A New Type of Conducting Ion-radical Salts containing 7,7,8,8-Tetracyanoquinodimethane and Halide Anion

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A new type of conducting ion-radical salts containing 7,7,8,8-tetracyanoquinodimethane and halide anion is described; the representative (**1**) of this type of simple salt shows good conducting properties.

Ion-radical salts based on 7,7,8,8-tetracyanoquinodimethane (TCNQ) are being extensively studied.[1] The known systems may be divided into two groups: (a) simple salts M^{n+}-$(TCNQ^-)_n$, and (b) complex salts $M^{n+}(TCNQ^-)_n(TCNQ)_m$.

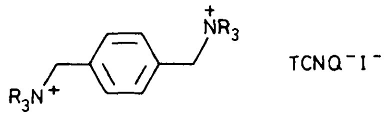
During our study of TCNQ salts of organylammonium dications we prepared a new type of simple salt containing $TCNQ^-$ *and* halide anion according to the formula $M^{(n+m)+}(TCNQ^-)_n(X^-)_m$. These compounds were synthesized by a metathesis reaction of ammonium salts[2] (iodide or bromide) with LiTCNQ.

The new salts differ from the halide ion-containing redox reaction products of some ammonium[3] and sulphonium[4] halides with TCNQ which are 'complex salts.' Normally 'simple salts' exhibit only poor electric conductivity because

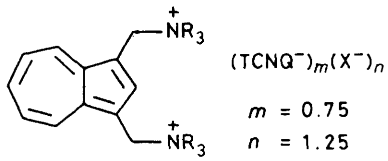
Table 1. Room-temperature conductivity data for compounds $M^{2+}(TCNQ^-)_n(X^-)_m$.

Compound	$M^{2+}:TCNQ^-:X^-$ [a]	$\sigma/\Omega^{-1}\,cm^{-1}$ [b]
(**1**)	1 : 1 : 1	1.6×10^{-2} [c]
(**2a**)	1 : 0.75 : 1.25	(7.7×10^{-2}) [c]
		3×10^{-6} [d]
(**2b**)	1 : 0.75 : 1.25	1.4×10^{-7} [e]
(**3**)	1 : 2	1×10^{-6} [e]

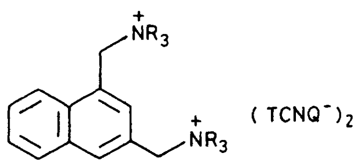
[a] Elemental analyses (C,H,N,X) indicated that the compounds were stoicheiometric. [b] Determined on polycrystalline compaction. [c] Four-probe technique. [d] Average value of several samples. [e] Two-probe technique.



(1)



(2) a; X = I
b; X = Br



(3)

R = Me

the TCNQ molecules are fully charged and thus do not crystallize in segregated stacks with small intermolecular distances,[5] whereas 'complex salts' are good to very good conductors. Only a few exceptions exist.[1,6] Nevertheless, the simple salt (**1**) also exhibits good conducting properties (Table 1).

Simple salts, in which $TCNQ^-$ is partly replaced by halide anion seem to be obtainable if bis(ammonium)-cations are used which have a rigid aromatic hydrocarbon core.

However, this assumption is not comprehensive enough as shown by compound (**3**), which is an ordinary simple salt with common conductivity. On the other hand, compounds (**2a**) and (**2b**) show that (**1**) is not a single exceptional case. They are other examples of these radical-cation salts containing a stoicheiometric mixture of diamagnetic and paramagnetic anions.

During our study there was evidence of a good conducting sample of (**2a**) also, but this phase was difficult to reproduce, so that it might be possible that high conductivity was induced by traces of the corresponding complex salt, as it was assumed for several cases of good conducting simple salts.[7] Only a poor conducting radical salt was formed when bromide was used to substitute TCNQ.

Elemental analyses obtained from several samples prepared independently always showed the same constant composition, even if a large excess of LiTCNQ was employed. Thus the stoicheiometry seems to depend on crystal packing effects. This might be the reason for the composition of the halide containing complex salts.[3]

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