Most organic superconductors that have been discovered are salts with \( \pi \)-cation molecules such as \((TMTSF)_2X\) and \((ET)_2X\). In contrast, \(\text{Ni(dmit)}_2\) is a \( \pi \)-anion molecule whose charge transfer salts also exhibit superconductivity. We include them in our discussion although they are not organic molecules in the strictest sense. In any case, the field of molecular superconductors has been expanded to include both cation radical and anion radical salts.

### 7.1 Ni(dmit)_2 Salts and Their Superconductivity

A new class of molecules, bis(4,5-dimercapto-1,3-dithiole-2-thione)-nickel, abbreviated \(\text{Ni(dmit)}_2\) and shown in Fig.1.1, has been found to form highly conducting compounds. The molecule has a large number of sulfur atoms on its periphery which is expected to enhance two-dimensionality through increased intercolumn interaction. On forming ion radical salts, this molecule is rather exceptional in that it acts as acceptor rather than donor.

The donor-acceptor compound \(\alpha\text{-TTF[Ni(dmit)}_2\text{]}\) has been found to show high electrical conductivity: at ambient pressure this reaches 300 S/cm at 300 K and increases to \(\sim 10^8\) S/cm at 4.2 K, with a maximum near 3 K. Furthermore, under 7 kbar, this compound shows superconductivity with \(T_c\) of 1.62 K, as illustrated by Fig.7.1 [7.1]. The upper critical transverse magnetic field is 1.3 T at 1.08 K and higher than 2.5 T at 0.4 K.

The crystal consists of stacks of \(\text{Ni(dmit)}_2\) and TTF. It has a centered monoclinic structure with space group \(C2/c\) with \(a = 46.22\) Å, \(b = 3.732\) Å.

![Fig.7.1. Superconducting transitions of \(\text{TTF[Ni(dmit)}_2\text{]}\) at 7 kbar. From [7.1]](image_url)
Fig. 7.2. End-on view of the Ni(dmit)$_2$ molecules in the bc-plane showing the two-dimensional arrangement of these units. From [7.1]

Fig. 7.3. A view of the crystal structure of TTF[Ni(dmit)$_2$]$_2$ parallel to the b axis. The TTF and Ni(dmit)$_2$ molecules are repeated along the b axis at the unit cell distance of 3.73 Å. The four Ni(dmit)$_2$ molecules along the z (or c) shown lie at different levels along the b axis. From [7.1]

c = 22.86 Å and $\beta = 119.19^\circ$. The molecules of TTF and Ni(dmit)$_2$ stack in distinct columns parallel to the b-axis, the needle axis (Fig. 7.2), where only Ni(dmit)$_2$ molecules are depicted, for simplicity. These columns make alternating sheets of TTF and Ni(dmit)$_2$ parallel to the bc-plane as shown in Fig. 7.3.

The electronic structure of this system is controversial. It has been proposed that three-dimensional electronic properties are promoted because the S...S distances are shorter than twice the van der Waals distance of 3.70