Electrocrystallised Metal–Tetracyanoquinodimethane Salts with High Electrical Conductivity

By Poopathy Kathirgamanathan and David R. Rosseinsky
(*Department of Chemistry, University of Exeter, Exeter* EX4 4QD)

Summary Conductivities/Ω^{-1} cm^{-1} from *ca.* 10^{-5} to 800 [for Cu(TCNQ)] are obtained for salts, often novel, of the formulation $M(TCNQ)_n$ or $M(TCNQ)_n$ (solvent)$_m$, prepared by cathodic electrocrystallisation from tetracyanoquinodimethane (TCNQ) in the presence of metal (M) salts, where the M are K, Mn, Fe, Co, Ni, Cu, Zn, Ag, and Cr.

Highly conductive adducts now assume increased importance in view of the recent discovery[1] of superconductivity in one of the group. Metal–tetracyanoquinodimethane salts might have been expected to exhibit high conductivity, but hitherto have not.

These salts have been prepared[2–4] by (i) metathesis of a cation source with Li^+TCNQ^- in water, (ii) reaction of a metal iodide with TCNQ° forming I_2 in hot acetonitrile, or (iii) reaction of TCNQ° with organometallics in acetonitrile. We have now applied the electrocrystallisation technique, which we have developed[5,6] for the preparation of conductive adducts, to the preparation of metal–TCNQ salts.

The method closely follows that used before.[5,6] Thus, a solution of, *e.g.*, 0·5 mmol of metal salt and 1 mmol of TCNQ in 200 ml of acetonitrile was electrolysed at the potential specified in the Table. If the reactant salt was insoluble, the excess was allowed to settle, remaining at all times separate from the product which adhered to the cathode. Careful lifting out and washing with acetonitrile avoided contamination of the product. Microcrystalline products were pulverised and compacted into discs ('d' in

TABLE 1 Preparation, composition, and conductivities of metal TCNQ salts[a]

Reactant, ratio[b] (% yield)	Potl /V *vs* S C E[c]	t/h	Product	σ/Ω^{-1} cm^{-1}	Ref 2 Product	Ref 2 σ(d)/Ω^{-1} cm^{-1}
KBr, 1 (60)	−0 513	194	K(TCNQ)	2×10^{-4} pd	K(TCNQ)	2×10^{-4}
$Mn(ClO_4)_2$, 2 (42)	−0 504	49	Mn(TCNQ) $\frac{2}{3}$MeCN	$4\ 4 \times 10^{-3}$ pd	$Mn(TCNQ)_2\ 3H_2O$	$1\ 1 \times 10^{-5}$
$FeCl_2\ 4H_2O$, 2 (30)	−0 430	72	$Fe_2(TCNQ)_3\ 5H_2O$	$4\ 8 \times 10^{-4}$ pd	$Fe(TCNQ)_2\ 3H_2O$	2×10^{-5}
$Co(ClO_4)_2\ 6H_2O$, 2 (50)	−0 540	72	$Co(TCNQ)_2\ 3H_2O$	$2\ 6 \times 10^{-4}$ pd	$Co(TCNQ)_2\ 3H_2O$	1×10^{-5}
$NiCl_2\ 6H_2O$ 2 (48)	−0 790	102	$Ni_2(TCNQ)_3\ 6H_2O$	$2\ 6 \times 10^{-4}$ pd	$Ni(TCNQ)_2\ 3H_2O$	1×10^{-5}
$CuCl_2$, 2 (21)	−0 513	10	Cu(TCNQ)	$2\ 9 \times 10^{-2}$ pd	Cu(TCNQ)	5×10^{-3}
			"	31 ps		
$CuCl_2$ 2 (72)	(g 221[d])	247	Cu(TCNQ)	784 gs		
$Zn(ClO_4)_2\ 6H_2O$, 2 (15)	−0 540	38	$Zn_2(TCNQ)_3(ClO_4)_2\ 3H_2O$	$2\ 1 \times 10^{-2}$ pd	—	—
$AgNO_3$ 1 (61)	−0 001	35	$Ag_4(TCNQ)_3$	6×10^{-4} pd	Ag(TCNQ)	$1\ 25 \times 10^{-6}$
			"	8 ps		
$AgNO_3$ 1 (83)	(g 990[d])	16	$Ag_4(TCNQ)_3$	44 gs		
$CrAc_3$ 3 (41)	(g 31[d])	408	$Cr(TCNQ)_3$	$5\ 1 \times 10^{-3}$ gd	$Cr_2Ac_4OH(TCNQ)\ 6H_2O$	1×10^{-9}

[a] Abbreviations p potentiostat, g galvanostat, s single crystal, d compacted disc [b] Amount of TCNQ per 1 reactant [c] Standard calomel electrode [d] Current density in μA cm^{-2}

the Table) for 2-probe D C conductivity studies, otherwise single crystals ('s' in the Table) were used Most preparations employed potentiostat ('p') conditions,[5] some the newer galvanostat ('g') technique[5] The chromium salt $Cr(TCNQ)_3$ was prepared from $CrAc_3$ in glacial acetic acid with a galvanostat current density of 30 5 μA cm^{-2} C, H, and N analyses accorded well with the compositions cited

The results in the Table demonstrate the accessibility of single crystals by the present method, the high conductivities σ of some, and the enhancement of conductivity achieved by the galvanostat preparation The particularly high σ value for Cu(TCNQ) indicates possibly metallic properties Here the contributing canonical forms (A)—(C) doubtless aid the required metal-like delocalisation, especially if the structure proves to be stacks of like upon like

$$\underset{\text{(A)}}{Cu^{2+}TCNQ^{2-}} \longleftrightarrow \underset{\text{(B)}}{Cu^{+}TCNQ^{-}} \longleftrightarrow \underset{\text{(C)}}{Cu^{\circ}TCNQ^{\circ}}$$

Similar considerations prevail for $Ag_4(TCNQ)_3$, in which $TCNQ^{2-}$ is a nominal unit (as in the Mn, Fe, and Ni salts) By contrast $TCNQ^{\circ}$ is, again nominally, incorporated in the Zn compound As observed earlier,[5,6] the electrochemical method often produces stoicheiometries or compositions different from those of the chemical preparations

We thank Mr T E Booty for the skilful mounting of the crystals

(*Received, 2nd June* 1980, *Com* 593)

[1] D Jerome, A Mazaud, M Ribault, and K Bechgaard, *J Phys* (*Paris*) *Lett*, 1980, **41**, L95
[2] L R Melby, R J Harder, W R Hertler, W Mahler, R E Benson, and W E Mochel, *J Am Chem Soc* 1962, **84**, 3374
[3] A R Siedle, *J Am Chem Soc* 1975, **97**, 5931
[4] A R Siedle, G A Candela, and T Finnegan *Inorg Chim Acta* 1979 **35**, 125
[5] P Kathirgamanathan, S A Mucklejohn, and D R Rosseinsky, *J Chem Soc Chem Commun*, 1979, 86
[6] P Kathirgamanathan and D R Rosseinsky, *J Chem Soc*, *Chem Commun*, 1980, 356