

Electrocrystallised Metal–Tetracyanoquinodimethane Salts with High Electrical Conductivity

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Summary Conductivities/ $\Omega^{-1}\text{cm}^{-1}$ from *ca.* 10^{-5} to 800 [for $\text{Cu}(\text{TCNQ})$] are obtained for salts, often novel, of the formulation $\text{M}(\text{TCNQ})_n$ or $\text{M}(\text{TCNQ})_n(\text{solvent})_m$, 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 discovery¹ 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

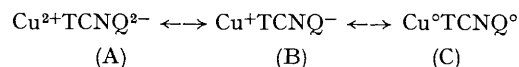
TABLE 1 Preparation, composition, and conductivities of metal TCNQ salts^a

Reactant, ratio ^b (% yield)	Potl/V vs S C E ^c	t/h	Product	$\sigma/\Omega^{-1} \text{ cm}^{-1}$	Ref 2	
					Product	$\sigma(\text{d})/\Omega^{-1} \text{ cm}^{-1}$
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) ₂ 3/2 MeCN	4.4×10^{-3} pd	Mn(TCNQ) ₂ 3H ₂ O	1.1×10^{-5}
FeCl ₂ 4H ₂ O, 2 (30)	-0 430	72	Fe ₂ (TCNQ) ₃ 5H ₂ O	4.8×10^{-4} pd	Fe(TCNQ) ₂ 3H ₂ O	2×10^{-5}
Co(ClO ₄) ₂ 6H ₂ O, 2 (50)	-0 540	72	Co(TCNQ) ₂ 3H ₂ O	2.6×10^{-4} pd	Co(TCNQ) ₂ 3H ₂ O	1×10^{-5}
NiCl ₂ 6H ₂ O 2 (48)	-0 790	102	Ni ₂ (TCNQ) ₃ 6H ₂ O	2.6×10^{-4} pd	Ni(TCNQ) ₂ 3H ₂ O	1×10^{-5}
CuCl ₂ , 2 (21)	-0 513	10	Cu(TCNQ)	2.9×10^{-2} pd 31 ps	Cu(TCNQ)	5×10^{-3}
CuCl ₂ , 2 (72)	(g 221 ^d)	247	Cu(TCNQ)	784 gs		
Zn(ClO ₄) ₂ 6H ₂ O, 2 (15)	-0 540	38	Zn ₂ (TCNQ) ₃ (ClO ₄) ₂ 3H ₂ O	2.1×10^{-2} pd		
AgNO ₃ 1 (61)	-0 001	35	Ag ₄ (TCNQ) ₃	6×10^{-4} pd 8 ps	Ag(TCNQ)	1.25×10^{-6}
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	5.1×10^{-3} gd	Cr ₂ Ac ₄ OH(TCNQ) 6H ₂ O	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 $\mu\text{A cm}^{-2}$

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 CrAc₃ in glacial acetic acid with a galvanostat current density of $30.5 \mu\text{A cm}^{-2}$. 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



Similar considerations prevail for Ag₄(TCNQ)₃, in which TCNQ²⁻ is a nominal unit (as in the Mn, Fe, and Ni salts). By contrast TCNQ⁰ is, again nominally, incorporated in the Zn compound. As observed earlier,^{5,6} the electrochemical method often produces stoichiometries 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 Rossemsky, *J Chem Soc Chem Commun*, 1979, 86

⁶ P Kathirgamanathan and D R Rossemsky, *J Chem Soc, Chem Commun*, 1980, 356