MEM(TCNQ)₂ at room temperature and 10 K, and the absence of a spin-Peierls transition

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Precise X-ray determinations of the crystal structure of the 1:2 complex of *N*-ethyl-*N*-methylmorpholinium and 7,7,8,8-tetracyano-*p*-quinodimethanide, abbreviated as MEM–TCNQ or MEM(TCNQ)₂ ($C_7H_{16}NO^+ \cdot 2C_{12}H_4N_4^{0.5-}$), have been performed at 293 and at 10 K. Evidence for the expected spin-Peierls transition at 19 K is not found, and this may follow from radiation damage to the crystal or from insufficient equipment sensitivity.

Comment

The charge-transfer salt morpholinium tetracyanoquinonate, MEM(TCNQ)₂, undergoes a first-order structural phase transition at 340 K (T_c), with dimerization of one-dimensional stacks of TCNQ units and a *ca* 1000-fold decrease in electrical conductivity (van Bodegom, 1981; van Bodegom & Bosch, 1981). There is also a second-order transition at 19 K (T_{sP}) associated with the electronically driven spin-Peierls dimerization of the antiferromagnetic Heisenberg spin-$\frac{1}{2}$ chain of $[(TCNQ)_2]^-$ dimers (van Bodegom *et al.*, 1981; Larson, 1995).
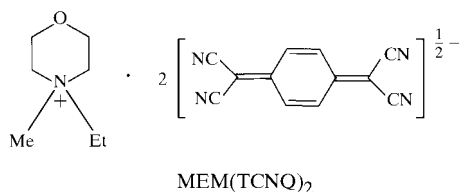
MEM(TCNQ)₂

The main structural changes in MEM(TCNQ)₂ at 340 K are related to the disorder of the MEM group through merohedral twinning, which causes a subtle dimerization of the TCNQ stacks. The degree of twinning is related to disorder of the MEM group around a local pseudo-inversion centre ($0, \frac{1}{2}, 0$ for the set of coordinates used here), which changes with temperature. With the assumption of two preferred orientations, the 100% occupancy of the MEM orientation observed

at 113 K (Bosch & van Bodegom, 1977) decreases to 84% at 294 K, 63% at 323 K, and reaches 50% above the high-temperature phase transition at T_c. A low-temperature crystallographic study has recently determined the dynamics of the *c*-doubling spin-Peierls transition (Lumsden & Gaulin, 1999), although structural data have yet to be collected below T_{sP}.

We present here results of an X-ray study of the compound at room temperature followed by one on the same crystal at 10 K. We undertook the low-temperature investigation with the aim of obtaining data for structural refinement of the spin-Peierls ground state, which would give information unique for a spin-Peierls system. At 10 K, however, we were unable to observe evidence for the doubling of the *c* axis associated with spin-Peierls dimerization.

A previous study on the same crystal used here, performed at 15 K on diffractometer ID11 at the European Synchrotron Radiation Facility, had been successful in locating discrete weak $c^*/2$ superstructure reflections associated with the spin-Peierls dimerization. Integration of image-plate data confirmed the existence of the $c^*/2$ modulation, whose superstructure reflection intensities were 10^{-3} to 10^{-4} of those of neighbouring Bragg reflections (Kepert *et al.*, 1999). Also, a magnetic study of fresh crystals from the same synthetic batch was successful in showing the presence of the spin-Peierls transition (Lovett *et al.*, 2000).

The room-temperature structure of MEM(TCNQ)₂ has been discussed in detail earlier (van Bodegom, 1981) and our data are somewhat more accurate. The general view of the compound with its atom-numbering scheme, as used by Bosch & van Bodegom (1977) for their 113 K structure, is given in Fig. 1. The structure of the compound in the crystal consists of TCNQ columns stacked along the *c* direction with MEM molecules between them. The geometrical characteristics found for our models are close to those in the final model of the 113 K structure of Bosch & van Bodegom (1977). The shortest CH⋯N separations between successive TCNQ columns and their nearest neighbour MEM molecules are listed in the tables of hydrogen bonds (Tables 1 and 2). The value obtained for the MEM site-population parameter x, 0.835 (5), is in very good agreement with the value of 0.84 reported by van Bodegom (1981).

In the molecule of TCNQ, there are five different kinds of non-hydrogen bonds: two endocyclic bonds, $Csp^2 = Csp^2$ 1.352 (10) Å and $Csp^2 - Csp^2$ 1.432 (12) Å, and three exocyclic bonds, $Csp^2 = Csp^2$ 1.392 (17) Å, $Csp^2 - Csp$ 1.427 (10) Å and $Csp \equiv N$ 1.144 (8) Å. The bond lengths given here are averaged distances taken from the Cambridge Structural Database (Allen *et al.*, 1979) and published in *International Tables for Crystallography* (1992, Vol. C, Table 9.5.1.1). They form the series of bonds C7—C8, C6—C7, C3—C6, C2—C3 and N1—C2 (Fig. 1). The averaged results for our room-temperature structures are 1.355 (8), 1.436 (6), 1.397 (7), 1.426 (7) and 1.144 (7) Å, respectively, and are in excellent agreement with literature data. The 10 K averaged results, *i.e.* 1.365 (4), 1.435 (5), 1.401 (8), 1.429 (3) and 1.157 (2) Å, are slightly different from those published for the 113 K structure

[1.359 (3), 1.446 (3), 1.392 (7), 1.439 (3) and 1.160 (4) Å; Bosch & van Bodegom, 1977], but may be considered normal within a 3σ limit. The C—H bond lengths vary from 0.92 to 1.02 Å, with an average value of 0.97 (2) Å. The dihedral angle between the best least-squares planes of the quinodimethane groups for the room-temperature and 10 K structures are 1.06 (6) and 1.81 (1)°, respectively. The dihedral angles between the benzene rings and the cyanide groups are 3.1 (1) and 3.15 (3)° (N1→N5 cyanide), and 1.4 (1) and 1.70 (3)° (N12→N16 cyanide) for molecule 1 of TCNQ, and 4.1 (1) and 4.29 (3)° (N17→N21 cyanide), and 2.5 (1) and 1.79 (3)° (N28→N32 cyanide) for molecule 2. The interatomic distances in the MEM molecule correspond to normal values and the ring is in the chair conformation.
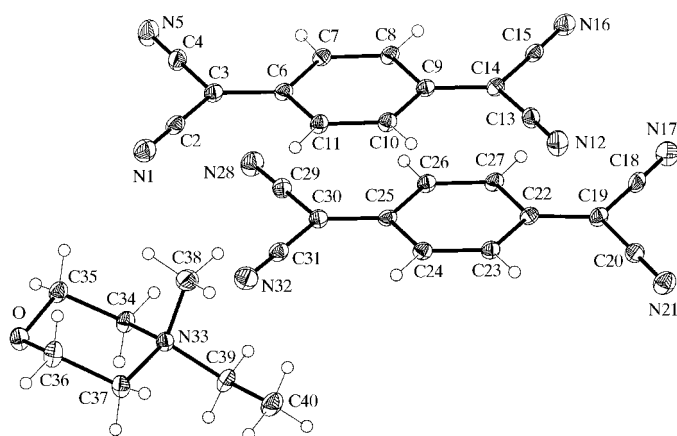

Figure 1
Environments of the atoms in MEM(TCNQ)$_2$ at 10 K. Displacement ellipsoids are shown at the 75% probability level.

In our experiment at 10 K, we were not able to detect the results of the spin-Peierls transition. It is possible that radiation damage arising from the earlier synchrotron study has led to a lowering of T_{sP} for the crystal studied. Such a lowering, which is well established for electronic transitions in one-dimensional electronic materials (Zuppiroli, 1988), arises from the inhibition of three-dimensional long-range ordering in the presence of radiation-induced defect sites. Although weak diffuse scattering is anticipated in such cases, the series of scans we performed along the c^* direction of reciprocal space showed no detectable systematic features above the background. It is possible that our equipment was not sufficiently sensitive to detect peaks as small as 10^{-3} of the nearby Bragg intensities in the presence of the noise from powder scattering from the Be thermal shields.

Experimental

A crystal used in an earlier synchrotron experiment (Kepert *et al.*, 1999) was employed.

MEM(TCNQ)₂ at 293 K

Crystal data

$C_7H_{16}NO^+ \cdot 2C_{12}H_4N_4{}^{0.5-}$	$Z = 1$
$M_r = 538.59$	$D_x = 1.258$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.803$ (1) Å	Cell parameters from 12
$b = 15.353$ (2) Å	reflections
$c = 6.985$ (1) Å	$\theta = 12.3–16.1°$
$\alpha = 112.30$ (1)°	$\mu = 0.08$ mm^{-1}
$\beta = 74.44$ (1)°	$T = 293$ (2) K
$\gamma = 111.84$ (1)°	Prism, black
$V = 710.7$ (2) Å^3	$0.55 \times 0.45 \times 0.25$ mm

Data collection

Huber 512 goniometer diffrac-	$h = 0 \rightarrow 10$
tometer	$k = -21 \rightarrow 20$
ω–2θ scans	$l = -9 \rightarrow 9$
4110 measured reflections	3 standard reflections
4110 independent reflections	every 100 reflections
2851 reflections with $I > 2\sigma(I)$	intensity decay: 1%
$\theta_{max} = 30.1°$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0808P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.049$	$+ 0.0567P]$
$wR(F^2) = 0.158$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.002$
4110 reflections	$\Delta\rho_{max} = 0.23$ e Å^{-3}
408 parameters	$\Delta\rho_{min} = -0.15$ e Å^{-3}
H atom-parameters constrained	Extinction correction: *SHELXL*
	Extinction coefficient: 0.046 (8)

Table 1
Hydrogen-bonding geometry (Å, °) for MEM(TCNQ)$_2$ at 293 K.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C8—H8$\cdots$N12^{i}	0.93	2.65	3.317 (5)	129
C11—H11$\cdots$N5^{ii}	0.93	2.68	3.359 (5)	131
C24—H24$\cdots$N28^{ii}	0.93	2.66	3.329 (6)	130
C27—H27$\cdots$N21^{i}	0.93	2.71	3.380 (5)	130
C34—H34$A\cdots$N32	0.97	2.53	3.402 (5)	149
C34—H34$B\cdots$N1^{iii}	0.97	2.81	3.742 (7)	162
C38—H38$C\cdots$N5^{ii}	0.96	2.73	3.395 (7)	127
C38—H38$B\cdots$N17^{iv}	0.96	2.68	3.267 (8)	120

Symmetry codes: (i) $1 + x, y, z$; (ii) $x - 1, y, z$; (iii) $x, y, z - 1$; (iv) $x, 1 + y, 1 + z$.

MEM(TCNQ)₂ at 10 K

Crystal data

$C_7H_{16}NO^+ \cdot 2C_{12}H_4N_4{}^{0.5-}$	$Z = 1$
$M_r = 538.59$	$D_x = 1.305$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.773$ (1) Å	Cell parameters from 12
$b = 15.315$ (2) Å	reflections
$c = 6.8347$ (9) Å	$\theta = 12.7–16.3°$
$\alpha = 113.249$ (8)°	$\mu = 0.09$ mm^{-1}
$\beta = 73.569$ (9)°	$T = 10.0$ (1) K
$\gamma = 111.796$ (9)°	Prism, black
$V = 685.2$ (2) Å^3	$0.55 \times 0.45 \times 0.25$ mm

Data collection

Huber 512 goniometer diffrac-	$\theta_{max} = 30.1°$
tometer	$h = -10 \rightarrow 10$
ω–2θ scans	$k = -21 \rightarrow 21$
8048 measured reflections	$l = -9 \rightarrow 9$
4024 independent reflections	3 standard reflections
3966 reflections with $I > 2\sigma(I)$	every 100 reflections
$R_{int} = 0.011$	intensity decay: 1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0698P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.030$	$+ 0.0427P]$
$wR(F^2) = 0.085$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
4024 reflections	$\Delta\rho_{max} = 0.44$ e Å^{-3}
467 parameters	$\Delta\rho_{min} = -0.25$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	Extinction correction: *SHELXL*
	Extinction coefficient: 0.046 (4)

Table 2
Hydrogen-bonding geometry (Å, °) for MEM(TCNQ)$_2$ at 10 K.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C8—H8$\cdots$N12^i	1.02 (2)	2.58 (2)	3.261 (2)	124.2 (16)
C11—H11$\cdots$N5^{ii}	0.98 (2)	2.57 (2)	3.294 (2)	130.3 (17)
C24—H24$\cdots$N28^{ii}	0.98 (2)	2.59 (2)	3.271 (2)	126.3 (15)
C27—H27$\cdots$N21^i	0.99 (2)	2.62 (2)	3.298 (2)	125.3 (16)
C34—H34$A\cdots$N32	0.95 (2)	2.49 (2)	3.331 (2)	149.0 (17)
C34—H34$B\cdots$N1^{iii}	0.94 (2)	2.79 (2)	3.703 (2)	163.1 (14)
C38—H38$C\cdots$N5^{ii}	0.99 (2)	2.60 (2)	3.351 (2)	132.6 (17)
C38—H38$B\cdots$N17^{iv}	0.95 (2)	2.59 (2)	3.203 (2)	122.6 (14)

Symmetry codes: (i) $1 + x, y, z$; (ii) $x - 1, y, z$; (iii) $x, y, z - 1$; (iv) $x, 1 + y, 1 + z$.

Both room-temperature and 10 K data sets were obtained on a locally assembled Huber 512 goniometer equipped with a Displex 202D cryogenic refrigerator (Henriksen *et al.*, 1986; Larsen, 1995). A series of continuous one-dimensional scans along the c^* direction of reciprocal space showed no detectable systematic features above the background between the Bragg peaks.

For the structure from the room-temperature data set, fractional populations x and $1 - x$ were refined for the atoms of the disordered MEM molecule in its two orientations relative to the pseudo-inversion centre. The positional parameters of the disordered part of the MEM molecule (atoms N33′ to O′) were refined using the *SAME* instruction of the *SHELXL*97 least-squares program, and with isotropic atomic displacement parameters for all atoms. Distances between *SAME* listed atoms are restrained to be the same length as those between the corresponding following atoms of the preferred molecule (atoms N33 to O) with an s.u. of 0.02 Å. For the ordered part of the MEM molecule, anisotropic atomic displacement parameters were employed for non-H atoms, with isotropic displacement parameters for H atoms. During refinement, the H atoms of MEM and TCNQ at 293 K were refined using 'riding-model' constraints, with fixed C—H distances of 0.93, 0.97 and 0.96 Å for the CH, CH$_2$ and CH$_3$ groups, respectively. Isotropic displacement parameters of the H atoms were constrained to the U_{eq}/U value of the bonded C

atoms with $U_H = 1.2U_C$ in CH and CH$_2$ groups, and $U_H = 1.5U_C$ for the H atoms of CH$_3$ groups. The absolute structure could not be determined reliably because of strong correlation between pseudo-centrosymmetrically related parameters of the two unique molecules of TCNQ. Flack parameters (Flack, 1983) were estimated to be 2 (3) at room temperature and 0.9 (8) at low temperature, but were not included among the refined parameters.

For both compounds, data collection: local diffractometer control software; cell refinement: local diffractometer control software; data reduction: *PROFIT* (Streltsov & Zavodnik, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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