane^{2+}	DPPP

Chemical analysis of the bis-4-pyridinium TCNQ salts gave cation : TCNQ : H_2O ratios of 1:n:1 where $3 \leqslant n \leqslant 5$ (see Table 2). An isostructural series of twelve TCNQ salts has been confirmed by X-ray powder diffraction studies.

STRUCTURAL PROPERTIES

X-ray oscillation photographs show two sets of layer lines for crystals mounted about b: (a) weak layer lines corresponding to d-spacings of 11.8 to 19.4 Å, and (b) strong layer lines corresponding to d-spacings of 3.84 to 3.93 Å. Oscillation and Weissenberg photographs of the strong layer lines indicate that the subcell is monoclinic, space group $P2_1/c$. The parameters are listed in Table 1.

TABLE 1 Crystal data.

Cation	DHPA	DHPP	DMPA	DMPP	DEPE	DPPP
TCNQ subcell (strong layer lines)						
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	12.91	12.93	12.90	12.93	12.72	12.73
b/Å	3.93	3.86	3.84	3.85	3.84	3.87
c/Å	27.62	27.48	27.34	27.50	27.67	28.47
β/°	109.9	109.1	107.4	108.1	107.8	107.9
Hydrated cation lattice (weak layer lines)						
d_w/Å	11.8	15.4	15.4[a]	17.1	17.4	19.4
d_w/b	3.0	4.0	4.0	4.44	4.53	5.0
Density (in Mg m^{-3})						
D_c (b	1.37	1.33	1.35	1.33	1.35	1.32
D_m (c	1.35	1.33	1.34	1.34	1.34	1.31

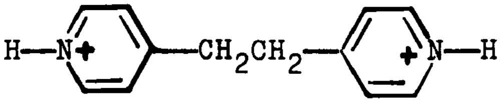
[a] X-ray oscillation photographs show weak DMPA layer lines corresponding to a d-spacing of 7.68 Å. They also show very faint intermediate layer lines which suggest that the d-spacing should be doubled to 15.4 Å.

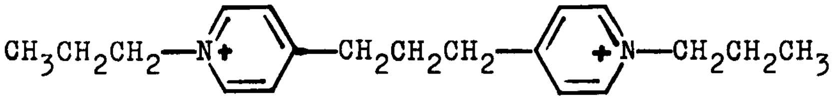
[b] Densities were calculated for one molecule of $(\text{cation})_x(\text{TCNQ})_4(\text{H}_2\text{O})_x$ per subcell. $x = 4b/d_w$.

[c] Experimental densities were obtained by floatation in mixtures of CCl_4/C_6H_{12}.

In three of the salts, previously reported[2], the weak layer lines were attributed to the H_2O lattice. From density measurements and chemical analyses, these salts are now known to have stoichiometries which are commensurate with the ratios of the d-spacings of the layer lines. Thus for the general formula, $(\text{cation})^{2+}(\text{TCNQ})_n^{2-}(H_2O)$, $n = d_W/b$ (Table 1). The strong layer lines correspond to the TCNQ lattice and the weak layer lines to the hydrated cation lattice.

Characteristics of these salts are (a) an isostructural TCNQ lattice and (b) a disordered cation lattice. The TCNQs are arranged in columns parallel to b with uniform spacings of ~3.2 Å. The cations extend in the general direction of the TCNQ stack and span three or more successive lattice spacings. The stoichiometry is defined by the cation length. Thus by systematically varying the size of the cation, for example from DHPA = $C_{12}H_{14}N_2$ to DPPP = $C_{19}H_{28}N_2$, the stoichiometry can be progressively varied from 1:3 to 1:5. Of particular interest in this isostructural series are the TCNQ salts of DMPP = $C_{15}H_{20}N_2$, DEPE = $C_{16}H_{20}N_2$ and DEPA = $C_{16}H_{22}N_2$. Preliminary crystallographic studies indicate that these salts are nonstoichiometric with cation : TCNQ ratios of 1:4.44 to 1:4.53. The cations span ~4½ lattice spacings.





ELECTRICAL PROPERTIES

The electrical properties of the bis-4-pyridinium TCNQ salts are listed in Table 1. The properties

TABLE 2 Electrical properties.

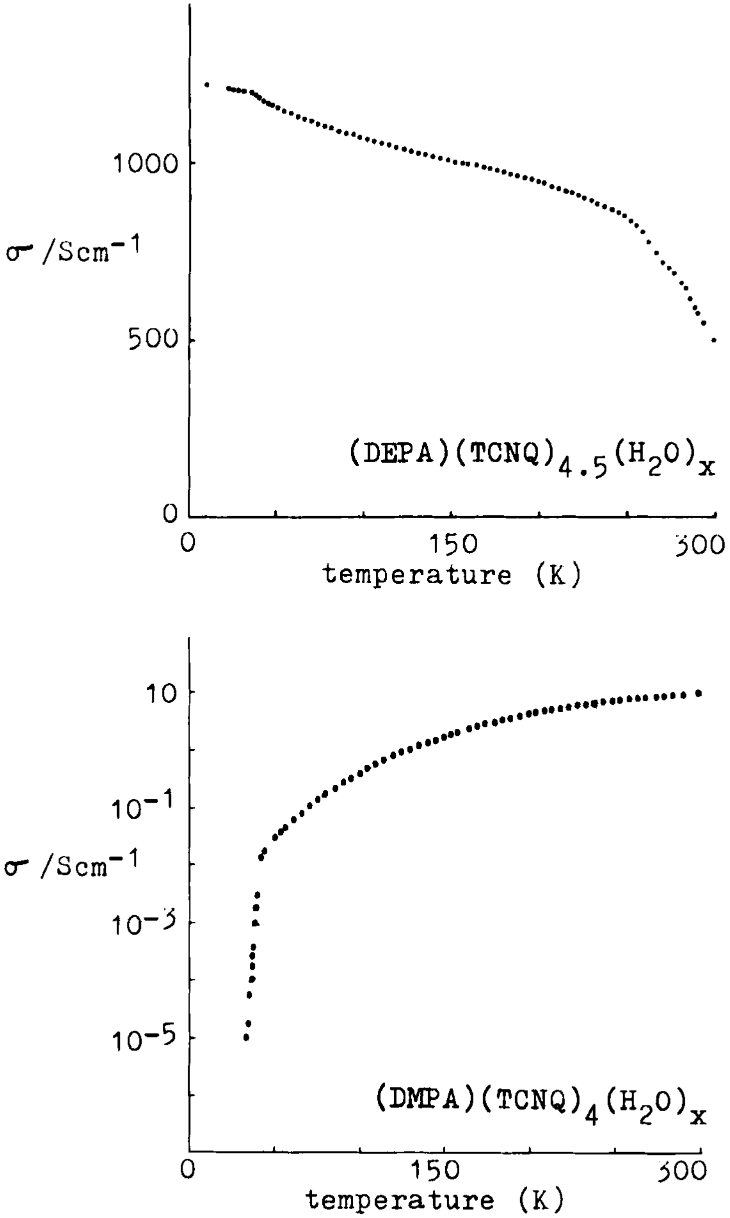
Cation		Ratio	Properties[b]	
Code	Formula	Cation:TCNQ	σ /Scm^{-1}	E_a/eV
DHPA	$C_{12}H_{14}N_2$	1:3[a]	0.3	0.15
DHPE	$C_{12}H_{12}N_2$	1:3	0.5[c]	0.11[c]
DHPP	$C_{13}H_{16}N_2$	1:4[a]	1-10	0.10
DMPA	$C_{14}H_{18}N_2$	1:4[a]	1-50	0.05
DMPE	$C_{14}H_{16}N_2$	1:4	1[c]	0.06[c]
DMPP	$C_{15}H_{20}N_2$	1:4.44[a]	10-100	0.05
DEPA	$C_{16}H_{22}N_2$	1:4.5	100-500	metallic
DEPE	$C_{16}H_{20}N_2$	1:4.53[a]	10-500	0.05 or 0
DEPP	$C_{17}H_{24}N_2$	1:5	1-10	0.06
DPPA	$C_{18}H_{26}N_2$	1:5	0.2[c]	0.07[c]
DPPE	$C_{18}H_{24}N_2$	1:5	0.05[c]	0.12[c]
DPPP	$C_{19}H_{28}N_2$	1:5[a]	0.05	0.11

[a] As determined from preliminary X-ray studies.

[b] Single crystal b-axis conductivities (300 K) and activation energies (200 to 300 K) unless stated otherwise.

[c] Compacted pellet values.

FIGURE 1 Conductivity versus temperature plots of $(DEPA)(TCNQ)_{4.5}(H_2O)_x$ and $(DMPA)(TCNQ)_4(H_2O)_x$.



range from metallic to semiconducting with σ_{300K} = 500 to 0.05 Scm^{-1} and E_a = 0 to 0.15 eV along b. Conductivity enhancement can be achieved by annealing the crystals in vacuum. Dehydration occurs with (a) a contraction of the unit cell and (b) loss of the weak layer lines. The layer lines correspond to the hydrated cation lattice and their loss indicates an increase in the disorder. For metallic behaviour the disorder must be sufficient to suppress those modulations of the TCNQ lattice which would otherwise give rise to a semiconducting state.

The dissimilar electrical properties of the isostructural congeners, $(DEPA)(TCNQ)_{4.5}(H_2O)_x$ and $(DMPA)(TCNQ)_4(H_2O)_x$, are shown in Figure 1. The former is metallic to below 10 K, whereas the latter is semiconducting. It is of interest to note that both salts show anomolous behaviour at 40 K. A semiconductor-to-insulator transition in $(DMPA)(TCNQ)_4(H_2O)_x$, at this temperature, is attributed to a distortion of the one-dimensional TCNQ lattice. Consequently a "kink" at 40 K in the metallic conductivity of $(DEPA)(TCNQ)_{4.5}(H_2O)_x$ is believed to reflect an attenuated Peierls distortion[4]. The dissimilar electrical behaviour is attributed to subtle differences in the degree of cation lattice disorder.

Further studies on this isostructural series are in progress. The crystal structures have been determined by Dr S.C.Wallwork and will be published separately[5], as will the magnetic and thermoelectric properties.

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