The Highly Conductive Nonstoicheiometric Tetrathiafulvalene Nitrate: Composition, Conductivity, and Structure

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The nonstoicheiometric tetrathiafulvalene (TTF) salt, $TTF(NO_3)_{0.55}$, has been prepared as single crystals by electrocrystallisation. At $\geqslant 291$ K it has unidimensionally metallic properties, with a (four-probe) conductivity of $1.2 \times 10^3 \Omega^{-1} cm^{-1}$ at 291 K, along the needle axis; at <291 K it is semiconducting. The crystals are monoclinic, space group $P2_1/n$, with $a = 10.976$, $b = 11.868$, $c = 3.607$ Å, and $\beta = 90.79°$, the nitrates are completely disordered around the centre of symmetry at ($\frac{1}{2}$, 0, $\frac{1}{2}$) with electron density smeared along the *c* axis, as in other TTF adducts. Disorder of the sulphur atoms gives electron density displacements above and below the TTF plane. Electronic motion associated with TTF stacks, comprising TTF^0–TTF^+ mixed charge entities, underlies the high *c*-axis conductivity.

THERE is widespread current interest in the new 'organic metals', of which TTF (tetrathiafulvalene)–TCNQ (tetracyanoquinodimethanide) is the progenitor,[1] one recently having been made superconductive.[2] Adducts of TTF with simple anions include[3,4] $TTF(NO_3)_{0.55}$, which we have prepared for the first time, and studied for structure and conductivity.

EXPERIMENTAL

Preparation.—We give a detailed account of the preparation, since conductive properties often depend critically on preparative history. 1 mmol TTF (Aldrich) and 10 mmol tetra-n-butylammonium nitrate (Fluorochem) dissolved in 100 ml of six-times distilled acetonitrile were electrolysed in a nitrogen-flushed cell using a triangular array of electrodes each separated by *ca.* 2 cm. The working electrode was a horizontal platinum disc 1 cm in diameter sealed to the bottom of its support so that only the nether face was exposed; the vertical auxiliary electrode was 2 cm of 22 gauge platinum wire at a depth such that its length was bisected by the plane of the platinum disc; a conventional porous-plugged saturated calomel electrode (s.c.e.) completed the array. The disc potential was potentiostatted at 0.750 ± 0.001 V *versus* s.c.e. This gave current–time traces leading in our experience to the formation of good crystals, *i.e.* current densities/$\mu A\ cm^{-2}$ of 6.4×10^2 initially, dropping to 5.1×10^2 in 20 s, rising to a maximum of 1.15×10^3 in 14 h, then dropping, finally, to 63.7 after 26.8 h. The crystals, carefully removed from the electrode, were washed extensively with acetonitrile. The product, as black needles, $5 \times 0.1 \times 0.1$ mm^3, was dried at room temperature at 10^{-2} Torr. C, H, and N analyses gave $TTF(NO_3)_{0.55}$, the stoicheiometry being reproducible from preparation to preparation to within experimental error (1.6%). The pulverised adduct dissolves in H_2O, MeCN, DMF, EtOH, MeOH, and $PhNO_2$, its growth in electrocrystallisation clearly depending on still conditions. In MeCN, u.v.–visible absorption maxima occurred at λ 308 (ε 4 400), 318 (4 550), 334 (3 080), 408 (2 650), 437

$Z = 2$; $F(000) = 242$; $D_x = 1.69$ g cm^{-3}, $D_c = 1.69$ g cm^{-3}. λ(Mo-K_α) = 0.710 69 Å; μ(Mo-K_α) = 9.3 cm^{-1}.

The crystal system and initial unit-cell parameters were determined from oscillation and Weissenberg photographs. Accurate values were derived from least-squares refinement to 25 θ values automatically centred on a Nonius CAD-4 diffractometer. The space group $P2_1/n$ (No. 14) was uniquely determined by systematic absences. The density D_x was the flotation value. Intensities were recorded using graphite-monochromated Mo-K_α and a θ—2θ step scanning mode. 442 of the 885 measured reflections were used in the structure determination [observed $F_o > 3\sigma(F_o)$]. Data were corrected for Lorentz and polarisation effects but no absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares procedures using the SHELX 76 program.[5] The diffraction pattern was (as is fairly typical of conductive adducts) of apparently mediocre quality, and the intensity distribution for each reflection was broad and associated with Laue-type streaks.

Difference electron-density synthesis showed the structure to be considerably disordered. The three carbon atoms in half-TTF were not disordered but the two sulphur positions had significant residual electron density above and below the TTF molecular plane: the final refinement yielding the best *R* employed an in-plane occupancy of 0.80 and the remaining 0.20 was equally distributed above and below. Carbon, and the sulphur with occupancy 0.80, were treated anisotropically, but the sulphur atoms with occupancy of 0.10 were refined isotropically. The nitrate ion is severely disordered around the centre of symmetry at ($\frac{1}{2}$, 0, $\frac{1}{2}$) and the electron density is smeared along the *c* axis with several broad regions having electron densities higher than others. Attempts to include six positions for NO_3 in the refinement with isotropic temperature factors yielded structurally unrealistic conformations, and the general disorder as found in SCN adducts[6] is clearly evident here. S–C and N–O distances were constrained at 1.76(1) and 1.20(1) Å, and hydrogen atoms were not located.

Though larger than the values between 1.73 and 1.75 Å been referred to above. Only four oxygens are cited since their dispositions within the nitrate are by inference totally disordered; the occupancy factors and the parameters U of their temperature factors are likewise fictions, and thus excluded from Table 1.

by a decrease which led to very low values $<10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 77 K.

The spectra of the dissolved product show the presence of TTF^0 (308 nm), TTF^+ (334, 437, and 584 nm), and $(\mathrm{TTF}^+)_2$ (408 nm) from comparison with work on TTF

TABLE 1

Refined positional parameters with e.s.d. in parentheses, assigned occupancy factors K, and temperature factor parameters U †

Atoms	x	y	z	K	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
S(1)	0.020 2(5)	−0.181 7(4)	−0.008(2)	0.80	0.086(4)	0.065(3)	0.089(4)	0.001(4)	0.003(3)	−0.004(2)
S′(1)	0.037(5)	−0.181(4)	0.302(33)	0.10	0.106(43)	0.06(2)	0.24(9)	0.03(4)	0.08(6)	0.01(2)
S″(1)	0.005(4)	−0.176(5)	−0.363(30)	0.10	0.05(2)	0.12(4)	0.19(7)	0.01(4)	−0.13(3)	−0.02(2)
S(2)	0.197 2(5)	−0.001 2(5)	−0.004(2)	0.80	0.068(3)	0.083(3)	0.095(4)	0.00(0)	0.00(0)	−0.011(2)

[redacted]

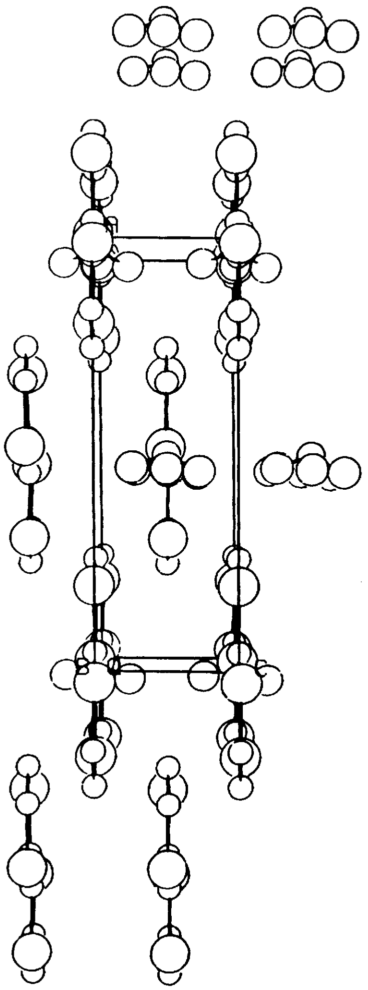

FIGURE 2 $TTF(NO_3)_{0.55}$ viewed along the *b* axis

charge and positive charge donor species, so on this time scale uniformity is imposed on what appear to be a discernibly dual population as indicated by i.r. That the implied residual times for conducting electrons on particular TTF molecules appear to exceed the lifetimes of the i.r.-excited species does not necessarily militate

TABLE 2

Conductivities of different samples by various techniques

Sample	Method	σ/Ω^{-1} cm^{-1}
Disc	2 probe DC	0.06
Disc	2 probe AC(1—20 kHz)	0.002
Single crystal		
c axis	2 probe DC	4
	4 probe DC	171; 1 200

agains a metallic conduction mechanism, though the implied localisation is notable.

The depicted structure (Figures 1—3) shows the stacked columns of TTF and NO_3^- typical of the genre. The interplanar distance 3.607 Å is close to that in $TTF(SCN)_{0.57}$ and comparable with that [4,6,12] in $TTF\text{-}Br_{0.71-0.76}$, 3.57 Å, and $TTFI_{0.71}$, 3.55 Å, slightly larger than that in TTF–TCNQ, 3.47 Å.[13–15]

TTF stacks in the nitrate show a new feature, the disorder in sulphur atoms, shown as density above and below the TTF molecular plane. Insofar as the sulphur atom orbitals are those principally involved in the conductivity interactions this is a significant observation. Conceivably such distortions coincide with electron residence or absence.

The metallic conduction in the new adduct is presumed to occur in the $TTF^{\delta+}$ stacks (δ 0.55). It is significant that the average δ is close to that in the stoicheiometric TTF–TCNQ, which however achieves

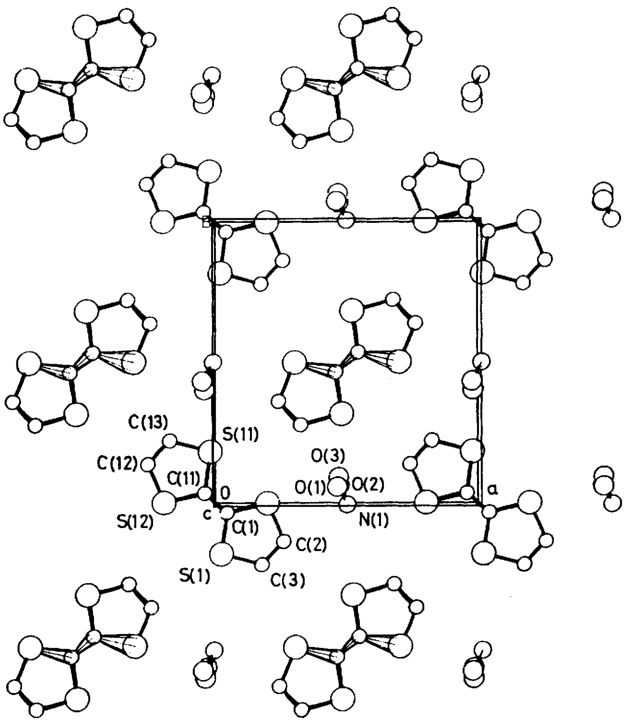

FIGURE 3 $TTF(NO_3)_{0.55}$ viewed along the *c* axis

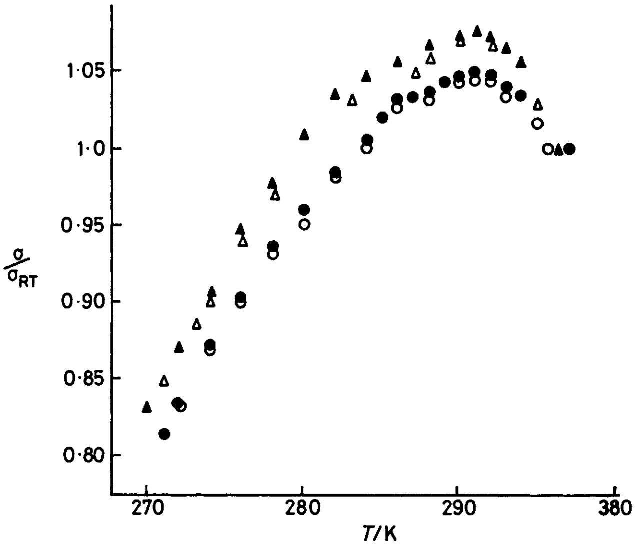

FIGURE 4 Ratio of σ at temperature *T* to σ_{RT}, the room temperature value, as a function of *T*. Two samples: filled symbols, *T* down; empty symbols, *T* up

this value by partial transfer to $TCNQ^{\delta-}$, itself becoming a conductive stack.[16] No conductive role is envisaged for NO_3^- in our compound, though it is not precluded. The disorder in NO_3^- must in part support the charge density waves to which the high conductivities are attributable.[16] The delocalisation of charge and its transfer along the TTF^0–TTF^+–TTF^0 *etc.* array provides a simplified but acceptable view of the conduction mechanism.

The σ temperature dependence is shown in Figure 4. Metallic conductivity appears above 291 K, but at that temperature a metal-semiconductor transition gives rise to a semiconductor which to 270 K gives a linear log σ–T^{-1} relation with activation energy 0.129 eV. Below 270 K the drop in σ is steeper than this. ($TTFI_{0.71}$ shows [17] a comparable value, 0.085 eV, below 220 K). Different samples show different conductivities but the same transition temperature. Cycling through the transition also generally introduces irreproducibility, since reversal through a transition involves a recrystallisation with inevitably different defect populations and the like.

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