

clearly shows the differences between the two phases regarding the h.b. distances and angles. In contrast to the γ phase the ethylammonium group is disordered in β C2Mn and so is the h.b. scheme. It is the superposition of two orientations. In both of them two h.b.'s run to axial Cl atoms, one to a bridging Cl. This scheme may be designated *aab*, replacing the term 'monoclinic' (Chapuis, Kind & Arend, 1976); correspondingly the term 'orthorhombic h.b. scheme' may be replaced by *abb*; the reason for this new designation is the fact that a 'monoclinic' orientation of the h.b. scheme does not correspond to the symmetry of the structure in cases where *n* of the general formula is not equal to 1.

The octahedra layer is puckered and this may be described by specifying the tilt system as $a^-a^-c^0$ (Glazer, 1972; Depmeier, 1977). The tilt angle about the pseudotetragonal *a* axes is 5° . The four Cl(1) atoms surrounding the central Mn do not form a regular square but a rectangle with $\text{Cl}(1)-\text{Cl}(1)'' = 3.630$ (3.591 Å) and $\text{Cl}(1)'\text{-Cl}(1)'' = 3.705$ (3.706 Å). The values in brackets refer to the γ phase and these values clearly show that the $\gamma \rightarrow \beta$ phase transition mainly affects *b* [$a_\beta - a_\gamma = 0.03$, $b_\beta - b_\gamma = 0.109$ Å, cf. also Fig. 6 of Depmeier, Felsche & Wildermuth (1977)]. This effect should be attributed to the stronger N-H(3)···Cl(1) h.b. in the γ phase.* The main

* This correlation between h.b. strength and lattice constants seems to be a valuable tool to explain phase transitions in compounds $(\text{C}_n\text{H}_{2n+1}\text{NH}_2)_2\text{MnCl}_4$ with $n > 3$ where single crystals are not available at the moment.

differences between the γ and the β phases have been discussed (Depmeier, 1977).

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2:3 Complex of Rubidium and 7,7,8,8-Tetracyanoquinodimethane

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(Received 31 October 1977; accepted 19 January 1978)

Abstract. $\text{Rb}_2(\text{C}_{12}\text{H}_4\text{N}_4)_3$, monoclinic, $a = 7.297$ (1), $b = 10.392$ (1), $c = 21.444$ (2) Å, $\beta = 97.45$ (1)°, $Z = 2$, $U = 1612.3$ Å³, $F(000) = 772$, $\mu(\text{Mo}) = 32.6$ cm⁻¹; systematic absences: $h0l$ absent for l odd, $0k0$ for k odd; space group $P2_1/c$. The final R_w is 0.063 for 2750 observed reflexions. Inspection of Weissenberg photographs showed the compound to be isomorphous with Cs_2TCNQ_3 .

Introduction. As part of a series of crystal structure determinations of TCNQ complexes to study the phase transitions common to most of these salts, the crystal structures of two modifications of RbTCNQ were determined in our laboratory (Hoekstra, Spoelder & Vos, 1972; van Bodegom, de Boer & Vos, 1977). The structure determination of a third modification was carried out by Shirota & Kobayashi (1973). Recently

we happened to discover crystals of Rb₂TCNQ₃ among crystals of RbTCNQ-I.

Cell constants were calculated by a least-squares program from the $(\sin^2 \theta)/\lambda^2$ values of 252 reflexions obtained from zero-layer-line Weissenberg photographs superimposed with NaCl reflexion spots [$\lambda(\text{Cu } K\alpha_2) = 1.54434 \text{ \AA}$, $\lambda(\text{Cu } K\alpha_1) = 1.54050 \text{ \AA}$, $a(\text{NaCl}) = 5.64006 \text{ \AA}$ at 21°C]. A crystal, 0.2 × 0.5 × 0.5 mm, was mounted on the tip of a glass fibre and aligned along the *b* axis. Intensities were collected on a three-circle automatic Nonius diffractometer with the θ - 2θ method and Zr-filtered Mo radiation. All independent reflexions were measured up to $\theta = 30^\circ$ at room temperature. Deviations from linearity of the scintillation-counting equipment were kept below 1% by the use of attenuation filters; every 2 h a reference reflexion was measured three times; corrections were made for intensity changes in the primary beam, for Lorentz and polarization effects and for absorption. The latter correction was calculated with the Busing & Levy (1957) scheme: 12 × 10 × 10 volume elements and nine accurately located bounding planes were taken into account. Of the 4690 reflexions measured, 3586 had a net intensity greater than zero. A zero

weight was given to the reflexions with negative intensity and to 64 high-order reflexions with inaccurate intensities because of inclusion of neighbouring reflexions in the scan.

The coordinates of Cs₂TCNQ₃ found by Fritchie & Arthur (1966) were taken as a starting point for the refinement. The parameters of one Rb atom, one TCNQ group at a general position and one TCNQ around an inversion centre needed to be determined. We refined by blocked-matrix least squares with the XRAY system (1973) set of programs. One block was used for scale and overall temperature factor, one for Rb and for each of the TCNQ groups. Only the 2750 reflexions with $|F_o| \geq 2\sigma(F_o)$ were taken into account with weights $w = [\sigma^2(F_o) + E|F_o|^2]^{-1}$, $\sigma(F_o)$ being the standard deviation in $|F_o|$ due to counting statistics and errors in the filter factors; the constant $E = 0.00025$ was chosen so as to make $\langle w(|F_o| - |F_c|)^2 \rangle$ as similar as possible for different values of $|F_o|$ and $(\sin \theta)/\lambda$. For the non-hydrogen atoms the scattering curves were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). For Rb, dispersion corrections as given by Dauben & Templeton (1955) were applied. H atoms were constrained at 1.08 Å relative to their respective C atoms. For the non-hydrogen atoms anisotropic and for H isotropic parameters were refined. Residual $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.063$, goodness-of-fit $G = [\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2} = 3.31$ with number of observed reflexions $N_o = 2750$ and number of variables $N_v = 233$. Final positional parameters are given in Table 1.*

Table 1. Final positional parameters ($\times 10^4$)

Hydrogen atoms were constrained relative to their respective C atoms. For numbering of the atoms see Fig. 1. Numbers in parentheses are the estimated standard deviations in the last significant digits.

| | x | y | z |
|-------|------------|----------|-----------|
| Rb(1) | 5111 (1) | 2468 (1) | 2634 (0) |
| N(2) | -3832 (8) | 125 (7) | 1712 (3) |
| N(3) | 2151 (8) | 108 (7) | 2406 (3) |
| N(4) | 4606 (8) | 2996 (7) | -962 (3) |
| N(5) | -1168 (8) | 2964 (6) | -1757 (3) |
| N(6) | -4280 (8) | 3402 (7) | 1264 (3) |
| N(7) | 1545 (8) | 3528 (6) | 2065 (3) |
| C(8) | -2339 (10) | 266 (7) | 1629 (3) |
| C(9) | -490 (8) | 453 (6) | 1501 (3) |
| C(10) | 956 (10) | 265 (6) | 2013 (4) |
| C(11) | -1447 (8) | 1114 (6) | 393 (3) |
| C(12) | -64 (8) | 916 (6) | 919 (3) |
| C(13) | 1795 (8) | 1240 (6) | 835 (3) |
| C(14) | 2214 (8) | 1721 (6) | 272 (3) |
| C(15) | 828 (8) | 1904 (6) | -249 (3) |
| C(16) | -1046 (8) | 1585 (6) | -165 (3) |
| C(17) | 3108 (9) | 2741 (7) | -904 (3) |
| C(18) | 1261 (7) | 2406 (7) | -823 (3) |
| C(19) | -91 (8) | 2706 (7) | -1340 (3) |
| C(20) | -2804 (9) | 3668 (7) | 1209 (3) |
| C(21) | -930 (8) | 4014 (6) | 1129 (3) |
| C(22) | 433 (9) | 3760 (7) | 1658 (3) |
| C(23) | -1853 (8) | 4679 (6) | 33 (3) |
| C(24) | -473 (8) | 4513 (6) | 575 (3) |
| C(25) | 1417 (8) | 4860 (6) | 512 (3) |
| H(26) | -2864 | 878 | 439 |
| H(27) | 2882 | 1106 | 1222 |
| H(28) | 3626 | 1971 | 226 |
| H(29) | -2130 | 1728 | -552 |
| H(30) | -3269 | 4420 | 70 |
| H(31) | 2479 | 4740 | 908 |

Discussion. The structure is isomorphous with that of Cs₂TCNQ₃ (Fritchie & Arthur, 1966). Both the TCNQ groups and the Rb atoms are arranged in stacks along **b**. As in Cs₂TCNQ₃ there are two types of TCNQ: one group at a centre of symmetry (centrosymmetric *c*) and another at a general position (non-centrosymmetric *nc*), the arrangement along **b** being *nc...c...nc...nc...c...nc*. The separation between adjacent TCNQ moieties in the stack, which is a frequently used parameter in the description of structures of TCNQ compounds, is not strictly defined in the present compound as best planes calculated for (parts of) the TCNQ moieties are not parallel. We define the separation between adjacent TCNQ groups as the difference in distance to the origin of the best least-squares planes through the quinodimethane groups of the molecules considered. For adjacent molecules of mixed type *nc...c* the calculated distance is 3.26 Å

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33332 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

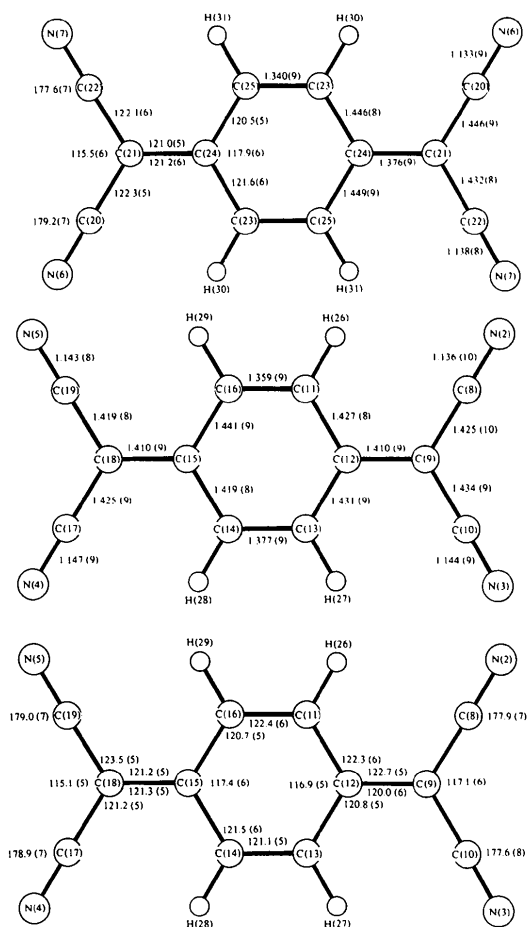


Fig. 1. Molecular geometry of the TCNQ units in Rb_2TCNQ_3 at 21°C . Values for bond lengths (\AA) are not corrected for libration effects. Numbering chosen according to Fritchie & Arthur (1966).

and for adjacent non-centrosymmetric molecules 3.12 \AA . The modes of overlap of TCNQ molecules in the stacks are of the same type as in Cs_2TCNQ_3 . For both

TCNQ groups bond angles and lengths are given in Fig. 1. The Rb ions are surrounded by a distorted cube of eight N atoms with $\text{Rb}\cdots\text{N}$ distances of $3.291(7)$, $3.263(7)$, $3.179(6)$, $2.941(6)$, $3.118(6)$, $2.892(6)$, $3.286(7)$ and $3.401(7) \text{ \AA}$.

A determination of the structure at liquid-nitrogen temperature is in progress. An account of the low-temperature work with full discussion of structure, including structural changes due to differences in atomic radii and temperature, will be published in a following paper.

The authors are grateful to Mr A. B. Verwey for growing the crystals. Part of the research has been supported by the Dutch Organization for the Advancement of Pure Research (ZWO). The computations were carried out at the Computing Center of the University of Groningen.

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