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The Crystal Structure of Rb(TCNQ)-II

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X-Ray studies of several TCNQ salts have revealed that the planar TCNQ molecules are stacked face-to-face to form columns in most of these crystal structures. The infinite columns hitherto reported consist of tetradic, triadic, diadic, and monadic units of TCNQ molecules.[1-6]

Rb(TCNQ) is polymorphic at room temperature.[7,8] The crystals of Rb(TCNQ)-I are monoclinic. The $TCNQ^-$ radical ions form columns contructed from diadic units of $TCNQ^-$. The crystal structure of Rb(TCNQ)-II will be reported in this paper.

Experimental

The dark purple crystal of Rb(TCNQ)-II was kindly supplied by Sakai. The cell dimensions were determined from Weissenberg photographs. The shape of the crystal used for the collection of the intensity data was approximate parallelepiped, with a maximum dimension of 0.3 mm. Equi-inclination Weissenberg photographs were taken around the c axis up to the third layer with Cu$K\alpha$ radiation (λ=1.5418 Å); the multiple film technique was used. In all, 811 reflections were observed. The intensities were estimated visually by comparison with a standard film strip and were converted to $|F(hkl)|$ by applying the usual Lorentz, polarization, and shape corrections.

The crystal data of Rb(TCNQ)-II are: $Rb^+(C_{12}H_4N_4)^-$, F.W. 290, triclinic, a=9.914±0.001, b=7.196±0.003, c=3.390±0.002 Å, α=92.70±0.10, β=86.22±0.11, γ=97.73±0.07, v=275.20Å^3, D_x=1.757, Z=1, space group $P\bar{1}$, $F(000)$=137

Determination of the Structure and Discussion

The space group $P\bar{1}$ was assumed tentatively and was then indeed verified at a later stage of the refinement. The trial structure was readily deduced from the three-dimensional Patterson synthesis. The atomic parameters were refined anisotropically by the block-diagonal least-squares method. The calculated positions of all the hydrogen atoms were included. The weighting scheme adopted was; w=1 for F>3.5 and w=0.2 for F<3.5. The final R value was 0.130.

The final positional and thermal prameters are given

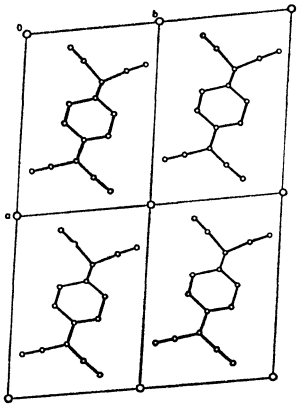

Fig. 1a. Projection of the structure along the b axis.

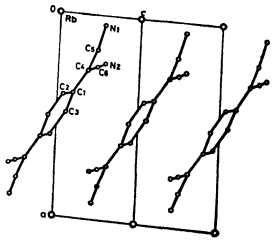

Fig. 1b. Projection of the structure along the c axis.

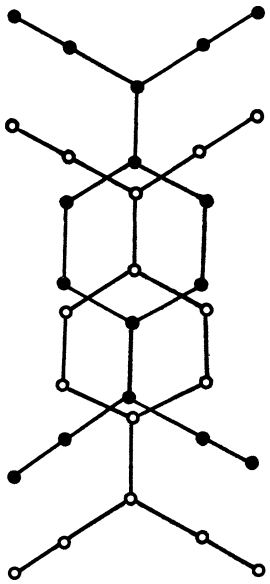

Fig. 2. Nearest neighbour overlap of $TCNQ^-$.

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Table 1. The final atomic parameters and their estimated standard deviations
Temperature factor $=\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]\times 10^4$

ATOM	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rb	0	0	0	80	124	260	33	72	36
	0	0	0	4	6	21	4	6	8
N(1)	905	3108	5373	116	123	677	31	113	−38
	21	25	50	28	43	178	29	55	66
N(2)	2410	9136	5693	95	150	1014	47	123	−18
	21	27	58	27	45	213	29	60	76
C(1)	3880	5349	1898	84	65	497	23	121	−26
	23	27	55	27	40	178	27	54	63
C(2)	3986	3509	763	66	150	722	38	101	−14
	23	31	62	29	53	214	32	60	80
C(3)	4883	6887	1053	98	120	724	261	147	12
	25	31	64	32	51	212	33	65	80
C(4)	2746	5814	3680	93	71	695	23	107	28
	24	28	61	30	43	206	29	61	72
C(5)	1732	4331	4724	105	114	871	33	130	−127
	25	31	66	33	52	241	34	71	84
C(6)	2562	7614	4837	60	165	681	31	35	1
	22	32	62	28	56	209	31	59	81

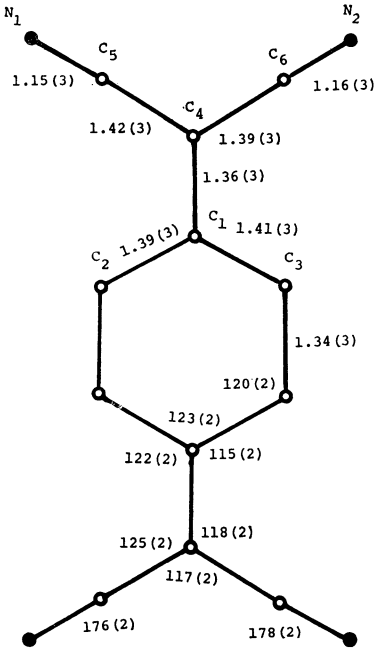

Fig. 3. Bond lengths (Å) and angles (°) with their standard deviations (in parenthses).

in Table 1. The observed and calculated structure factors are given in Table 2.[9] The structure within one unit cell is shown in Figs. la and 1b as viewed along the c axis and the b axis respectively. $TCNQ^-$ ions are stacked in a plane-to-plane manner and form columns of monadic units. This columnar structure is very similar to those found in the crystals of *N*-methylphenazinium(TCNQ).[1] The inter-planar spacing of TCNQ is 3.43 Å. The mode of overlapping is illustrated in Fig. 2. This type of overlapping has been observed in various TCNQ salts.[1-6] The bond lengths and angles of the $TCNQ^-$ are shown in Fig. 3. These values show that the $TCNQ^-$ ion has a quinoid character. It is known that crystals of Rb-(TCNQ)-I have monoclinic symmetry and that $TCNQ^-$ ions are stacked face-to-face to form columns of diadic units of $TCNQ^-$. Within a column, two different intermolecular spacings, 3.159 and 3.484 Å, appear alternately.[10]

Table 3. The pysical properties of both Rb(TCNQ)

	Rb(TCNQ)-II	Rb(TCNQ)-I
Electrical resistivity Ω cm (R. T.)	10^2	10^5
Activation energy eV	0.16∼0.19	0.53∼0.41 below the transition point 0.37∼0.28 above the transition point
Transition temperature K	230	374
The electrical anomalies at high pressure Kbar	unobservable	1, 3.5
Absorption peaks cm^{-1}	6250 16250, 26380	8500 15750, 26500

The physical properties of both Rb(TCNQ) substances are summarized in Table 3.[7] The resistivity of Rb(TCNQ)-I is about 10^3 times that of Rb(TCNQ)-II. The near-infrared absorption band of salt-II, which is due to the inter-radical charge transfer in the crystal, shifted toward a longer length than that of salt-I. The difference in the physical properties may arise from the difference in the columnar structures.

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9) Table 2 is kept by the office of the Chemical Society of Japan (Document No. 7313).

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