Crystal chemistry of TCNQ complexes role of cation, composition and temperature

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I. Introduction and summary

The organic electron acceptor tetracyanoquinodimethane (TCNQ, I)

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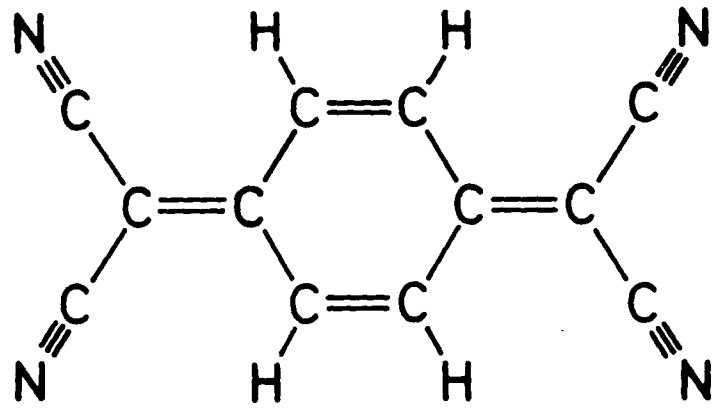

is known to form crystalline complexes with a great variety of donors which may be of organic or inorganic origin (1). During the last two decades these complexes have been the field of extensive study by chemists and physicists, because of their large variation of electric and magnetic properties and the diversity of solid modifications. The room temperature electric conductivities range from 10^{-10} to $10^{2}\Omega^{-1}cm^{-1}$. Some TCNQ salts have activation energies at low temperatures larger than 0.35 eV, whereas HMTSF(TCNQ)(2) is still highly conducting below 1 K. The magnetic susceptibility is sometimes activated, in other cases roughly constant, whereas in some complexes it rises sharply at low temperatures. On the basis of the mutual arrangement of the donor and TCNQ molecules, crystals of TCNQ complexes can be divided into three main groups. In crystals of the first group there are linear arrays in which planar donor and TCNQ molecules alternate, the so called mixed stacks. Crystals of the second group contain stacks composed out of TCNQ moieties only (segregated stacks). In some cases donor stacks are present as well. Finally there are crystals in which the TCNQ units occur as isolated entities (monomers, or dimers). As it soon became clear that the physical properties of TCNQ complexes with mixed stacks or with isolated TCNQ units do not differ essentially from those of other known charge transfer complexes (3), most attention has been paid to the second group of complexes. This group is also the subject of study of the present thesis.

The compounds will be briefly referred to as TCNQ complexes or TCNQ salts.

In explanations of the strong variations in physical properties encountered for the TCNQ complexes, a huge variation of effects, interactions or structural details has been reported in the literature. As examples may be mentioned Coulomb interactions, bandwidth arising from the strong π molecular overlap between molecules along the stack, exchange interactions between neighbouring spins, the average number of electrons per TCNQ and the coupling of electrons to inter- and intramolecular vibrations. In a recent approach (4) to explain the gross features of the electric conductivity, magnetic susceptibility, optical absorption, and stack distortions, it has been suggested that the Coulomb interactions are the dominant interactions and that the key variable is ρ, the number of electrons per TCNQ. Such models with only one variable parameter are attractive by their simplicity, but have the disadvantage that in many cases they do not explain subtle variations in properties as occur, for instance, as a function of temperature, pressure, disorder, or due to phase transitions. For a more detailed analysis of the effects involved, both the crystal structures and the physical properties of a group of related TCNQ complexes must be determined. A project in which this is realized is carried out in the Departments of Physical Chemistry and Chemical Physics of the University of Groningen, in close cooperation with chemists and physicists in Budapest, Vancouver, Grenoble and Oak Ridge. The Xray and neutron diffraction (or scattering) investigations described in the present thesis are meant to provide the structural basis for the research. The results of physical measurements are, or will be, reported elsewhere (5).

To study the influence of the size and shape of the cations on the structures and properties, Xray diffraction studies have been done on the related N-substituted morpholinium complexes N-methyl-N-ethyl-morpholinium $(TCNQ)_2$ [$MEM(TCNQ)_2$] , N,N-(diethyl)-morpholinium $(TCNQ)_2$ [$DEM(TCNQ)_2$], N,N-(dimethyl)-morpholinium $(TCNQ)_2$ [$DMM(TCNQ)_2$], and N-hydrogen-N-ethyl-morpholinium $(TCNQ)_2$ [$HEM(TCNQ)_2$] , (Chapter II), and of some Rubidium TCNQ complexes (Chapter IV). For both groups it may be assumed that each donor molecule supplies one electron to the

TCNQ molecules. The structures determined for $Rb_2(TCNQ)_3$ at 113 and 294 K have been compared with the isostructural complex $Cs_2(TCNQ)_3$ at 294 K(IV.4). It turned out that within the TCNQ stacks the shifts 'parallel' to the TCNQ planes do not depend on the temperature but quite strongly on the atomic radii of the cations. For the distances between the planes the reverse is the case.

The observed structure at 113 K of one of the morpholinium type complexes, $MEM(TCNQ)_2$, resulted in a new interpretation of its phase transition at 19 K and in the discovery of a second phase transition at 340 K. Measurements of the physical properties (6) showed not only anomalies at the phase transitions but also at intermediate temperatures. The electrical conductivity increases anomalously between 290 and 320 K. Even more remarkable is its sudden increase with a factor 10^3 at the first order phase transition at 340 K. To link these observations with changes in the crystal structure Xray diffraction studies were carried out at 294, 323 and 348 K (Chapter III). Two major changes have been observed: (a) an increasing disorder of the MEM molecule with increasing temperature, which sets in at about room temperature, (b) a further sharp enhancement of the disorder at the phase transition, at which temperature also the strongly dimerized TCNQ stacks become almost regular. The enhancement of the disorder and the accompanying stack regularity are evidently favorable for the conductivity.

The high temperature phase transition has been described by Sawatzky, Huizinga & Kommandeur (7), in terms of a one electron theory for a $\frac{1}{4}$ filled band system with high on-site Coulomb interaction U. In this picture the transition from a regular to a dimerized chain corresponds to a $4\,k_f$ anomaly ($k_f = \frac{\pi}{4a}$ is the Fermi wave vector of the regular stack with periodicity a). For such a system another anomaly ($2k_f$) is expected at lower temperatures, resulting in a tetramerization of the TCNQ stacks. To check whether the expected doubling of the cell dimension along the stack could be observed elastic neutron and Xray diffraction studies were performed below 19 K. Both techniques revealed the expected doubling, but the detailed structure has not been determined yet. At temperatures well above 19 K diffuse Xray scattering occurs, in accordance with a phonon softening detected at 20 K by inelastic neutron scattering (III.3).

Apart from the structure of $MEM(TCNQ)_2$, in Chapter II the crystal structure determinations of $DEM(TCNQ)_2$, $DMM(TCNQ)_2$ and $HEM(TCNQ)_2$ are described. The common feature of these complexes is the presence of sheets of TCNQ units. The details of the sheets, are, however, strongly different for various structures. $MEM(TCNQ)_2$, $DMM(TCNQ)_2$ and $HEM(TCNQ)_2$ contain only one crystallographically independent sheet, for $DEM(TCNQ)_2$ two independent sheets occur. Structural characteristics of the complexes, as detailed sheet features, number of independent sheets and cation-TCNQ sheet interactions, will effect their physical properties. Preliminary results (8) of ESR measurements show the differences expected on the basis of the structural aspects mentioned above.

In Chapter V a qualitative discussion of TCNQ complexes with segregated stacks shows under which circumstances sheets of TCNQ molecules as encountered in the present 1:2 complexes are likely to occur. Especially steric considerations as imposed by size and shape of the cations and strong electrostatic interactions, as present in the alkali TCNQ salts, have been used to classify the compounds. Idealized sheet features are formulated in V.2. The idealized sheet structure contains short N...H distances between the TCNQ molecules of successive stacks, and the overlap in the stack is assumed to be of the ring-external bond or the ring-ring bond type. For the class of flat cations, idealized sheet features are expected only if the cations meet certain criteria (Table 8 in V.5.5.). For the 1:1 salts in the literature only the flat cation NMP obeys the criteria, making the salt NMP(TCNQ)-I with its idealized sheet characteristics, unique among the 1:1 salts.

TCNQ complexes with long cations (V.4.) do not contain the idealized overlap modes along the stacks. Only favorable (V.4.) "polymolecule formation" of the cations due to partial overlap can prevent stack distortion at the head and tails of the cations. In the sheets of the 1:2 complexes with medium size cations stack distortions occur even more frequently, which may result in sheets built up out of dimers. The structures of the morpholinium type salts described in this thesis, demonstrate that intra- and inter-dimer stacking and sheet orientation strongly depend on the outer shape of the cations. The flexibility of these cations and the possibility of disorder make à priori predictions

of these structures nearly impossible. The 1:1 salts of the medium size cation class possess strongly distorted sheets or no sheets at all.

For the 1:1 alkali TCNQ salts the size of Rb^+ just enables this cation to combine strongest possible electrostatic interaction with $N^{\delta-}$ atoms of TCNQ, with (slightly distorted) idealized sheet characteristics. One Rb(TCNQ) modification crystallizes in such a structure type. For the smaller cations large deviations from the idealized sheet are expected. In the actual structures of two Rb(TCNQ) modifications and of the TCNQ complexes with smaller cations, the TCNQ stacks are related by pseudo fourfold symmetry and sheets do not occur. The structures of 1:1 TCNQ complexes containing cations related to TTF (V.9.), roughly follow the rules of Table 8 for the flat cations. Because of its small size, in the TTF(TCNQ) family the TTF cation itself is the least able to form a TCNQ complex with structural features as encountered in NMP(TCNQ)-I. A herringbone type packing as found in TTF(TCNQ) for both TTF and TCNQ, occurs frequently in crystals of organic complexes, but is (apart from the compound TMA.I.(TCNQ)) not observed for any other TCNQ complex.

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