The Crystal Structure of the Ionic 1:1-Complex of Ditoluenechromium and 7,7,8,8-Tetracyanoquinodimethane, $[(C_6H_5CH_3)_2Cr]^+(C_{12}H_4N_4)^-$

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Summary The structure of $[(C_6H_5CH_3)_2Cr]^+(C_{12}H_4N_4)^-$ consists of stacks of ditoluenechromium cations and stacks of TCNQ⁻ anions, with interplanar spacings of 3·42 Å.

SALTS of the stable anion-radical 7,7,8,8-tetracyanoquinodimethane (TCNQ⁻) are among the best organic electrical conductors known. The range of conductance in these salts is very wide (from about 10^{-12} ohm^{-1}cm.$^{-1}$ to 10^2 ohm^{-1} cm.$^{-1}$ at room temperature). The conductance of such compounds is directly associated with their crystal structures.[1]

Using *X*-ray analysis, we have investigated TCNQ⁻ salts with diarene derivatives, *viz.* with ditoluenechromium and dibenzenechromium: $[(C_6H_5{\cdot}CH_3)_2Cr]^+TCNQ^-$ (I), $[(C_6H_5{\cdot}CH_3)_2Cr]^+$ $TCNQ^-TCNQ^0$ (II), and $[(C_6H_6)_2Cr]^+TCNQ^-$ (III).

We report the crystal structure of compound (I). Crystal data: $C_{26}H_{20}N_4Cr$, dark violet needles developed along the *a* axis are monoclinic, space group $P2_1/n$, $a = 7{\cdot}00 \pm 0{\cdot}02$; $b = 15{\cdot}45 \pm 0{\cdot}03$; $c = 20{\cdot}50 \pm 0{\cdot}06$ Å; $\beta = 97 \pm 1°$; $U = 2200{\cdot}4$ Å^3; $M = 440{\cdot}5$ for $Z = 4$, $D_c = 1{\cdot}34$ g./cm.^{3}

The intensities of 1754 independent non-zero reflections (0*kl*—6*kl* and *h*0*l* layers) were taken with a multiple-film equi-inclination Weissenberg goniometer with unfiltered Cu radiation and estimated visually. Absorption corrections were deemed to be unnecessary ($\mu = 46{\cdot}4$ cm.$^{-1}$).

The packing of the ions $[(C_6H_5{\cdot}CH_3)_2Cr]^+$ and $TCNQ^-$ was deduced from analysis of projections of Patterson functions $p_0(vw)$ and $p_1(vw)$. The crystal structure was refined by a full-matrix least-squares method with individual isotropic temperature factors to $R = 0{\cdot}14$. Individual isotropic temperature factors for carbon atoms in the cation are considerably higher than those for atoms in the anion. This is due to the ease of rotation of the toluene rings and to some disorder in the location of methyl groups. This will be discussed in detail later.

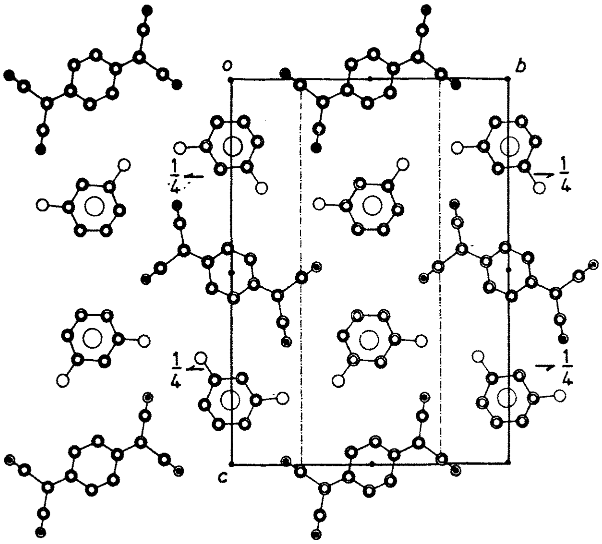

FIGURE 1. *The* [100] *projection of structure* (I).

Stacks of $TCNQ^-$ anions and $[C_6H_5{\cdot}CH_3)_2\ Cr]^+$ cations are essential features of the structure of (I). The [100] projection of structure (I) is given in Figure 1. Two ions of $TCNQ^-$ with interplanar spacing of $3{\cdot}42 \pm 0{\cdot}03$ Å fall within the period *a* in the anion stack. The overlapping of two neighbouring $TCNQ^-$ ions in the stack is shown in Figure 2a.

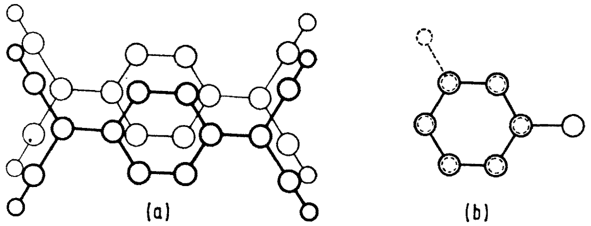

FIGURE 2. (a) *Overlapping of two neighbouring* $TCNQ^-$ *ions* (b) *Overlapping of two toluene rings in the* $[(C_6H_5{\cdot}CH_3)_2Cr]^+$ *cation*

The distribution of bond lengths in $TCNQ^-$ is of the pseudo-aromatic type, *i.e.* the double bonds are longer, and the single bonds are shorter as compared with those in a neutral $TCNQ^0$.[2]

In the cation stack, one $[(C_6H_5{\cdot}CH_3)_2Cr]^+$ ion falls within the period *a*. The ditoluenechromium cation has a twisted prismatic configuration (Figure 2b). The interplanar spacing of aromatic rings is $3{\cdot}21 \pm 0{\cdot}04$ Å. $(Cr{-}C)_{av} = 2{\cdot}11 \pm 0{\cdot}03$ Å; $(C_{ar}{-}C_{ar})_{av} = 1{\cdot}38 \pm 0{\cdot}04$ Å.

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