Novel Conductive Adducts of Tetrathiafulvalene and Tetrathiatetracene

By POOPATHY KATHIRGAMANATHAN and DAVID R. ROSSEINSKY
(*Department of Chemistry, The University, Exeter* EX4 4QD)

Summary. Adducts of thia-donors have been prepared as single crystals by a new galvanostatic electrocrystallisation method usually yielding better products than the potentiostatic method, although $TTTI_{0.72}$ (TTT = tetrathiatetracene) from the latter shows a metallic conductivity of $1.1 \times 10^3\ \Omega^{-1}\ cm^{-1}$ at 300 K.

Electrocrystallised[1] TTF adducts (TTF = tetrathiafulvalene) of novel composition have quite high conductivities and are usually unidimensionally metallic. Potentiostatic growth was employed originally,[1] but we now find that a marked improvement on that already effective method ensues with galvanostatic (constant current) control, and the conduction properties and compositions of a number of new adducts of three thia donors are listed in Table 1. Galvanostatted products often occur as substantially larger single crystals 20 × 0·1 × 0·1 mm, or as single crystals [TTF(N$_3$)$_{0\cdot74}$] rather than microcrystalline powders, and sometimes as products which are[2] unobtainable by chemical means (TTF azide and isocyanate compounds[2]). Galvanostatic preparation usually yields higher σ values (TTF-SO$_3$OMe, TTFAc$_{0\cdot70}$, and TTFBr$_{0\cdot70}$) but not always (TTFI $_{0\cdot70}$). Some unusual adducts, such as TTF(AgNO$_3$)$_{0\cdot67}$, have been obtained, in this case using a sacrificial silver anode after a method for preparing cadmium organometallic complexes.[3]

Table 1. Conductivities σ of samples from galvanostatic (g) or potentiostatic (p) preparations, measured on discs with 2 or 4 probes (d2 or d4) or on single crystals with 2 or 4 probes (s2 or s4).

	σ/Ω^{-1} cm^{-1}
TTFTCNQ(p)	100 (s4)
TTF(N$_3$)$_{0\cdot74}$(p, g)	0·096 (d4), 0·10 (s2)
TTF(OSO$_2$OMe) (p, g)	5·1 × 10^{-8} (d4 p), 8·2 (s4 g)
TTF(SCN)$_{1\cdot14}$ (p, g)	4 (s2 p); 0·2 (s4 g), 530 (s4 g)
TTF(HSO$_4$)$_{1\cdot2}$ (p, g)	4·7 × 10^{-2} (s4 p); 0·9 (s4 g), 4 (s4 g)
TTF(OCN)$_2$ (g)[a]	1·1 × 10^{-7} (d2)
TTF(Ac)$_{0\cdot70}$ (p, g)	3 (s2 p), 38 (s2 g)
TTFI$_{0\cdot70}$ (p, g)	10 (s2 p), 7·5 (s2 g)
TTFBr$_{0\cdot70}$ (p, g)	0·3 (s2 p), 1·4 (s4 p), 800 (s2 g)
TTF(ClO$_4$)$_{0\cdot71}$ (p)[b]	9 (d2)
TTF(BPh$_4$)$_{0\cdot86}$ (p)[b]	2·5 (d2)
TTF [Fe(CN)$_6$]$_{0\cdot25}$ (p)[a]	10·5 (d2)
TTF(AgNO$_3$)$_{0\cdot67}$ (g)[a]	0·4 (d2)
TTTI$_{0\cdot72}$ (p)	1·1 × 10^3 (s2)
TTT(NO$_3$)$_{0\cdot74}$ (p)	500 (s2)
Thia Ni (mnt)$_2$ (p)	10^{-4} (d4)

[a] Microcrystalline. [b] Polycrystalline. [c] mnt = maleonitriledithiolate.

A further benefit of the galvanostatic method is the possibility of linking cells in series for multiple preparations of the adduct. Indeed, with a fixed (say) donor, and a different acceptor in each cell, a variety of adducts can be prepared in one experiment. For the TTF halides the reproducibilities of σ in two batches of three crystals are good (Table 2) but for TTF(SCN)$_{1\cdot14}$ (Table 1) they are much less so.

Table 2. Conductivities σ of series-grown halide complexes of TTF: 3 crystals from each of 2 batches (s2).

	Batch 1: σ/Ω^{-1} cm^{-1}	Batch 2: σ/Ω^{-1} cm^{-1}
TTFI$_{0\cdot70}$	7·4, 7·6, 7·5	7·4, 7·6, 7·5
TTFBr$_{0\cdot70}$	820, 820, 860	800, 810, 880
TTFCl$_{1\cdot1}$	1·0, 4·2, 5·5	2·1, 3·1, 5·7

For tetrathiatetracene (TTT) iodine complexes σ varies with stoicheiometry, *e.g.* TTTI$_{1\cdot5}$ from cosublimation[4] or cocrystallisation[5] has a σ of 600 to 10^4 Ω^{-1} cm^{-1},[6,7] while the 1 : 1 adduct[5,8] has σ *ca.* 1·4—70 Ω^{-1} cm^{-1}. Other stoicheiometries are also known.[7,9,10] We have now prepared TTTI$_{0\cdot72}$ for the first time, again with a high σ value, 10^3 Ω^{-1} cm^{-1} (Table 1).

The electrocrystallisation potential is determined voltammetrically (Bruker E44 polarograph) on Pt or W electrodes, TTT adducts being grown at 0·500 V (s.c.e.) in MeCN, thianthrene adducts at 1·138 V. The corresponding current was controlled on a locally constructed galvanostat in the galvanostatic preparations. A tentative suggestion[1] that crystallisation selectively occurred fastest on the most conductive axis by virtue of that conductivity needs some qualification in the light of electrocrystallisations effected near the gas/solution surface: crystals were forced up through the surface, showing growth to occur on the metal electrode. The improvements effected by galvanostatting may thus be attributed to resultant better control of the potential at the metal face, which would soon become screened by crystals from displaying its true local potential with respect to a reference in the bulk solution.

We thank Dr M. A. Mazid for *X*-ray examination of some of the samples, and Mr T. E. Booty for substantial technical assistance throughout.

(*Received, 4th December* 1979; *Com.* 1265.)

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[1] P. Kathirgamanathan, S. A. Mucklejohn, and D. R. Rosseinsky, *J. Chem. Soc., Chem. Commun.*, 1979, 86.
[2] F. Wudl, G. A. Thomas, D. E. Schaffer, and W. M. Walsh, Jr., *Mol. Cryst. Liq. Cryst.*, 1976, **32**, 147.
[3] A. Osman and D. G. Tuck, *J. Organomet. Chem.*, 1979, **169**, 255.
[4] B. Hilti and C. W. Mayer, *Helv. Chim. Acta.*, 1978, **61**, 801.
[5] L. I. Buravov, G. I. Zvereva, V. F. Kaminskii, L. P. Rosenberg, M. L. Khidekel, R. P. Shibaeva, I. F. Shchegolev, and E B. Yagubskii, *J. Chem. Soc., Chem. Commun.*, 1976, 720.
[6] S. K. Khanna, S. P. S. Yen, R. B. Somoano, P. M. Chaikin, C. Lowe, R. Williams, and S. Samson, *Phys. Rev., Sect. B*, 1979, **19**, 655.
[7] L. C. Isett, *Phys. Rev., Sect. B*, 1978, **18**, 439.
[8] E. A. P. Albuerne, H. Johnson, J. R. Trevor, and D. J. Trevor, *J. Chem. Phys.*, 1971, **55**, 1547.
[9] E. Abrahams, L. P. Gorkov, and G. A. Kharadze, *Solid State Commun.*, 1978, **25**, 521.
[10] G. Mikaly, A. Janossy, and G. Grüner, *Solid State Commun.*, 1977, **22**, 771.