The Crystal Structure of the 1:2-Complex of Ditoluenechromium and 7,7,8,8-Tetracyanoquinodimethane, $[(C_6H_5CH_3)_2Cr]^+(C_{12}H_4N_4)^-(C_{12}H_4N_4)$

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Summary The structure of $[(C_6H_5CH_3)_2Cr]^+$ TCNQ$^-$ TCNQ^0 consists of stacks of ditoluenechromium cations and stacks of alternate TCNQ$^-$ and TCNQ^0, with interplanar spacings of 3·29 Å.

EARLIER, we reported the crystal structure of the ionic 1 : 1-complex of ditoluenechromium and 7,7,8,8-tetracyanoquinodimethane, $[(C_6H_5CH_3)_2Cr]^+$ TCNQ$^-$ (I),[1] and we now present the results of an *X*-ray study on the 1 : 2-complex of ditoluenechromium and 7,7,8,8-tetracyanoquinodimethane $[(C_6H_5CH_3)_2Cr]^+$ TCNQ$^-$ TCNQ^0 (II). A comparison between the structures of the two compounds is of importance, as they differ significantly in electrical conductivity.[2] For (I), the specific resistance measured on monocrystals is $\rho = 2{\cdot}5\ 10^5$ ohm/cm., with activation energy $E_a = 0{\cdot}36$ ev; for (II), $\rho = 0{\cdot}5$ ohm/cm., at $E_a = 0{\cdot}08$ ev.

Crystal data for (II): $C_{38}H_{24}N_8Cr$, dark violet needles developed along the *b* axis, triclinic, space group $P\bar{1}$, $a = 8{\cdot}25 \pm 0{\cdot}02$; $b = 7{\cdot}76 \pm 0{\cdot}02$; $c = 13{\cdot}77 \pm 0{\cdot}03$ Å; $\alpha = 94{\cdot}7° \pm 0{\cdot}5°$; $\beta = 92{\cdot}3° \pm 0{\cdot}5°$; $\gamma = 112{\cdot}5° \pm 0{\cdot}5°$; $U = 813{\cdot}3$ Å^3; $M = 644{\cdot}7$; for $Z = 1$ $D_c = 1{\cdot}32$ g./cm.^{3}

The intensities of *ca.* 1770 independent non-zero reflections (*h*0*l*-*h*6*l* and 0*kl* layers) were taken with a multiple-film equi-inclination Weissenberg goniometer with unfiltered Cu radiation, and estimated visually. A spot-size correction was applied.[3] Absorption corrections were deemed to be unnecessary ($\mu = 33{\cdot}6$ cm.$^{-1}$).

If the space group is $P\bar{1}$, the lone $[(C_6H_5CH_3)_2Cr]^+$ ion must occupy a centre of symmetry, while the two TCNQ molecules may lie either in two other centres of symmetry or else take a general position. A trial structure consistent with these assumptions was readily deduced by inspection of the three-dimensional Patterson synthesis. The structure (II) was refined by means of Fourier synthesis, followed by a full-matrix least-squares method with isotropic temperature factors to $R = 0{\cdot}13$.

Isolated stacks of $[(C_6H_5CH_3)_2Cr]^+$ cations and stacks of alternate TCNQ$^-$ and TCNQ^0 are essential features of the structure (II) (Figure 1). In the cation stack, one ion $[(C_6H_5CH_3)_2Cr]^+$ falls within the period *b*. The cation of ditoluenechromium has a prismatic *trans*-configuration. The interplanar spacing of aromatic rings within a cation is $3{\cdot}34 \pm 0{\cdot}04$ Å and for two adjacent cations in the stack it is $3{\cdot}68 \pm 0{\cdot}04$ Å. $(Cr–C)_{av} = 2{\cdot}18 \pm 0{\cdot}03$ Å; $(C_{ar}–C_{ar})_{av} = 1{\cdot}40 \pm 0{\cdot}04$ Å.

The molecules of TCNQ$^-$ and TCNQ^0 occupy two crystallographically independent centres of symmetry, but the accuracy of determination of bond lengths ($\pm 0{\cdot}03$ Å) does not permit us to distinguish between TCNQ$^-$ and TCNQ^0. The interplanar spacing of molecules TCNQ$^-$ and TCNQ^0 is $3{\cdot}29 \pm 0{\cdot}03$ Å. The overlapping of neighbouring TCNQ$^-$ and TCNQ^0 in the stack is shown in Figure 2.

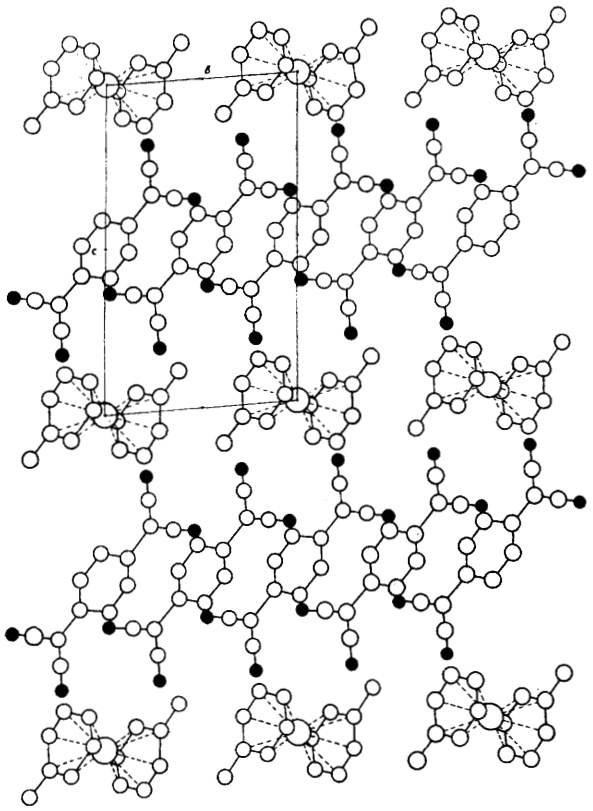

FIGURE 1. *The* [100] *projection of the* $[(C_6H_5CH_3)_2Cr]^+$ TCNQ$^-$ TCNQ^0 *structure.*

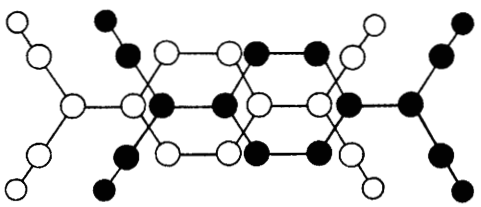

FIGURE 2. *Overlapping of adjacent* TCNQ$^-$ *and* TCNQ^0 *in a stack.*

If in the structure (I) each stack of TCNQ is surrounded by six stacks of cations as though making a barrier for interaction between TCNQ stacks, then the stacks of TCNQ in the structure (II) form layers parallel to the plane *ab*.

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