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Crystal Structure of (DPPP) $(TCNQ)_5$ (H_2O) and Electrical Properties of the Mixed Valence TCNQ Salts of Diquaternised 1,3-BiS (4-pyridyl) propane

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The conductivities and thermoelectric e.m.f.'s of an isostructural series of TCNQ salts are reported together with the crystal structure of $(DPPP)(TCNQ)_5(H_2O)$, representative of the series. The 1:5 salt has a monoclinic subcell, space group $P2_1/c$, with $a = 12.73(2)$, $b = 3.87(2)$, $c = 28.47(10)$ Å, $\beta = 107.9(4)°$. The TCNQs stack plane-to-plane in columns, parallel to **b**, with (i) an average interplanar spacing of ~3.3Å and (ii) an exocyclic double bond to quinonoid ring overlap of adjacent molecules. The hydrated cation lattice shows no long-range order. $(DPPP)(TCNQ)_5(H_2O)$ and its isostructural congeners, $(DHPP)(TCNQ)_4(H_2O)$, $(DMPP)(TCNQ)_{4\text{-}1/2}(H_2O)$ and $(DEPP)(TCNQ)_5(H_2O)$, are small band gap semiconductors. The room temperature conductivities, determined parallel to **b**, are in the range 0.05 to 100 S cm^{-1}.

INTRODUCTION

The electrical and structural properties of the mixed valence TCNQ salts of diquaternised 1,3-bis(4-pyridyl)propane (DRPP), where **R** = **H** (hydro),

M (methyl), **E** (ethyl) and **P** (n propyl), have been investigated as part of a series of studies on low-dimensional conductors. They are isostructural with the corresponding salts of diquaternised 1,2-bis(4-pyridyl)ethylene (DRPE) and 1,2-bis(4-pyridyl)ethane (DRPA) and form part of an isostructural series of twelve known compounds.[1] In this work, the crystal structure of (DPPP)(TCNQ)$_5$(H$_2$O), its electrical properties and those of its congeners are reported.

SYNTHESIS AND ANALYSIS

Black needles of (DHPP)(TCNQ)$_4$(H$_2$O) were obtained when a hot aqueous acetonitrile solution of 1,3-bis(4-pyridinium)propane dichloride, LiTCNQ and TCNQ (1:2:2 mole ratio) was allowed to cool slowly to ambient temperature. Microcrystalline samples of (DMPP)(TCNQ)$_{4\text{-}1/2}$(H$_2$O), (DEPP)(TCNQ)$_5$(H$_2$O) and (DPPP)(TCNQ)$_5$(H$_2$O) were obtained by reacting the corresponding 1,3-bis(1-alkyl-4-pyridinium)propane diiodide with TCNQ (1:4 mole ratio) in aqueous acetonitrile. Black needles and elongated plates were obtained upon recrystallization. The stoichiometries were determined partly by comparison of the spacings of the weak and strong layer lines (see below); partly by spectroscopic and elemental analyses, and partly by calculations based on the crystal densities (Table 1). From the density and unit cell volume the total relative molecular mass contained within the unit cell may be calculated. Subtraction from this of the relative molecular masses of the TCNQs within the cell gives the remainder attributable to the hydrated cations, and hence, the stoichiometry.

TABLE I

Elemental data, crystal densities (*D*) and the ratio of the unit cell dimensions, *b'* and *b*, corresponding to the weak and strong layer lines on the X-ray oscillation photographs. (4/*n* gives the number of TCNQs per cation, where *n* is the number of cations in the subcell, determined from *D* and the subcell volume).

Complex salt*		C	H	N	O	D/Mg m^{-3}	4/n	b'/b
(DHPP) (TCNQ)$_4$(H$_2$O)	Calc.	70.79	3.31	24.36	1.55	1.33(2)		
	Found	70.52	3.58	24.23	1.68	1.33(2)	4.0(3)	4.0(1)
(DMPP) (TCNQ)$_{4\text{-}1/2}$(H$_2$O)	Calc.	71.13	3.46	24.04	1.37	1.32(2)		
	Found	71.64	3.59	23.93	1.15	1.32(2)	4.5(4)	4.4(2)
(DEPP) (TCNQ)$_5$(H$_2$O)	Calc.	71.40	3.58	23.79	1.24			
	Found	71.78	3.54	23.78	1.34			
(DPPP) (TCNQ)$_5$(H$_2$O)	Calc.	71.70	3.81	23.28	1.21	1.32(2)		
	Found	71.33	3.77	23.33	1.30	1.31(2)	5.1(4)	5.0(1)

*The stoichiometries have been rounded off to the nearest integer or half-integer value.

In earlier studies[2–5] on the DEPE salt, now known to have a stoichiometry of 1:4½, a cation to TCNQ ratio of 1:4 was assumed from its elemental, spectroscopic and density data. Such techniques are, however, insensitive to small changes in the cation to TCNQ ratio and, by these methods, it is not possible to distinguish between the integer and half-integer values for stoichiometries greater than 1:4. In particular, for $TCNQ^0:TCNQ^- > 1$, Beer's Law is not obeyed (Figure 1).

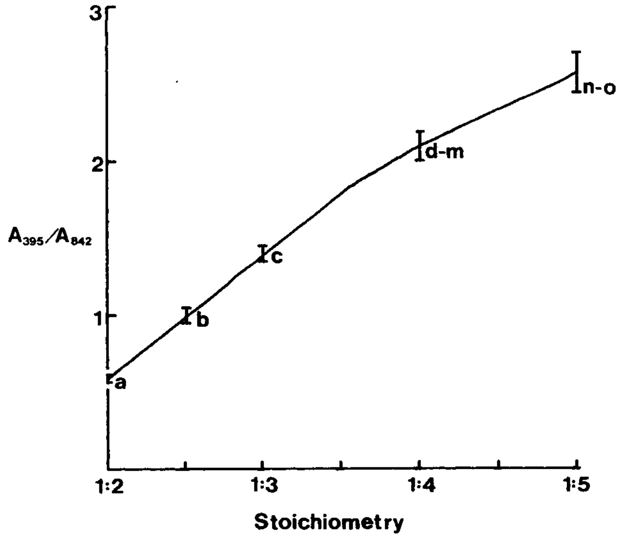
Studies on (DPPE)(TCNQ)$_5$(H$_2$O) and (DPPP)(TCNQ)$_5$(H$_2$O) provided the first indication of a varying stoichiometry in this isostructural series. For the 1:5 salts, the ratios of absorbances at 395 and 842 nm are in the range 2.5 to 2.7. These values compare favorably with those obtained for [1,2-bis(1-benzyl-4-pyridinium)ethylene](TCNQ)$_5$ and [1,2-bis(1-benzyl-4-pyridinium)ethane](TCNQ)$_5$, whose structures are known. The stoichiometries, which have also been calculated from the crystal densities and unit cell volumes, closely resemble those deduced from the X-ray diffraction pattern by the method explained below.

STRUCTURE DETERMINATION

X-ray photographs of the DHPP, DMPP and DPPP salts were taken with the crystals oscillating about their needle axes. In each case there were some weak reflections on the oscillation photographs lying on intermediate layer lines between the strong main layers. For the DHPP and DMPP salts, the weak reflections were few in number and diffuse, whereas in the case of the DPPP salt, the reflections were sharper and more numerous. For each salt, the main layer lines occurred at virtually the same spacing corresponding to unit cell dimensions of 3.85 to 3.87 Å. The intermediate layer lines, however, occurred with different spacings which increased with increasing cation size.

Weissenberg photographs of the zero and first main layer lines showed reflections with similar spacings and intensities for each of the salts. These could be interpreted in terms of a common monoclinic subcell of space group $P2_1/c$. This same subcell had previously been found[3] for (DEPE) (TCNQ)$_{4\text{-}1/2}$(H$_2$O) and since its dimensions, subsequently refined from several reflections located by diffractometer, change very little from salt to salt (Table 2), it is interpreted as defining the TCNQ lattice. Crystal structure determinations, based only on the X-ray reflections of the subcell, have been carried out for (DEPE) (TCNQ)$_{4\text{-}1/2}$(H$_2$O) and (DPPP) (TCNQ)$_5$(H$_2$O) using poor quality X-ray data measured on a Hilger and Watts four-circle diffractometer. The positions and orientations of the four TCNQs in each subcell have been determined by Patterson syntheses and refined by

FIGURE 1 Ratio of the molar absorption coefficients at 395 and 842 nm vs stoichiometry for fifteen bipyridinium TCNQ salts whose structures have been determined.[6–20] Note that Beer's Law is obeyed for stoichiometries of 1:2 to 1:4 only, corresponding to TCNQ°:TCNQ⁻ ratios <1. Similar behavior has been observed by Rembaum *et al*[21] for mixtures of TCNQ and LiTCNQ.



(a) $[1,2\text{-bis(1-ethyl-4-pyridinium)ethylene}]^{2+}(\text{TCNQ})_2^{2-}$
(b) $[1,2\text{-bis(1-ethyl-4-pyridinium)ethane}]_2^{4+}(\text{TCNQ})_5^{4-}$
(c) $[1,1'\text{-bis(methyl)-4,4'-bipyridinium}]^{2+}(\text{TCNQ})_3^{2-}$
(d) $[1,1'\text{-bis(ethyl)-4,4'-bipyridinium}]^{2+}(\text{TCNQ})_4^{2-}$
(e) $[1,1'\text{-bis(n propyl)-4,4'-bipyridinium}]^{2+}(\text{TCNQ})_4^{2-}$
(f) $[1,1'\text{-bis(benzyl)-4,4'-bipyridinium}]^{2+}(\text{TCNQ})_4^{2-}$
(g) $[1,1'\text{-bis(p-cyanophenyl)-4,4'-bipyridinium}]^{2+}(\text{TCNQ})_4^{2-}$
(h) $[1,2\text{-bis(1-methyl-4-pyridinium)ethane}]^{2+}(\text{TCNQ})_4^{2-}$
(i) $[1,2\text{-bis(1-ethyl-4-pyridinium)ethane}]^{2+}(\text{TCNQ})_4^{2-}$
(j) $[1,2\text{-bis(1-ethyl-4-pyridinium)ethylene}]^{2+}(\text{TCNQ})_4^{2-}$
(k) $[1,3\text{-bis(1-pyridinium)propane}]^{2+}(\text{TCNQ})_4^{2-}$
(l) $[1,4\text{-bis(1-pyridinium)butane}]^{2+}(\text{TCNQ})_4^{2-}$
(m) $[1,4\text{-bis(1-pyridiniummethyl)benzene}]^{2+}(\text{TCNQ})_4^{2-}$
(n) $[1,2\text{-bis(1-benzyl-4-pyridinium)ethylene}]^{2+}(\text{TCNQ})_5^{2-}$
(o) $[1,2\text{-bis(1-benzyl-4-pyridinium)ethane}]^{2+}(\text{TCNQ})_5^{2-}$

least-squares calculations to $R = 0.32$ and 0.19 for the DEPE and DPPP salts respectively.

CRYSTAL STRUCTURE

The crystal structure of (DPPP)$(\text{TCNQ})_5(\text{H}_2\text{O})$, projected along **b**, is shown in Figure 2. The TCNQs stack plane-to-plane, in columns parallel to **b**,

TABLE II

Dimensions of the subcell for three 1,3-bis(4-pyridinium) propane salts and the cell dimension (b') corresponding to the intermediate layer line spacings. The figures in parentheses are probable errors.

Cation	a/Å	b/Å	c/Å	β/deg	Volume/Å^3	b'/Å
DHPP	12.93(2)	3.86(1)	27.48(5)	109.1(1)	1296(8)	15.4(5)
DMPP	12.93(2)	3.85(1)	27.50(5)	108.1(2)	1301(9)	17.1(6)
DPPP	12.73(2)	3.87(2)	28.47(10)	107.9(4)	1335(17)	19.4(2)

with (i) a mean perpendicular spacing of ~3.3 Å and (ii) an exocyclic bond to quinonoid ring overlap of adjacent molecules along the conducting chains (Figure 3). Adjacent columns form "zig-zag" sheets parallel to the (001) plane, an arrangement which gives rise to two cation channels per unit cell, extended along **b** and centered at $x = 0$, $z = \frac{1}{4}$ and $x = 0$, $z = \frac{3}{4}$. The channels are of relatively small cross section showing that the cations must be tilted not far from parallel with **b** and must extend over more than one subcell. It is therefore suggested that the diffuse intermediate layer lines correspond to a repeat distance spanning the hydrated cations

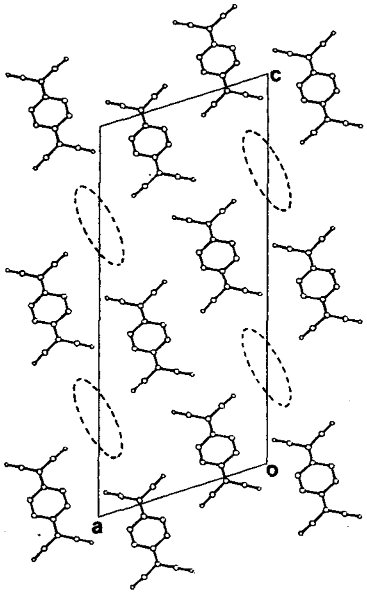


FIGURE 2 Projection of the structure of (DPPP) $(TCNQ)_5(H_2O)$ along **b**, the stacking axis. The hydrated cation channels are indicated by the broken lines.

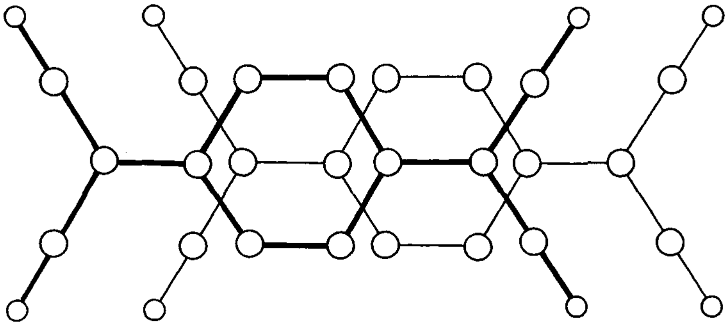


FIGURE 3 TCNQ molecular overlap in (DPPP)(TCNQ)$_5$(H$_2$O).

with the cation lattice showing no long-range order. If this is so, the ratio of the **b**′ : **b** cell dimensions, corresponding to the weak and strong layers respectively, should equal the ratio of TCNQs to cations in the overall structures (see Table 1). The fact that the ratios obtained, though only approximate in view of the weakness of the intermediate layer lines, resemble closely the stoichiometries derived from the densities suggests that this interpretation of the data is correct.

Fourier difference maps, phased on the TCNQ molecules and using only the subcell reflections show, not surprisingly, uninterpretable electron-density fluctuations in the cation channels. These arise partly from the fact that each cation spans more than one subcell; partly because the positions of the cation channels correspond with the positions of two-fold screw axes (the cations probably occupy randomly the two positions related by this symmetry operation); and partly because there may well be further linear disordering of the cations and water molecules along the length of the channel. The possibility of a partial ordering within the **b**′ cell length, in the case of the DPPP salt, which shows sharper intermediate layer lines, is still under investigation.

ELECTRICAL CONDUCTIVITY

Conductivity temperature dependences (log σ vs $10^3/T$) of the isostructural congeners are shown in Figure 4. The conductivities, determined parallel to **b**, exhibit semiconducting behavior. Within a narrow temperature range, the data give a reasonable fit to the expression $\sigma = \sigma_0 \exp(-E_a/\mathrm{k}T)$ where $\sigma_{300\mathrm{K}} = 1$ to 100 S cm^{-1} and $E_a = 0.04$ to 0.06 eV in (DMPP)(TCNQ)$_{4\text{-}1/2}$(H$_2$O); 1 to 10 S cm^{-1} and 0.06 to 0.10 eV in (DHPP)

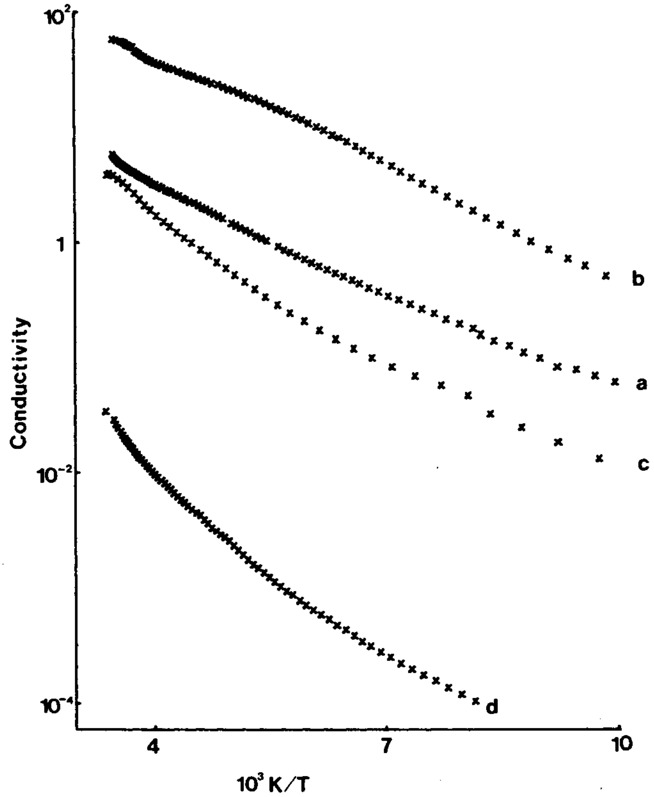


FIGURE 4 Variation of the *b*-axis conductivities (in S cm^{-1}) with reciprocal temperature of (a) (DHPP) $(TCNQ)_4(H_2O)$, (b) (DMPP) $(TCNQ)_{4\text{-}1/2}(H_2O)$, (c) (DEPP) $(TCNQ)_5(H_2O)$ and (d) (DPPP) $(TCNQ)_5(H_2O)$.

$(TCNQ)_4(H_2O)$ and (DEPP) $(TCNQ)_5(H_2O)$; and 0.05 S cm^{-1} and 0.11 to 0.14 eV in (DPPP) $(TCNQ)_5(H_2O)$. The activation energies were determined in the range 200 to 300 K. Over a wider temperature range correlation is poor, which suggests that either E_a or σ_0 is temperature dependent or alternatively that the conductivity does not follow an activated law.

For the isostructural congener, (DEPE) $(TCNQ)_{4\text{-}1/2}(H_2O)$, reported previously,[1] the properties are also sample dependent and range from semiconducting to metallic with $\sigma_{300K} = 10$ to 500 S cm^{-1}. For the semiconducting crystals, Somoano *et al.*[3] have reported anisotropic conductivities at 300 K of 0.33, 50 and 0.03 S cm^{-1} along **a**, **b**, and **c** respectively. In the current work, corresponding values of 0.05, 0.05 and 0.007 S cm^{-1} have been obtained for (DPPP)$(TCNQ)_5(H_2O)$. The lower anisotropy ratio of 7:7:1, compared with 10:1500:1 in (DEPE)$(TCNQ)_{4\text{-}1/2}(H_2O)$, and the lower conductivities are attributed to cation ordering (see below). The ordering is consistent with the fact that X-ray oscillation photographs of the DPPP salt show sharper intermediate layer lines.

THERMOELECTRIC POWER

The thermoelectric e.m.f.'s of the isostructural mixed valence TCNQ salts are sample dependent, but for each the thermoelectric e.m.f. (Figure 5) tends to saturate to a constant value in the high temperature region. Similar behavior[22] in, for example, quinolinium$(TCNQ)_2$ and acridinium$(TCNQ)_2$ has been interpreted by Chaikin and Beni[23] in terms of correlated carrier motion, which may well also apply to our salts. Thus for a system of localized carriers, with strong on-site electron-electron repulsion, the

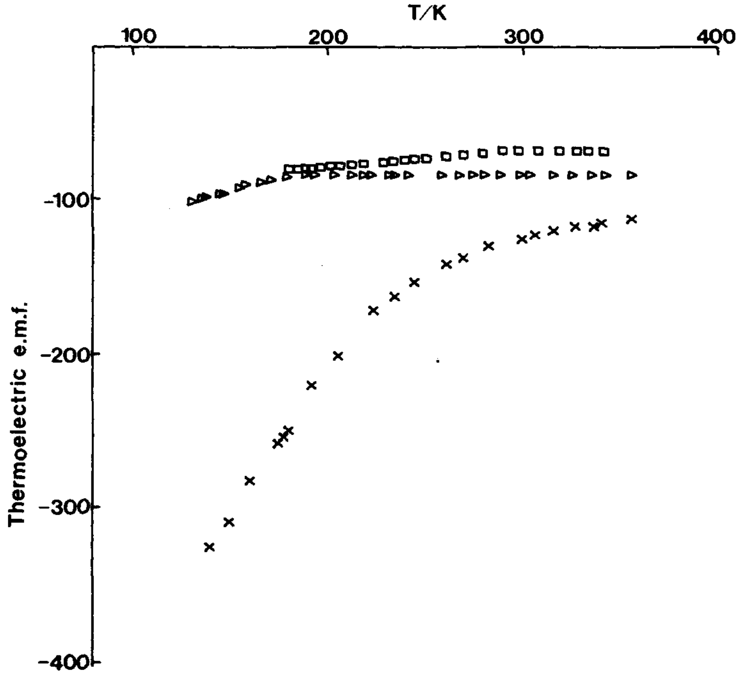


FIGURE 5 Variation of the thermoelectric e.m.f.'s (in $\mu V\ K^{-1}$) with temperature of the DHPP (□), DMPP (▷) and DEPP (x) salts.

thermoelectric e.m.f. (S) is given[23] by

$$S = -k/e \ln[2(1 - \rho)/\rho],$$

where ρ is the ratio of carriers to TCNQ sites. In the absence of back charge transfer, the calculated thermoelectric e.m.f.'s of the 1:4, 1:4.5 and 1:5 TCNQ salts are −59.8, −79.0 and −94.8 μV K^{-1} respectively. The experimental values, obtained for the isostructural series of salts of diquaternised 1,3-bis(4-pyridyl)propane (DRPP) and diquaternised 1,2-bis(4-pyridyl)ethylene (DRPE), demonstrate the same progression as the theoretical values. The thermoelectric e.m.f.'s are, however, sample dependent and there is some overlap of values, the typical ranges in the saturation region being −50 to −75 μV K^{-1} for (DHPP)(TCNQ)$_4$(H$_2$O) and (DMPE)(TCNQ)$_4$(H$_2$O), −65 to −95 μV K^{-1} for (DMPP)(TCNQ)$_{4\text{-}1/2}$(H$_2$O) and (DEPE)(TCNQ)$_{4\text{-}1/2}$(H$_2$O) and −80 to −120 μV K^{-1} for (DEPP)(TCNQ)$_5$(H$_2$O) and (DPPE)(TCNQ)$_5$(H$_2$O). The fact that the experimental data correspond reasonably closely with the calculated values suggests that the Chaikin and Beni expression is applicable but, in view of the overlap and the sample dependence, this cannot be stated with any certainty.

A few samples of the dehydrated DEPE salt have also shown smaller, temperature independent values of −25 to −35 μV K^{-1}. The data cannot be fitted to the above expression as it would be necessary for the cation to take a valency in excess of 2+. It is therefore assumed that this small thermoelectric e.m.f. corresponds to the infrequently observed metallic state.

CONCLUSION

We have shown for the isostructural salts of diquaternised 1,3-bis(4-pyridyl)propane that the TCNQ lattice (Figure 2) can accommodate cations ranging in size from DHPP (M_r = 200.3) to DPPP (M_r = 284.4), causing the stoichiometry to change from 1:4.0(1) to 1:5.0(1). This adaptability, combined with the fact that the hydrated cation lattice shows no long-range order, leads us to suggest that the cation channels may also accommodate "impurities" such as CH$_3$CN. Flandrois *et al.*[24] have reported CH$_3$CN inclusion as high as 2 mole % in (N-methyl-o-phenanthrolinium)(TCNQ)$_2$ and > 0.1% in other samples investigated. In the isostructural salts of diquaternised 1,3-bis(4-pyridyl)propane and 1,2-bis(4-pyridyl)-ethylene, variable solvent inclusion within the cation channels may cause further small changes in stoichiometry. Such nonstoichiometry could account for the higher conductivities sometimes observed.

In the salts investigated, the TCNQ lattice is isostructural, yet the conductivities span four orders of magnitude, from 0.05 S cm^{-1} in (DPPP)$(TCNQ)_5(H_2O)$ to 100 S cm^{-1} in the more highly conducing crystals of (DMPP)$(TCNQ)_{4\text{-}1/2}(H_2O)$ and 500 S cm^{-1} in the metallic form of (DEPE)$(TCNQ)_{4\text{-}1/2}(H_2O)$. Differences in the properties are attributed to differences in the degree of cation disorder, as in these quasi-one-dimensional systems disorder is necessary to stabilize the conducting chains. A qualitative guide to the degree of disorder is obtained by studying the intermediate layer lines which are attributed to the hydrated cation lattice. Thus it is of interest to note that in (DPPP)$(TCNQ)_5(H_2O)$, which has the lowest conductivity, the intermediate layer lines show some structure; whereas in (DMPP)$(TCNQ)_{4\text{-}1/2}(H_2O)$ and (DEPE)$(TCNQ)_{4\text{-}1/2}(H_2O)$, which are highly conducting, even in the semiconducting crystals, the layer lines are very weak and diffuse.

Our crystallographic and electrical studies have shown that the conductivity decreases significantly as the hydrated cation lattice orders.

CORRIGENDA

In earlier studies, the intermediate layer lines were assigned to the water lattice only, as it was assumed that each of the complexes had a common stoichiometry of 1:4. This assignment was based on the fact that the intermediate layers were unobserved when crystals were annealed in vacuum at 80 to 100°C, and under such conditions analysis had indicated that dehydration occurred. From density measurements and single crystal X-ray studies, the intermediate layer lines are now attributed to the hydrated cation lattice. Their disappearance, upon annealing, indicates an increase in the cation disorder and it is assumed that dehydration plays an important role in the disordering process.

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References

1. G. J. Ashwell, *Proceedings of The International Conference on Low Dimensional Conductors*, Boulder (1981). Published in *Molecular Crystals and Liquid Crystals*, (1982).

2. G. J. Ashwell, D. D. Eley, and M. R. Willis, *Nature*, **201**, 259 (1976).
3. R. B. Somoano, V. Hadek, S. P. S. Yen, A. Rembaum, C. H. Hsu, R. J. Deck, T. Datta, and A. M. Hermann, *Physica Status Solidi (b)*, **81**, 281 (1977).
4. M. A. Shaikh, *Solid State Commun.*, **33**, 991 (1980).
5. G. J. Ashwell, *Nature*, **290**, 686 (1981).
6. S. C. Wallwork, to be published.
7. G. J. Ashwell, D. D. Eley, S. C. Wallwork, M. R. Willis, G. D. Welch, and J. Woodward, *Acta Cryst.*, **B33**, 2252 (1977).
8. G. J. Ashwell and S. C. Wallwork, *Acta Cryst.*, **B35**, 1648 (1979).
9. G. J. Ashwell, D. D. Eley, S. C. Wallwork, and M. R. Willis, *Proc. Roy. Soc. Lond. A*, **343**, 461 (1975).
10. G. J. Ashwell, I. Diaconu, D. D. Eley, S. C. Wallwork, and M. R. Willis, *Z. Naturforschung*, **34a**, 1 (1979).
11. T. Sundaresan and S. C. Wallwork, *Acta Cryst.*, **B28**, 2474 (1972).
12. G. J. Ashwell, D. A. Kennedy, I. W. Nowell, and J. G. Allen, *Acta Cryst.*, submitted for publication.
13. G. J. Ashwell, D. D. Eley, N. J. Drew, S. C. Wallwork, and M. R. Willis, *Acta Cryst.*, **B33**, 2598 (1977).
14. G. J. Ashwell, D. A. Kennedy, I. W. Nowell, and J. G. Allen, in preparation.
15. G. J. Ashwell, D. D. Eley, R. J. Fleming, S. C. Wallwork, and M. R. Willis, *Acta Cryst.*, **B32**, 2948 (1976).
16. G. J. Ashwell, V. E. Bartlett, J. K. Davies, D. D. Eley, S. C. Wallwork, M. R. Willis, A. Harper, and A. C. Torrance, *Acta Cryst.*, **B33**, 2602 (1977).
17. G. J. Ashwell, W. Waclawec, and S. C. Wallwork, in preparation.
18. G. J. Ashwell and S. C. Wallwork, *Acta Cryst.*, **B31**, 1174 (1975).
19. G. J. Ashwell, D. D. Eley, A. Harper, A. C. Torrance, S. C. Wallwork, and M. R. Willis, *Acta Cryst.*, **B33**, 2258 (1977).
20. G. J. Ashwell, D. D. Eley, N. J. Drew, S. C. Wallwork, and M. R. Willis, *Acta Cryst.*, **B34**, 3608 (1978).
21. A. Rembaum, V. Hadek, and S. P. S. Yen, *J. Amer. Chem. Soc.*, **93**, 2532 (1971).
22. I. F. Schegolev, *Physica Status Solidi (a)*, **12**, 9 (1972).
23. P. M. Chaikin and G. Beni, *Phys. Rev.*, **B13**, 647 (1976).
24. S. Flandrois, P. Libert, and P. Dupuis, *Prace Naukowe Instytutu Chemii Organicznej i Fizycznej Politechniki Wroclawskiej*, **7(1)**, 269 (1974).